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Principles and Practice

OF

AGRICULTURAL ANALYSIS

A Manual for the Study of Soils, Fertilizers, and
Agricultural Products

For the Use of Analysts, Teachers, and Students of Agricultural
Chemistry

SECOND EDITION, REVISED AND ENLARGED

VOLUME II

FERTILIZERS AND INSECTICIDES

BY HARVEY W. WILEY, A.M., Ph.D.

EASTON, PA.
THE CHEMICAL PUBLISHING CO.

1908

39854

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W64p
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PREFACE TO VOLUME SECOND

In this volume an attempt has been made to treat the subject of fertilizers and fertilizing materials in the manner followed in the first volume with soils. The general principles of fertilizer manufacture and application have been presented in so far as they seemed to throw light on the rational method of examination and analysis. The standard methods of analysis in use in this and other countries, have been presented with sufficient fullness for the guidance of the skilled worker, and the information of the student. To those who make use of a book only for routine work or for preparation for an examination, this volume, as its predecessor, will be found to have little attraction. This fact, however, will not be a cause of regret to the author whose purpose has been, avowedly, to present to the busy worker and student a broad view of a great subject which each one does not have the time to search out for himself.

It is a matter of regret, however, that the contents of the volume have again exceeded all expectations. It was found impracticable to secure any greater condensation without departing from the purpose, and impairing the completeness of the work. When work is done with no prospect of financial compensation, it is gratifying to find it appreciated, and the author will be content to have this volume meet with as kindly a reception as has been accorded volume one.

HARVEY W. WILEY.

WASHINGTON, D. C.,
End of July, 1895.

PREFACE TO SECOND EDITION

A great part of the material relating to the occurrence and analysis of ammonia, nitrous and nitric acid printed in the first volume of the first edition of this work has been rewritten and transferred to this volume. This rearrangement has resulted in making the first and second revised volumes of approximately the same size.

All the matter of this volume has been rewritten and brought down to date. New features of moment are those relating to the production of nitric acid for manurial purposes from cyanamid and by direct electric oxidation of the nitrogen of the air. A chapter on the analysis of insecticides has also been added.

While not intended in any way as a laboratory guide it is hoped this volume may be even more highly appreciated than in its first form by the student, the investigator and the teacher.

H. W. WILEY.

November, 1908.

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EXAMINATION OF FERTILIZING MATERIALS, FERTILIZERS, AND MANURE

PART FIRST

DEFINITIONS, SAMPLING AND PRELIMINARY TREATMENT

1. **Introduction.**—The principal plant foods occurring in soils are named and the methods of estimating them described in the first volume. As fertilizers are classed those materials which are added to soils to supply deficiencies in plant foods or to render more available the stores already present. There is little difference between the terms fertilizer and manure. In common language the former is applied to materials prepared for the farmer by the manufacturer or mixer, while the latter is applied to those accumulated about the stables or made elsewhere on the farm. Thus it is common to speak of a barn-yard or stall manure and of a commercial fertilizer. This distinction is more nominal than real. If a choice is to be made between terms, manure is preferable. The term fertilization, moreover, is applied biologically to the effective congress of the male and female elements of the egg, and thus confusion may arise by the application of that term to any process of manuring.

In harmony with the common practice in this country, however, the words will be used in this volume in the sense indicated above.

One of the objects of the analysis of soils is to determine the character of the fertilizer which should be added to a field in order to secure its maximum fertility.

One purpose of the present manual is to determine the fitness of offered fertilizing material to supply the deficiencies which may be revealed by a proper study of the needs of the soil.

2. **Occurrence of Fertilizers in Nature.**—In the succession of geological epochs which has marked the natural history of the earth there have been brought together in deposits of greater or less magnitude the stores of plant food unused by growing crops

or which may once have been part of vegetable and animal organisms.

For a full description of the extent and origin of these deposits the reader is referred to works on economic geology. A brief description of them is given further on in connection with the fertilizing materials which they furnish. These deposits are the chief sources of the commercial fertilizers of a mineral nature which are offered to the farmers of to-day and to which the agricultural analyst is called upon to devote much of his time and labor. The methods of determining the chemical composition and agricultural value of these deposits, as practiced by the leading chemists of this country and Europe, will be fully set forth in the following pages.

3. Waste Matters as Fertilizing Materials.—In addition to the natural products just mentioned, the analyst will be called on also to deal with a great variety of waste materials which, in the last few years, have been saved from the débris of factories, abattoirs and other sources and prepared for use on the farm. Among these waste matters may be mentioned bones, horns, hoofs, hair, tankage, dried blood, fish scrap, oil cakes, ashes, sewage and sewage precipitates, offal of all kinds, leather scraps, and organic débris in general.

It is important, before beginning an analysis, and especially before passing a final judgment on the data obtained, to know the origin of the substances to be determined. As has already been pointed out in the first volume, the process which would be accurate with a substance of a mineral origin might lead to error if applied to the same element in organic combination. This is particularly true of phosphorus and potash. A simple microscopic examination will usually enable the analyst to determine the nature of the sample. In this manner, in the case of a phosphate, it would at once be determined whether it is derived from bone, mineral, or basic slag. The odor, color and general consistence will also aid in the determination.

4. Valuation of Fertilizing Ingredients.—Perhaps there are no more numerous and perplexing questions propounded to the analyst than those which relate to the value of fertilizing materials.

There is none harder to answer. As a rule, these questions are asked by the farmer, and refer to the money value of the fertilizers put on his fields. In such cases the cost of transportation is an important factor in the answer. The farther the farmer is removed from the place of fertilizer manufacture the greater, as a rule, will be the cost. Whether the transportation is over land or by water also plays an important part in the final cost. The discovery of new stores of fertilizing materials has also much to do with the price. This fact is especially noticeable in this country, where the price of crude phosphates at the mines has fallen in a few years from nearly six dollars to three dollars per ton.¹

This decrease has been largely due to discoveries of vast beds of phosphatic deposits in Florida, North Carolina, Tennessee and Wyoming. The state of trade, magnitude of crops and the vigor of commerce also affect, in a marked degree, the cost of the raw materials of commercial fertilizers.

Since 1904 there has been some improvement in prices, as is seen by the data on the following page.

5. Trade Values of Fertilizing Ingredients in Raw Materials and Chemicals.—As has already been mentioned, the task of fixing a money value for fertilizer ingredients is difficult. In fact, it is a very general opinion that such values should be left to the usual mandates of trade and the function of the analyst should cease when he has disclosed the character and amount of each ingredient of commercial value. The market price is then regulated by the ordinary conditions of demand, supply and transportation. In some cases the laws of the State require the construction of a table showing the money value of each of the component parts. In such a case the analyst is guided by trade conditions and further by the character or origin of the material in question. Thus soluble phosphoric acid is far more valuable than the insoluble variety, and nitrogen in the form of blood or saltpeter than nitrogen in horns, hoofs or hair.

The values proposed for 1907 by the Massachusetts experiment station are given below.²

¹ *The American Fertilizer*, 1905, 22 : 17.

² *Massachusetts Experiment Station*, 1907, *Bulletin* 119 : 16.

	Cents per pound
Nitrogen in ammonia salts.....	17.5
“ “ nitrates.....	18.5
Organic nitrogen in dry and fine-ground fish, meat, blood, and in high-grade mixed fertilizers.....	20.5
“ “ “ fine-ground bone and tankage.....	20.5
“ “ “ coarse bone and tankage.....	15.0
Phosphoric acid soluble in water.....	5.0
“ “ soluble in ammonium citrate.....	4.5
“ “ in fine-ground fish bone and tankage.....	4.0
“ “ in coarse fish bone and tankage.....	3.0
“ “ in cottonseed meal, castor pomace, and wood ashes.....	4.0
“ “ insoluble (in water and in neutral ammonium citrate) in mixed fertilizers.....	2.0
Potash as sulfate, free from chlorids.....	5.0
“ as muriate, (chlorid).....	4.25
“ as carbonate.....	8.0

The above schedule of trade values is adopted by Massachusetts, Connecticut, Rhode Island, Maine, Vermont, New York and New Jersey. It is based on the current market prices in ton lots of the materials.

The values assigned by the Maryland station differ but slightly from the above.³

	Cents per pound
In mixed fertilizers:	
For nitrogen as ammonia.....	20.0
“ potash (K_2O) free of chlorids.....	6.0
“ “ (K_2O) as chlorid or in kainit.....	5.0
“ phosphoric acid soluble in water and ammonium citrate...	5.0
“ insoluble phosphoric acid.....	2.0
“ “ “ “ from rock phosphate.....	1.0
In dissolved rock:	
For phosphoric acid soluble in water and ammonium citrate...	4.5
In ground bone:	
For nitrogen as ammonia in fine bone.....	16.0
“ “ “ “ “ medium bone.....	15.0
“ “ “ in medium bone.....	14.0
“ “ “ coarse bone.....	13.0
“ phosphoric acid in fine bone.....	5.0
“ “ “ “ “ medium bone.....	4.5
“ “ “ “ “ medium bone.....	4.0
“ “ “ “ “ coarse bone.....	2.0
In tankage and ground fish:	
For nitrogen as ammonia.....	15.0
“ phosphoric acid.....	3.0

³ The Maryland Agricultural College Quarterly, 1907, No. 37 : 3.

The organic nitrogen in superphosphates, special manures and mixed fertilizers of a high grade is usually valued at the highest figures laid down in the trade values of fertilizing ingredients in raw materials; namely, eighteen and one-half cents per pound, it being assumed that the organic nitrogen is derived from the best sources; viz., animal matter, as meat, blood, bones or other equally good forms, and not from leather, shoddy, hair or any low priced, inferior form of vegetable matter, unless the contrary is evident. In such materials the insoluble phosphoric acid is not given any value or only a mere trifle per pound. These values change as the markets vary.

The scheme of valuation prepared by the Massachusetts station does not include phosphoric acid in basic slags. By many experimenters the value of the acid in this combination, tetracalcium phosphate, is fully equal to that in superphosphates soluble in water and ammonium citrate. It would perhaps be safe to assign that value to all the phosphoric acid in basic slags soluble in a five per cent. citric acid solution.

Untreated fine-ground phosphates, especially of the soft variety so abundant in many parts of Florida, have also a high manurial value when applied to soils of an acid nature or rich in humus. On other soils of a sandy nature, or rich in calcium carbonate, such a fertilizer would have little value. The analyst in giving an opinion respecting the commercial value of a fertilizer must be guided not only by the source of the material, its fineness or state of decomposition, and its general physical qualities, but also by the nature of the crop which it is to nourish and the kind of soil to which it is to be applied.

GENERAL PRINCIPLES OF SAMPLING

6. **Directions.**—It is impracticable to give definite directions for getting samples of fertilizers which will be applicable to all kinds of material and in all circumstances. If the chemist himself have charge of the sampling it will probably be sufficient to say that it should accurately represent the total mass of material at hand. Generally the samples which are brought to the chemist have been procured without his advice or direction, and he is simply called upon to make an analysis of them as they are presented.

7. General Principles of Sampling.—The report of the chairman of the committee charged with presenting to the Sixth International Congress at Rome the principles of sampling and suggestions in respect of the method in which they should be carried out contains the following directions.⁴

The subject of sampling for analysis may be very properly divided into a general and a special part. I therefore shall discuss the problem in this way: First, with a brief statement of the general principles which should underlie sampling, followed by some special observations on sampling in special cases.

8. Object of Sampling.—The object of securing a sample for analysis is self-evident; namely, that the sample should represent exactly, or as nearly as possible, the mean composition of the whole deposit or substance from which it has been separated. For this reason, much must be left in all cases to the sound judgment of the person in charge of the sampling. This person, whenever possible, should be the analyst himself, as no one can judge so well as the one who is called upon to do the analytical work the character of the sample necessary to secure a proper material on which the analysis is to be conducted. Therefore, it is almost impossible to lay down any general principles which should guide the expert in securing the sample of his material unless the character of that material be known.

9. Classes of Materials.—The materials which are to be operated upon by the analyst are naturally divided into three states, namely, gaseous, liquid and solid. These bodies pass gradually from one state to another, and especially is this true of those passing from a solid to a liquid condition. The transition from the liquid to the gaseous form is very sharp and well defined.

10. Sampling a Gas.—In general, in the sampling of a gaseous material it is only necessary that the gaseous contents of the vessel, room or space should be thoroughly mixed in order that any given portion of the gas may represent the whole sample. This is especially true if the gases be of a mixed character or of different specific gravities. Where, for instance, carbon dioxid

⁴ Wiley, *Methods of Sampling Materials for Analysis*, Atti del VI Congresso internazionale di Chimica applicata, 1907, 7: 170.

is generated in the lower part of a room filled with air, being a heavier gas it would naturally accumulate as a heavy liquid would accumulate under a lighter one. A sample of the gas, therefore, in a confined space of this kind would not be representative of the whole contents unless previous to the sampling the whole were subjected to violent stirring. An ordinary electric fan properly placed in a room will within a short time so thoroughly mix its gaseous contents that a sample may be drawn which will represent fully the character of the whole.

In order that a sample of the gas may be unmixed and unabsorbed, it is well that it should be aspirated into a vessel filled with a liquid with which the gas is not miscible. Mercury, of course, is the best liquid for this purpose for most gases, but on account of its great weight and cost is unsuitable. As a rule, water will be found entirely satisfactory for the aspirating material, especially if the vessel be of considerable size so that the total volume of gas drawn in is rather large. The small quantity of gas which will be absorbed may be practically neglected.

A very good sample of gas may also be secured by pumping gas from any room or confined space into a dry rubber bag which is previously completely flattened out so as to expel any air which it may contain. In order that the last traces of air may be expelled, it is advisable in a case of this kind to fill the rubber bag at least partially full of gas, remove it from the room where the sampling is made, and express the contents, then carry back into the room and refill.

Gases may also be sampled into eudiometers or other vessels in which the analytical processes are to be carried out. In all these cases the study of the nature of the case, the experience of the analyst and the character of the analysis will determine the methods which are best adapted to the purpose.

II. Sampling a Liquid.—The sampling of liquid bodies is to be accomplished in the same general way. A thorough stirring of the liquid should always precede the sampling in order that the sample may be uniform in character. The stirring may be made either by mechanical means, as usually practiced, or, if the liquid be one which does not contain a large amount of

gas, pure air may be blown through it. The mechanical method by paddles or other stirrers, however, is to be preferred when it can be practiced. The sampling of water for analytical purposes requires special methods which will be given later.

12. Sampling a Solid.—The general principles which should underlie and regulate the sampling of solid materials are more difficult to enunciate. Here we have the greatest variety of conditions. Solid materials may be of such a character that they may be easily mixed; as, for instance, in the case of a powder or any substance in a finely subdivided state. On the other hand, a material from which a sample is to be taken may be solid, extremely hard and difficult of disintegration, as is the case with a rock or a piece of metal or of wood. The difficulties which obtain, therefore, are very great in this class of bodies and require special precautions, great experience and knowledge of the subject and the exercise of patience in order that good results may be secured. Where bodies can be perforated—as in the case of wood—very good samples may be taken by means of augers which are made to penetrate the wood at different places, and thus a sample secured. If the material is contained in bags or barrels which are easily penetrated, the ordinary trier which is used for sampling is, as a rule, sufficient to give an average sample. In the case of metal, boring may be practiced with a small drill and reasonably satisfactory samples secured.

The local conditions which obtain, the character, size and shape of the body, the facilities at hand for sampling, the purpose for which the analysis is to be made, and the general environment will be sufficient to guide the expert analyst in his work and enable him to get a sample of material which to him is a reasonably satisfactory representative. In a little more general way it may be said in regard to liquids which are supposed to have been mixed at one time and which have been barreled or bottled—as in the case of wine, vinegar or beer—it is always advisable to take a portion of the sample from each package. Solids which are finely divided and evenly mixed according to a uniform standard and which have been taken from a single source, as, for instance, in the case of fertilizers which are contained in bags, should have at

least a sample taken from every tenth bag. If there are less than ten bags, however, not less than three or four of the bags should be sampled.

In regard to the preservation of samples after they are secured, ordinary fruit jars which are furnished with rubber gaskets may be used for liquids without any fear of loss. In the case of liquids, where a narrow-necked receptacle is employed, and especially where it is necessary or advisable to secure a small volume of sample, a bottle which is closed with a rubber stopper may be used. A cork stopper which has been coated with paraffin and afterwards secured with sealing wax may be substituted sometimes to advantage for a rubber stopper. Of course, in many cases the presence of paraffin is objectionable, and in such cases it should not be used.

13. Subdivision of Sample.—The extent of the subdivision of the sample depends entirely on its nature and the character of the examinations to be made. In general it may be said that the finer the subdivision the better the analytical results. When substances are dry and can be easily pulverized, they should be powdered and passed through a sieve with a millimeter or, better still, a half millimeter mesh. The sample may be selected advantageously from a large amount of material by repeated quartering, the subsamples being passed successively through the crusher from time to time so as to have only a small amount of the sample in a fine state of subdivision when the final grinding occurs. In the case of a tough and difficultly reduced substance like meat, as large a quantity as possible should be passed repeatedly through a sausage mill, mixing the whole at once for each grinding, quartering the residue and regrinding, and mixing the subsamples.

Many products which consist of relatively small particles which can not be ground may be thoroughly mixed together and subdivided by means of quartering until a sample of proper size is obtained. If this material is soluble in water, the whole of the sample may be weighed, dissolved in water and an aliquot portion of the mixture taken for analysis. If soluble in other solvents than water, a similar process is to be employed. It appears that

the complete mixture of many substances which are soluble and which are of such a nature that they can not be readily ground is best effected by dissolving them in water or some other satisfactory solvent, mixing the solution and taking an aliquot part thereof, as above suggested.

If liquids have solids in suspension it is often necessary to thoroughly mix them in order that the sample may contain its proportionate part of the solid matters. Milk may be sufficiently mixed by pouring several times from one receptacle to another before the sample is removed. Carbonated liquids may be withdrawn from the casks or bottles in which they are held by means of a spigot with a stop-cock. In the case of viscous substances a large spatula, cheese-knife or cheese-sampler may be conveniently employed. For instance, this method of sampling may be practised with a substance like massecoite. In case the degree of fluidity is too great to admit of such a method of sampling, a slotted tube may be used which is inserted in the semi-liquid mass until filled and then withdrawn and its contents removed for the sample. Sirups and molasses in which the sugar has been partially crystallized offer unusual difficulties in sampling, owing to the great difficulty of breaking up the crystals and mixing them uniformly with the liquid portions. In such cases it is better to dissolve the crystals if possible by gentle heating and stirring of the products, or even the addition of a known amount of water until the whole of the crystallized portions are dissolved.

There are some plastic materials which it is almost impossible to sample in a uniform way. In these cases it may be found necessary to subdivide the material by cutting a selected and occasional piece representing, as nearly as possible, the whole material. Materials like street sweepings and garbage may be sampled when they are loaded or unloaded by taking an occasional shovelful and throwing it off to itself, until a carload or other large quantity has thus been sampled. These materials which are removed may then be thoroughly mixed together and resampled in the same way.

Sugar-cane and sugar-beets may be sampled by taking at random every tenth or hundredth beet or cane. The same is true

of apples and other fruits. In such sampling care must be exercised not to select the particular individual to be sampled, but to take every one which comes within the prescribed limit. In general, it may be said that it would be advisable to divide the materials which are the usual subjects of analysis into different classes and subdivisions, and that uniform methods for these classes and subdivisions be recommended.

14. Sampling of Fertilizers.—Perhaps there are no more numerous and perplexing questions connected with the subject of sampling than those which arise in the case of fertilizers. In many countries the method of sampling the fertilizing materials is prescribed by law. It is impracticable to give definite directions in all cases which will be applicable to all kinds of materials and in all instances. The chemist himself having charge of securing the sample should see that it accurately represents the total amount of the material sampled. Too often the samples which are brought to the chemist have been secured without his advice or direction and really are not representative.

For sampling manufactured fertilizers, which in this country are usually very finely divided, I have found nothing better than a slotted brass tube. The tube may be from 1 to 1½ inches in diameter, with a half or three-quarter inch slot. It should be long enough to reach the full length of the package, and the lower end should be provided with a cutting edge that it may be forced into the package easily. For a handle a smaller tube 3 to 4 inches long is brazed at right angles to the upper end of the larger tube. In sampling, the package of fertilizer is thrown on the side, and if the contents are hard they are broken up by rolling and by blows on the container. The slotted tube is now forced into the package with the slot down, turned over, shaken slightly to fill the tube, withdrawn, and the content emptied on a rubber or oil cloth. Samples are drawn from at least five per cent. of the packages, but should always be drawn from at least three packages. These samples are thoroughly mixed on the cloth, a subsample secured by quartering, placed in a screw-top can and labeled for identification. This instrument and method are suitable for sampling all finely ground fertilizers and fertilizer materials, but

are not suitable for raw phosphate rock, coarse raw tankage, fish scrap, farm manures, tobacco stems, unground kainit, nor for very lumpy nitrate of soda and sulfate of ammonia, all of which, except when mechanical devices are used, leave much to the judgment of the sampler, and for which only general instructions can be given.

Large samples should be secured from five to ten per cent. of the material, being careful to maintain the proper relation between the coarse and fine portions, and to protect the sample from loss or absorption of moisture. When the material is very wet, as fish scrap, or may take up much moisture, as sulfate of ammonia, the sample should be weighed and brought into an air-dry condition, and again weighed. It is now coarsely ground, thoroughly

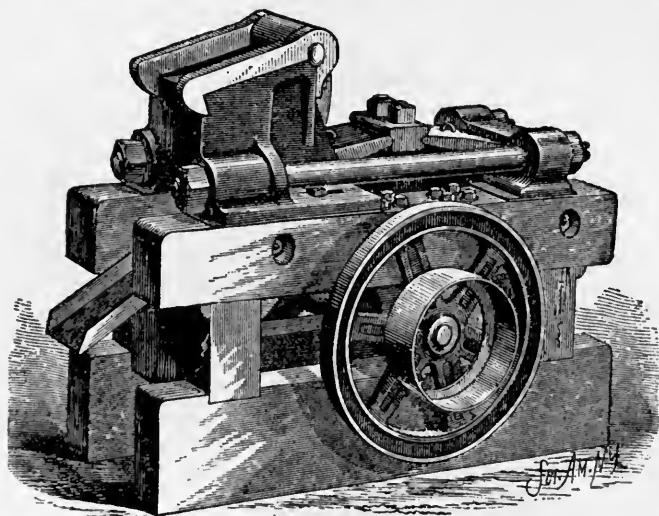


Fig. 1. Apparatus for Crushing Mineral Fertilizers.

mixed and a subsample taken, which may be again ground and subsampled if necessary. The loss or gain in bringing to an air-dry condition must be carefully noted and the results of the analysis corrected thereby.

15. Minerals Containing Fertilizing Materials.—When possible, the samples should be accompanied by a description of the mines where they are procured and a statement of the geologic condi-

tions in which the deposits were made. As large a quantity of the material as can be conveniently obtained and transported should be secured. Where a large quantity of mineral matter is at hand it should first be put through a crusher. Many forms of crusher, driven by hand and other power, are on the market. They are all constructed essentially on the same principle, the pieces of mineral being broken into small fragments between two heavy vibrating steel plates. The general form of these crushers is seen in Fig. 1.

The fragments coming from the crusher can be reduced to a coarse powder by means of the iron plate and crusher shown in Fig. 2.

Where only a small quantity of mineral is at hand the apparatus just mentioned may be used at once after breaking the sample into small fragments by means of a hammer.

Finally the sample, if to be dissolved in an acid for soluble materials only, is reduced to a powder in an iron mortar until it will pass a sieve with a one, or, better, one-half millimeter

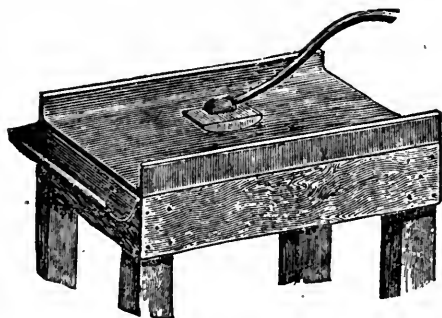


Fig. 2. Plate Grinder for Minerals.

circular mesh. The powder thus obtained must be stirred with a magnet to remove all iron particles that may have been incorporated with the mass by abrasion of the instruments employed.

If a complete mineral analysis of the sample is to be secured, the material freed from iron, as above described, is to be rubbed to an impalpable powder in an agate mortar.

16. Mixed Fertilizers.—In securing a sample of mixed fertilizers the first requisite is that they should be homogeneous. If a part of one kind of a fertilizer be in excess in any part of the whole,

the sample is apt to be nonrepresentative. The finer the materials in the original state and the more thoroughly they have been mixed the better the sample will be. If the materials be in bags it will be sufficient to take portions from every tenth bag or from three or four of the bags if there be less than ten, by means of an ordinary trier which is thrust through the bag and filled with the material therein contained. This consists of a long metal implement such as would be formed by a longitudinal section of a tube. The end is pointed and suited for penetrating into the sack and the materials contained therein. On withdrawing it, the semi-circular concavity is found filled with the material sampled. Samples in this way are removed from various parts of the bag and these samples well mixed together and a subsample of the amount necessary for the laboratory is then obtained. Quite a great deal more of the sample should be secured than is necessary for the analysis and this quantity may be called the "Industrial Sample." When the industrial sample, more or less voluminous, reaches the laboratory, the chemist is to begin by taking a note of the marks, labels and descriptions found thereon, and of the nature and state of the package which contains it and the date of its arrival. All this information should be entered upon the laboratory book and afterwards transcribed on the paper containing the results of the analysis, as well as the name of the person sending it. This having been done, the sample is to be properly prepared in order that a portion may be taken representing the mean composition of the whole.

If it is in a state of fine powder, such as ground phosphates and certain other fertilizers, it is sufficient to pass it two or three times through a sieve with meshes one millimeter in diameter, taking care to break up the material each time in order to mix it and to pulverize the fragments which the sieve retains. The whole is afterwards spread in a thin layer upon a large sheet of paper and a portion is taken here and there upon the point of a knife until about twenty grams are removed, and from this the portion subjected to analysis is afterwards taken.

If the sample comes in fragments, more or less voluminous, such as phosphatic rocks or coarsely pulverized guanos contain-

ing agglomerated particles, it is necessary first to reduce the whole to powder by rubbing it in a mortar or by using a small drug mill. It is next passed through a sieve of the size mentioned above and that which remains upon the sieve pulverized anew until all has passed through. This precaution is very important, since the parts which resist the action of the pestle most have often a composition different from those which are easily broken.

When the products to be analyzed contain organic materials, such as horn, flesh, dry blood, etc., the pulverization is often a long and difficult process, and results in a certain degree of heating, which drives off some of the moisture in such a way that the pulverized product is at the last drier, and, consequently, richer than the primitive sample. It is important to take account of this desiccation, and since the pulverization of a mass so voluminous can not be made without loss, the determination of the total weight of the sample before and after pulverization does not give exact results. In such a case it is indispensable to determine the moisture both before and after pulverizing, and to calculate the analytical results obtained upon the pulverized sample back to the original sample. In order to escape this necessity, as well as the difficulties resulting from the variations in moisture during transportation, some chemists have thought it better to always dry the commercial products before submitting them to analysis, and to report their results in the dry state, accompanied by a determination of the moisture, leaving thus to the one interested the labor of calculating the richness in the normal state, that is to say, in the real state in which the merchandise was delivered.

In addition to the fact that this method allows numerous chances of errors, many substances undergoing important changes in their composition by drying alone, it has been productive of the most serious consequences. The sellers have placed their wares on the market with the analysis of the material in a dry state, and a great number of purchasers have not perceived the fraud concealed under this expression so innocent in appearance. It is thus that there has been met with in the markets guano containing twenty-five per cent. of water, which was guaranteed to

contain twelve per cent. of phosphoric acid, when in reality it contained only eight per cent. in the moist state.

17. Barn-Yard Manures.—The sampling of stall and barn-yard manures is more difficult on account of the fact that the materials are not homogeneous and that they are usually mixed with straw and other débris from the feed trough, and only the greatest care and patience will enable the operator to secure a fair sample.

In the case of liquid manures the liquid should be thoroughly stirred before the sample is taken. In a given case the difficulty of securing representative samples of stall manure is described and also methods of removing it.⁵ The stall manure sampled had been piled in the cattle-yard for a time and the cattle were allowed to run over the heaps for an hour or two each day. Pigs were allowed free access to the heaps in order to insure a more perfect mixture of the ingredients.

Twenty-nine loads of 3000 pounds each were sampled from the exposed heap and 34 loads of 2000 pounds each were sampled from the covered heap. From each load were removed two carefully selected portions of 10 pounds each, which were placed in separate covered boxes numbered A and B. When the sampling was completed these boxes were covered. After being removed to the laboratory the boxes were weighed and the contents thoroughly mixed. Two samples of 12 liters each were drawn from each box. One-third of this was chopped in a large meat chopper and the other two-thirds taken into the laboratory without being cut. These samples, on entering the laboratory, were weighed and dried at a temperature of 60° to secure the samples for analysis.

18. Sampling of Materials Used for Road Building.—The materials of which roads are built, especially the rock materials, have of late years been subjected to careful scientific examination. The methods may be applied also to minerals containing fertilizer ingredients. In the examination of rocks and rock materials which are used to build roads, the sample which is sent should be large enough to give assurance that it practically represents the materials employed. For this purpose not less than 30 pounds

⁵ Proceedings 12th and 13th Meetings of the Society for the Promotion of Agricultural Science, 1891-2 : 139.

of the sample should be secured. If there seems to be any reasonable doubt regarding the character of the sample, its source should be investigated and a proper sample secured. In general, the principles which should guide the securing of samples of this kind of material are those which are in vogue for ordinary mineral analyses, save the larger quantity of road material which is usually required.

19. Absence of Official Methods.—Although the proper study of a fertilizer has its chief economic value when the analysis is conducted on a representative sample, the official chemists have given but scant attention to the subject of sampling. It is evident that a detailed description of the procedure to be followed in each case would be practically impossible. In such a variety of compounds as is presented by fertilizing materials and fertilizers, and especially manures, the good judgment of the chemist in charge of the sample must point the way to securing reasonably satisfactory results. Patience and ingenuity will lead to the solution of the most intricate problems which may arise.

20. Method of the French Experiment Stations.—In the method employed by the French experiment stations, it is directed that in no case should stones or other foreign particles be removed from the fertilizer sampled, but they should enter into the sample in, as nearly as possible, the same proportions as they exist in the whole mass.

In the case of stones or other solid masses which are to be sampled, as many portions as possible should be taken from all parts of the heap and these should be reduced to a coarse powder, thoroughly mixed together and sampled.

In case the material is in the form of a paste, if it is homogeneous, it will be sufficient to mix it well; but in case there is a tendency for the pasty mass to separate into two parts, of which the one is a liquid and the other more of a solid consistence, it may be well to get samples from each in case they can not be thoroughly incorporated by stirring.

21. Method of the French Association of Sugar Chemists.—The method adopted by the French sugar chemists directs that the sampling should begin with the fertilizer in bulk or from a portion

used for industrial purposes. The part for analysis is to be taken from the above sample after it has been sent to the laboratory. The method of procedure should be varied according to the condition of the substances to be analyzed.

The large sample selected from the goods delivered to commerce having been delivered at the laboratory, the analytical sample is obtained as described in 16.

22. Method of the International Congress of Applied Chemistry.

—The committee designated by the Fifth International Congress of Applied Chemistry has formulated the following general principles of sampling fertilizers and component materials thereof.⁶

1. Samples not drawn in accordance with these regulations are to be refused by official analysts, such refusal being recorded on the certificate.

2. Samples are only to be considered as properly identified, if drawn during unloading on railway or quay, in the presence of representatives of both parties, or by a sworn sampler, and in accordance with these regulations.

3. In the case of manufactured products, a sample is to be secured by means of a sampling iron from every tenth bag, or if the material is in bulk, from at least ten different places throughout the parcel.

4. In the case of shiploads of raw materials every fiftieth bag or bucketful during discharge (corresponding to two per cent. of the whole) is to be set aside, and from this, after first crushing to at least the size of a hazel-nut, a sample is to be removed for the determination of moisture; a further sample for the determination of the constituents of value is to be obtained in the same way as in the case of manufactured products after the sample has been reduced to a fine state by grinding and sifting.

5. The samples—in weight about 300 grams—are to be filled loosely into strong, clean and absolutely dry glass bottles.

6. At least three samples are to be prepared. The bottles are to be hermetically closed and sealed by the persons conducting the sampling.

⁶ Fünfter, Internationaler Kongress für angewandte Chemie, Bericht, 1904, 4 : 937.

7. The labels are to be signed by the persons supervising the sampling and are to be attached by means of the wax used in sealing the bottles.

8. The samples are to be kept in a cool, dark and dry place.

9. Materials of heterogeneous composition must be sufficiently reduced in size and mixed before bottling.

23. Influence of State of Subdivision.—The importance of good sampling in securing reliable analytical data is shown by Rivière by comparing the results of analysis of samples from different parts of the same bulk material.⁷ The substance examined was dried blood. A sample received from a farmer was passed as customary through a mill and contained 9.95 per cent. of nitrogen. This being lower than the guaranty, led to asking for a new sample of not less than 500 grams. In this sample there were found 11.20 per cent. of nitrogen. The sample was then divided into two portions by means of a sieve. The fine part, 204 grams, contained 9.40 per cent. of nitrogen and the coarse part 12.10 per cent. The two portions were again mixed and a sample analyzed contained 11.14 per cent. of nitrogen. It is evident from the above data that in transportation the fine particles tend to go to the bottom and the large to be collected on the top of the mass so that even were it well mixed at the start, at the end of the journey samples from different parts would show varying contents of nitrogen.

24. Preparation of Sample in Laboratory.—The method of preparing mineral fertilizers for analysis has been given under the directions for sampling. Many difficulties attend the proper preparation of other samples, and the best approved methods of procedure are given below.

According to the directions given by the Association of Official Agricultural Chemists the sample should be well intermixed, finely ground, and passed through a sieve having circular perforations one millimeter in diameter.⁸ The processes of grinding and sifting should take place as rapidly as possible so that there may be no gain or loss of moisture during the operation.

⁷ L'Engrais, 1905, 20 : 233.

⁸ Division of Chemistry, Bulletin 46, Revised, 1899 : 11.

25. Method of the International Commission.—The methods adopted by the international commission are as follows:

(a) Dry samples of phosphates or other artificial manures may be simply sifted and then mixed.

(b) In the case of damp materials, where the above procedure is not possible, the preparation must be confined to a careful mixing by hand.

(c) In the case of raw phosphates and animal charcoal, a water determination is to be made, as confirmatory evidence.

(d) In dealing with substances which are apt to lose water during grinding, the moisture is to be determined both before and after the preparation of the sample, the results of the analysis being afterwards calculated back into the original hygroscopic condition of the sample as received.

26. Method of the French Agricultural Stations.—The manner of proceeding recommended by the French stations varies with the fertilizer.⁹ If it is not already in the form of a powder it is necessary to pulverize it as finely as possible by rubbing it up in a mortar. In certain cases, as with superphosphates, the material should be passed through a sieve having apertures of one millimeter diameter, all the larger parts being pulverized until they will pass this sieve.

When the matters are too pasty to be divided in the mortar they should be divided by means of a knife or a spatula. They should then be incorporated with a known weight of inert, pulverulent matter such as fine sand, with which they should be thoroughly mixed and in subsequent calculations the quantity of sand or other inert matter added must be taken into consideration. Usually a pasty state of a fertilizer is due to the humidity of the mixture. In this case a considerable volume of the sample is dried and then reduced to a pulverulent state. In the subsequent calculations, however, the percentage of moisture lost must be taken into consideration.

Before drying a sample it is necessary to take into consideration whether or not the product will be modified by desiccation

⁹ Grandeau, *Traité d'Analyse Matières des agricoles*, 3rd Edition, 1897, 1 : 409.

as would be the case, for instance, with superphosphates. With these, which are often in a state more or less agglomerated, it is recommended to introduce, in order to divide them, a certain quantity of calcium sulfate to reduce them to a pulverulent state.

In the case of animal débris they should be divided as finely as possible with the aid of scissors and then passed through a drug mill if dry enough. They are then mixed by hand and may finally be obtained in a state of considerable homogeneity.

When fertilizers are in a pasty state or more or less liquid, they are dried at 100° , first introducing a little oxalic acid in case they contain any volatile ammoniacal compounds. The product of desiccation is then passed through a mill. Before treating in this way it is necessary to be sure that the composition will not be altered by drying. In the case of a mixture containing superphosphates and nitrate, for instance, drying would eliminate the nitric acid. In such a case the free phosphoric acid should be neutralized with a base like lime. In the case of fertilizers containing both nitrates and volatile ammoniacal compounds, the addition of oxalic acid might also set free nitric acid during the desiccation. In such a case it is necessary to dry two samples; one with the addition of oxalic acid for the purpose of estimating the ammonia, and the other without the acid for the purpose of estimating the nitrate. A qualitative analysis should precede all the operations so as to determine the nature of the material to be operated on.

27. German Method.—In the method pursued by the German experiment stations the manipulation is conducted as follows:¹⁰

(1) Dry samples of fertilizers must be passed through a sieve and afterwards well mixed.

(2) With moist fertilizers, which can not be subjected to the above process, the preparation should consist in a careful and thorough mixing, without sieving.

(3) On the arrival of the samples in the laboratory their weight should be determined. The half of the sample is prepared for analysis and the other part, to the amount, at least, of a kilogram, should be placed in a glass vessel, closed air-tight, and

¹⁰ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 303.

left in a cool place for at least a quarter of a year from the time of its reception, in order that it may be subjected to any subsequent investigations which may be demanded.

(4) In the case of raw phosphates and bone-black the amount of water which they contain should be determined at from 105° to 110° . Samples which in drying lose ammonia in any way, should have this ammonia determined.

(5) Samples which are sent to other laboratories for control analyses should be securely packed in air-tight glass bottles.

(6) The weight of the samples should be entered in the certificates of analysis.

(7) Samples which, on pulverizing, change their content of water, must have the water content estimated in both the coarse and powdered condition and the results of the analysis must be calculated to the water content of the original coarse substance.

28. Special Cases.—Many cases arise of such a nature as to make it impossible to lay down any rule which can be followed with success. As in almost every other process in agricultural chemistry, the analyst in such cases must be guided by his judgment and experience. Keeping in view the main object, viz., to secure in a few grams of material a fair representation of large masses, he will generally be able to reach the required result by following the broad principles already outlined. In many cases the details of the work and the adaptations necessary to success must be left to his own determination. In all special cases the methods of securing the samples should accompany the analytical data.

DRYING SAMPLES OF FERTILIZERS

29. Difficulties of Desiccation.—The determination of the uncombined moisture in a sample of fertilizer is not an easy task. In some cases, as in powdered minerals, drying to constant weight at the temperature of boiling water is sufficient. In organic matters containing volatile nitrogenous and other compounds these must first be fixed by oxalic or sulfuric acid, before the desiccation begins. If any excess of sulfuric acid be added, however, drying at 100° becomes almost impossible. Particular precautions must be observed in drying superphosphates. In

drying samples preparatory to grinding for analysis it is best to stop the process as soon as the materials can be pulverized. In general, samples should be dried only to determine water, and the analytical processes should be performed on the undried portions. It is not necessary, as a rule, to dry samples of mineral fertilizers in an inert atmosphere, such as hydrogen or carbon dioxide. Drying in vacuo may be practiced when it is desired to secure a speedy desiccation or one at a low temperature.

30. Official Methods.—The official agricultural chemists direct, in the case of potash salts, sodium nitrate, and ammonium sulfate, to heat from one to five grams at about 130° until the weight is constant.¹¹ The loss in weight is taken to represent the water. For all other fertilizers heat two grams, or five grams if the sample be very coarse, for five hours in a steam bath. The international commission prescribes heating to constant weight at 100° , using 10 grams of material. Substances containing gypsum are dried for three hours. Potash salts are dried in harmony with the regulations prescribed by the potash syndicate at Leopoldshall, Stassfurt.

In the German stations in the case of untreated phosphates and bone-black the moisture is estimated at from 105° to 110° . Samples which lose ammonia should have the weight of ammonia given off at that temperature, determined separately.

31. General Observations.—For purposes of comparison it would be far better to have all contents of moisture determined at the boiling point of water. While this varies with the altitude and barometric pressure yet it is quite certain that the loss on drying to constant weight at all altitudes is practically the same. Where the atmospheric pressure is diminished for any cause the water escapes all the more easily. This, practically, is a complete compensation for the diminished temperature at which water boils.

Only in the case where free sulfuric or phosphoric acid is present would this method be ineffective. The highly hygroscopic nature of these acids in a concentrated state renders desiccation at such a temperature practically impossible. In such cases a weighed ex-

¹¹ Division of Chemistry, Bulletin 46, 1899 : 11.

cess of base should be added to convert the acids into sulfates or phosphates.

Where the samples contain no ingredient capable of attacking aluminum, they can be conveniently dried, in circular dishes of this metal about seven centimeters in diameter and one centimeter deep, to constant weight, at the temperature of boiling water.

32. Moisture in Monocalcium Phosphates.—In certain fertilizers, especially superphosphates, containing the monocalcium salt, the estimation of water is a matter of extreme difficulty on account of the presence of free acids and of progressive changes in the sample due to different degrees of heat.

Stoklasa has studied these changes and reaches the following results:¹²

A chemically pure monocalcium phosphate of the following composition, viz.,

CaO.....	22.36 per cent.
P ₂ O ₅	56.67 " "
H ₂ O.....	21.53 " "

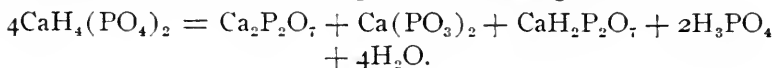
was subjected to progressive dryings. The loss of water after 10 hours was 1.83 per cent.; after 20 hours, 2.46 per cent.; after 30 hours, 5.21 per cent.; after 40 hours, 6.32 per cent.; after 50 hours, 6.43 per cent. The loss of water remained constant at 6.43 per cent. This loss represents one molecule of water as compared with the total molecular magnitude of the mass treated. A calcium phosphate, therefore, of the following composition, CaH₄(PO₄)₂.H₂O loses, after 40 hours drying at 100°, its water of crystallization. The calcium phosphate produced by this method forms opaque crystals which are not hygroscopic and which give, on analysis, the following numbers:

CaO.....	24.02 per cent.
P ₂ O ₅	60.74 " "
H ₂ O.....	15.00 " "

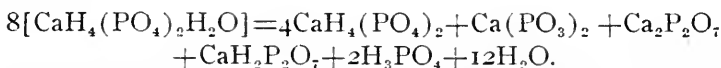
The temperature can be raised to 105° without marked change.

¹² Zeitschrift für analytische Chemie, 1890, 29 : 390.

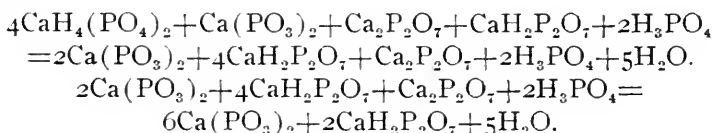
If the temperature be raised to 200° the decomposition of the molecule is hastened according to the following formula:



The chemical changes during the drying of monocalcium phosphates can be represented as follows, temperature 200° for one hour:



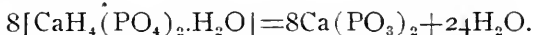
The further drying at 200° produces the following decomposition:



Finally, pyrophosphate at 210° is completely decomposed into metaphosphate and water according to the following formula:



Provided the drying is made at once at 210° the sum of the changes produced as indicated above, can be represented by the following formula:



The equations are to be considered as applying only to a pure monocalcium salt.

MINERAL PHOSPHATES

33. Natural Occurrence of Phosphates.—Gautier calls attention to the fact that the oldest phosphates are met with in the igneous rocks, such as basalt, trachyte, etc., and even in granite and gneiss.¹³ It is from these inorganic sources, therefore, that all phosphatic plant food must have been drawn. In the second order in age Gautier places the phosphates of hydro-mineral origin. This class not only embraces the crystalline apatites but also those phosphates of later formation formed from hot mineral waters in the jurassic, cretaceous, and tertiary deposits. These deposits are not directly suited to nourish plants.

¹³ *Comptes rendus*, 1893, **116**: 1271.

The third group of phosphates in order of age and assimilability embraces the true phosphorites containing generally some organic matter. They are all of organic origin.

In caves where animal remains are deposited there is an accumulation of nitrates and phosphates. Not only do the bones of animals furnish phosphates but they are also formed in considerable quantities by the decomposition of substituted glycerids such as lecithin. The ammonia produced by the nitrification of the albuminoid bodies combines with the free phosphoric acid thus produced, forming ammonium or diammonium phosphates. The presence of ammonium phosphates in guanos was first noticed by Chevreul.

If such deposits overlay a pervious stratum of calcium carbonate, such as chalk, and are subject to leaching, a double decomposition takes place as the lye percolates through the chalk. Acid calcium phosphate and ammonium carbonate are produced. By further nitrification and solution the latter becomes finally converted into calcium nitrate. In like manner aluminum phosphates are formed by the action of decomposing organic matter on clay.

Davidson explains the origin of the Florida phosphates by suggesting that they arose chiefly through the influx of animals driven southward during the glacial period.¹⁴ According to his supposition, the waters of the ocean, during the cenozoic period, contained more phosphorus than at the present time. The waters of the ocean over Florida were shallow and the shell fish existing therein may have secreted phosphate as well as carbonate of lime. This supposition is supported by an analysis of a shell of *lingula ovalis*, quoted by Dana, in which there was 85.79 per cent. of lime phosphate. In these waters were also many fishes of all kinds and their débris served to increase the amount of phosphatic material. As the land emerged from the sea came the great glacial epoch, driving all terrestrial animals southward. There was, therefore, a great mammal horde in the swamps and estuaries of Florida. The bones of these animals contributed largely to the phosphatic deposits. In addition to

¹⁴ Wyatt, *Phosphates of America*, 4th Edition, 1892 : 66.

this, the shallow sea contained innumerable sharks, manatees, whales, and other inhabitants of tropical waters, and the remains of these animals added to the phosphatic store.

While these changes were taking place in the quarternary period, the Florida peninsula was gradually rising, and as soon as it reached a considerable height the process of denudation by the action of water commenced. Then there was a subsidence and the peninsula again passed under the sea and was covered with successive layers of sand. The limestone during this process had been leached by rain water containing an excess of carbon dioxid. In this way the limestone was gradually dissolved while the insoluble phosphate of lime was left in suspension. During this time the bones of the animals before mentioned by their decomposition added to the phosphate of lime present in the underlying strata, while some were transformed into fossils of phosphate of lime just as they are found to-day in vast quantities.

Wyatt explains the phosphate deposits somewhat differently.¹⁵ According to him, during the miocene submergence there was deposited upon the upper eocene limestone, more especially in the cracks and fissures resulting from their drying, a soft, finely disintegrated calcareous sediment or mud. The estuaries formed during this period were swarming with animal and vegetable life, and from this organic life the phosphates were formed by decomposition and metamorphism due to the gases and acids with which the waters were charged.

After the disappearance of the miocene sea there were great disturbances of the strata. Then followed the pliocene and tertiary periods and quarternary seas, with their deposits and drifts of shells, sands, clays, marls, boulders, and other transported materials supervening in an era when there were great fluctuations of cold and heat.

By reason of these disturbances the masses of the phosphate deposits which had not been infiltrated in the limestone became broken up and mingled with the other débris and were thus deposited in various mounds or depressions. The general result

¹⁵ Engineering and Mining Journal, 1890, 50 : 218.

of the forces which have been briefly outlined was the formation of bowlders, phosphatic débris, etc. Wyatt therefore classifies the deposits in Florida as follows:

1. Original pockets or cavities in the limestone filled with hard and soft rock phosphates and débris.
2. Mounds or beaches, rolled up on the elevated points, and chiefly consisting of huge bowlders of phosphate rock.
3. Drift or disintegrated rock, covering immense areas, chiefly in Polk and Hillsboro counties, and underlying Peace River and its tributaries.

Darton ascribes the phosphate beds of Florida to the transformation of guano.¹⁶ According to this author, two processes of decomposition have taken place. One of these is the more or less complete replacement of the carbonate by the phosphate of lime. The other is a general stalactitic coating of phosphatic material. Darton further calls attention to the relation of the distribution of the phosphate deposits as affecting the theory of their origin, but does not find any peculiar significance in the restriction of these deposits to the western ridge of the Florida peninsula.

As this region evidently constituted a long narrow peninsula during early miocene time it is a reasonably tentative hypothesis that during this period guanos were deposited from which was derived the material for the phosphatization of the limestone either at the same time or soon after.

Darton closes his paper by saying that the phosphate deposits in Florida will require careful detailed geologic exploration before their relations and history will be fully understood.

According to Dr. N. A. Pratt the rock or bowlder phosphate had its immediate origin in animal life and to his view the phosphate bowlder is a true fossil. He supposes the existence of some species in former times in which the shell excreted was chiefly phosphate of lime. The fossil bowlder, therefore, becomes the remains of a huge foraminifer which had identical composition in its skeleton with true bone deposits or of organic matter.

¹⁶ American Journal of Science, 1891, 41 : 104.

Perhaps the most complete exposition of the theory of the recovery of waste phosphates, with especial reference to their deposit in Florida, has been given by Eldridge.¹⁷ He calls attention to the universal presence of phosphates in sea water and to the probability that in earlier times, as during the miocene and eocene geological periods, the waters of the ocean contained a great deal more phosphate in solution than at the present time. He cites the observations of Bischof, which show the solubility of different phosphates in waters saturated with carbon dioxid. According to these observations apatite is the most insoluble form of lime phosphate, while artificial basic phosphate is the most soluble. Among the very soluble phosphates, however, are the bones of animals, both fresh and old. Burnt bones, however, are more soluble than bones still containing organic matter. Not only are the organic phosphates extremely soluble in water saturated with carbon dioxid, but also in water which contains common salt or chlorid of ammonium. The presence of large quantities of common salt in sea water would, therefore, tend to increase its power of dissolving lime phosphates of organic origin. It is not at all incredible, therefore, to suppose that at some remote period the waters of the ocean, as indicated by these theories, were much more highly charged with phosphates in solution than at the present time.

According to Eldridge, the formation of the hard-rock and soft phosphates may be ascribed to three periods: First, that in which the primary rock was formed; second, that of secondary deposition in the cavities of the primary rock; third, that in which the deposits thus formed were broken up and the resulting fragments and comminuted material were redeposited as they now occur.

“The first of these stages began probably not later than the close of the older miocene, and within the eocene area it may have begun much earlier. Whether the primary phosphate resulted from a superficial and heavy deposit of soluble guanos, covering the limestones, or from the concentration of phosphate

¹⁷ Preliminary Sketch of Florida Phosphates, Author's Edition : 18.

of lime already widely and uniformly distributed throughout the mass of the original rock, or from both, is a difficult question. In any event, the evidence indicates the effect of the percolation of surface waters highly charged with carbonic and other acids, and thus enabled to carry down into the mass of the limestone dissolved phosphate of lime, to be redeposited under conditions favorable to its separation. Such conditions might have been brought about by the simple interchange of bases between the phosphate and carbonate of lime thus brought together; or by the lowering of the solvent power of the waters through loss of carbonic acid. The latter would happen whenever the acid was required for the solution of additional carbonate of lime, or when, through aeration, it should escape from the water. The zone of phosphate deposition was evidently one of double concentration, resulting from the removal of the soluble carbonate thus raising the percentage of the less soluble phosphate, and from the acquirement of additional phosphate of lime from the overlying portions of the deposits.

“The thickness of the zone of phosphatization in the eocene area is unknown, but it is doubtful if it was over 20 feet. In the miocene area the depth has been proved from the phosphates *in situ* to have been between six and 12 feet.”

The deposits of secondary origin, according to Eldridge, are due chiefly to sedimentation, although some of them may have been due to precipitation from water. This secondary deposition was kept up for a long period, until stopped by some climatic or geological change. The deposits of phosphates thus formed in the Florida peninsula are remarkably free from iron and aluminum in comparison with many of the phosphates of the West Indies.

The third period in the genesis of the hard rock deposits embraces the time of formation of the original deposits and their transportation and storage as they are found at the present time. The geological time at which this occurred is somewhat uncertain but it was probably during the last submergence of the peninsula. In all cases the peculiar formation of the Florida limestone must be considered. This limestone is extremely porous and

therefore easily penetrated by the waters of percolation. A good illustration of this is seen on the southwestern and southern edges of Lake Okeechobee. In following down the drainage canal which has been cut into the southwest shore of the lake, the edge of the basin which is composed of this porous material may be seen. The appearance of the limestone would indicate that large portions of it have already given way to the process of solution. The remaining portions are extremely friable, easily crushed, and much of it can be removed by the ordinary dredging machines. Such a limestone as this is peculiarly suited to the accumulation of phosphatic materials due to the percolation of the water containing them. The solution of the limestone and consequent deposit of the phosphate of lime is easily understood when the character of this limestone is considered.

Shaler as quoted by Eldridge in the work already referred to, refers to this characteristic of the limestone and says that the best conditions for the accumulation of valuable deposits of lime phosphate in residual débris appear to occur where the phosphatic lime marls are of a rather soft character; the separate beds having no such solidity as will resist the percolation of water through innumerable incipient joints such as commonly pervade stratified materials, even when they are of a very soft nature.

Eldridge is also of the opinion that the remains of birds are not sufficient to account for the whole of the phosphatic deposits in Florida. He ascribes them to the joint action of the remains of birds, of land and marine animals, and to the deposition of the phosphatic materials in the waters in the successive subsidences of the surface below the water line.

An important contribution to our knowledge of the origin of Florida phosphates has been made by Dall.¹⁸ After describing the early geological epochs in the southern part of the United States, Dall calls attention to the abundance of foraminifera, whose shells form deposits of limestone, which, in southern Florida, have been found to be nearly 2000 feet in thickness.

The deposit of rocks which is known geologically as the Vicks-

¹⁸ The American Fertilizer, 1898, 8 : 108.

burg type is composed entirely of organic material, that is, lime, clay, siliceous and iron taken up by marine animals from the water in which they lived and deposited as limestone.

Toward the end of the Vicksburg epoch a movement in elevation began which brought above the sea level a part of the land in the vicinity of Ocala, forming an island or group of islands between Cuba and the mainland, and the evidence is very strong that these low islands, containing numerous lagoons of fresh water and wooded with palms, reeds and other subtropical vegetation, remained as dry land from that time to the present. At the same time the low borders of the continent began to rise above the sea, forming a coastal plain of marshes and lagoons inhabited by tortoises, birds and other shore animals. It is well known that birds, seals and similar animals select for their rookeries, when possible, such islets as those described. Such locations give them security from predaceous animals, and an undisturbed breeding place for their young.

As phosphoric acid has a greater affinity for lime than carbonic acid, the carbonate of lime in such localities became converted into the less soluble phosphate of lime, and as the process was continued for thousands of years, in all probability, the first steps in the formation of the invaluable phosphate beds of Florida were taken in this way.

34. Character and Origin of the Tennessee Phosphates.—Some of the most extensive and valuable deposits of phosphates in the United States occur in Tennessee. The existence of these deposits in commercial quantities was first pointed out in 1893 and since that time elaborate examinations of the extent and character of the deposits have been made by the U. S. Geological Survey.¹⁹

35. Classification.—The phosphates of Tennessee are divided

¹⁹ Hayes, *The Tennessee Phosphates*, 17th Annual Report of the Geological Survey, 1895-96, Part II : 519.

Hayes, *Tennessee White Phosphate*, 21st Annual Report of the Geological Survey, 1899-1900, Part III : 478.

Geological Atlas of the U. S., Columbia Folio, Tennessee.

Hovey, *The Production of Phosphate Rock in 1903*, Geological Survey, Mineral Resources of the United States, 1903 : 1047.

into two principal classes each of which has a number of varieties. The two main groups are designated by their color, the black phosphate, which represents the original deposition, and the white phosphate, which is a secondary deposition or replacement. The first group belongs to the Devonian age, and its members have been changed from their original form only by the process of consolidation which affects all deeply buried sediments; that is, they have been changed from a condition of mud and sand into compact rock exactly in the same manner as the non-phosphatic bodies above and below them. The white phosphates, on the other hand, probably do not occupy the position and form they had when first deposited. The material composing them has been translated from its original position and redeposited in an entirely different form.

The white phosphates are of comparatively recent origin, probably having been formed in the last geological period preceding the present.

36. Occurrence of Black Phosphate.—The black phosphates occur first in a nodular condition associated with green sandy shale. The nodules vary in size and shape from nearly spherical bodies from one-half to one and a half inches in diameter, to irregular flattened ellipsoids, sometimes two feet in length and one-third or one-quarter as thick. Their surfaces are smooth and show no external evidence of organic origin. In weathering they produce almost a white powder, with fine and concentric banding of different shades of gray. Thin sections examined under the microscope appear to be chiefly amorphous, with grains of pyrite and organic matter. In some of the nodules there is a concentric arrangement of the material, which is easily separated. The nodules in the lower layers are the largest. The number of nodules varies largely within short distances. The nodules contain from 60 to 70 per cent. of tricalcium phosphate. There is a somewhat larger percentage of this substance in the weathered than in the unweathered rock. The nodules are easily separated from the materials in which they are imbedded, so that even when they are not sufficiently numerous to form almost continuous layers they can be mined with profit.

The black phosphate also occurs in a bedded form and presents several varieties. Among these may be mentioned oolitic phosphate, which has the appearance of a rusty, porous sandstone. The general appearance of the ovules of which the mass is made indicates that they were formed while lying free upon the sea bottom. In the phosphatic limestone which at some points underlies the phosphate bed, the same ovules and rounded fossil casts are seen scattered through the mass of calcitè. Another variety of this bedded stone is known as compact phosphate, resembling a homogeneous, finely grained sandstone. The phosphatic grains of this rock are so small that they are distinguished with difficulty even with a magnifying glass. The composition of the rock, however, is revealed in a thin section under the microscope, and it is shown to be made up of small ovules and fossil casts closely packed together. The ovules are nearly all flattened and are arranged with their long axes parallel.

Another variety is the conglomerate phosphate, which is closely associated with the oolitic and compact varieties, often entirely replacing them and consisting of beds of coarse sandstone or conglomerate containing various amounts of phosphate. These conglomerates are usually black or gray and the constituent grains are embedded in a matrix of fine material. They vary in size from extremely fine grains to coarse particles one-fourth of an inch in diameter. They are partly phosphate ovules, similar to those composing the oolitic rock, and partly quartz. The conglomerate also contains many weather worn pebbles which are an inch or more in diameter and composed of hard, black phosphate so fine grained and homogeneous as to resemble black flint.

There is also another variety known as shaly phosphate, in which the laminated structure is pronounced, the rock splitting into extremely thin sheets. In other instances the layers are an inch or several inches in thickness, having a black glazed surface even more carbonaceous than the remainder of the rock.

37. Occurrence of White Phosphates.—The white phosphates apparently present two types; namely, the breccia and the bedded phosphate. Closer examination shows that the two varieties are more nearly related than was at first supposed, and they are found

grading into each other imperceptibly, so that the distinctions which were supposed to exist tend to disappear on more careful examination. The result of this gradual merging has led to the dropping of the original classification and the bringing of the white phosphate into one group with a few slightly different varieties.

Whatever may have been the original form of this rock, the phosphatic deposit is evidently secondary and is intimately associated with the rocks of the carboniferous period. The sections of this variety of phosphatic rock exhibit under the microscope masses of silica in which are bedded rhombohedral crystals, sometimes very small and widely scattered, but perfect and sharply defined. In the granular portions of the rock the crystals are larger, appearing as sections of rhombohedrons which are not perfectly independent, but are segregated into irregular groups. These crystals, which have the form of calcite, have been entirely changed in their structure by the secondary deposit. Phosphate of lime, in other words, has practically taken the place of the carbonate of lime in these crystals. The following analyses, made under the direction of Monroe, show the composition of this form of Tennessee white phosphate:²⁰

ANALYSES OF TENNESSEE WHITE STONY PHOSPHATE.

	1	2	3	4	5	6
Silica, SiO ₂	61.34	49.43	54.30	54.88	50.18	56.46
Lime, CaO	20.30	26.40	22.87	22.76	25.57	22.01
Phosphoric acid, P ₂ O ₅	12.55	15.12	14.86	15.30	15.21	13.15
Corresponding to:						
Lime phosphate, Ca ₃ P ₂ O ₈ , and..	27.40	33.00	32.45	33.40	33.20	28.60
Lime carbonate, CaCO ₃	9.75	15.21	9.36	8.23	13.45	11.56

38. Breccia Phosphate.—The breccia is the most abundant variety of the white phosphate. It occurs in irregular masses composed of slightly angular fragments of carboniferous chert imbedded in a matrix of phosphate of lime. The phosphatic matrix before exposure to the weather is of a white or slightly reddish color and somewhat harder than compact chalk.

39. Lamellar Phosphate.—Another variety of the phosphate is the white lamellar, consisting of even, parallel layers or plates. It

²⁰ 17th Annual Report of the U. S. Geological Survey, Part II, 1895-6: 539.

has evidently been formed by deposition of solutions, successive layers being slightly different in color and texture. In numerous cases the deposition seems to have taken place in a rather smooth cavity which was but partly filled with the deposited solution, so that deposition took place only on the bottom.

40. Origin of the White Phosphates.—According to Hayes, the white phosphates of Tennessee originated as follows:²¹

From the nature of the deposits of white phosphate, their relations to other formations of the region, and the physical characteristics of the several varieties of the rock, there can be little doubt as to their mode of deposition. It seems reasonably certain that the rock is entirely a secondary deposit, accumulated subsequently to the deposition of the carboniferous, Devonian and Silurian formations, with which it is now associated. The latter were laid down on the sea bottom as horizontal beds of sand, mud and shells, having great lateral extent. They were buried beneath other beds of sediment many hundred feet in thickness, which have since been removed by erosion. The black phosphate, as has already been explained, is one such sedimentary bed which was deposited when the conditions were favorable for the accumulation of lime phosphate on the sea bottom. It was afterwards deeply buried by later deposited sediments, and has been brought to light by elevation of the sea bottom and erosion of the overlying strata.

Entirely different is the formation of the white phosphate. The lime phosphate of which these deposits are composed was doubtless originally extracted from sea water by organisms and accumulated together with other sediments, either segregated in beds and concretions or disseminated through limestones and shales. When these rocks were brought near the surface by uplift and erosion they were attacked by percolating surface waters, which contain carbonic and other organic acids. These acids readily dissolve carbonate of lime, and to some extent also phos-

²¹ The Tennessee Phosphates, by C. W. Hayes. Abstract from the 17th Annual Report of the Geological Survey, 1895-6, Part II, Economic Geology and Hydrography : 356. Also, Extract from the 21st Annual Report of the Geological Survey, 1899-1900, by C. W. Hayes, Part III, General Geology, Ore and Phosphate Deposits : 479.

phate of lime. When water which has slowly percolated through the rocks at some depth emerges at the surface or into a cavity in which it is no longer subjected to pressure, the excess of carbonic acid escapes, and the substances which had been held in solution by means of that acid may be redeposited. Thus many springs are now forming about their exits extensive deposits of materials which they have dissolved in the course of their underground passage. The most common spring deposits are calcareous, although siliceous and aluminous deposits are not uncommon, particularly in the case of thermal waters. When several substances are held in the same solution the least soluble will generally be the first to separate, and hence will form deposits nearer the exits. Also, when a solution of a difficultly soluble substance, as lime phosphate, comes in contact with one which is more easily soluble, as lime carbonate, there is generally an exchange effected—the more soluble substance is taken up and the less soluble one is deposited in its place.

A simple application of these principles suggests the probable mode of formation of these deposits. The altitude at which they are found indicates that they were formed when the valleys of the region had about two-thirds of their present depth. The region was probably heavily forested, the decay of vegetation furnishing an abundant supply of organic acids to the percolating surface waters. It was also a region of sluggish streams, the valleys of which may have been to some extent occupied by swamps. The waters, thus highly charged with organic acids, descending through the more or less porous formations which occupy the higher portions of the country, dissolved calcium carbonate, and, in less quantity, calcium phosphate. The former, by reason of its greater solubility, was carried into the streams and thence to the sea. The phosphate, however, was deposited, the form of the deposits being modified by local conditions. In some cases the waters containing these substances in solution found an outlet in a mass of fragmental chert derived from the decay of the overlying formations. Under such conditions the breccia was formed, the phosphate merely cementing the fragmental material. In other cases the waters flowed through open cavities of consid-

erable size. When these were the interstices among blocks of chert, there resulted the coarse breccia. The cavities were wholly or in part filled with compact phosphate, which shows, by differences of texture and color, that it was deposited from solution in successive layers. In some cases it appears that the cavities were in a pure limestone. After they had been to a greater or less extent filled by the phosphate, by reason of some change in conditions, the limestone was dissolved, leaving the phosphate disseminated through the residual clay, which represents the original insoluble constituents of the limestone. Finally, in some places, instead of finding open cavities in which the phosphate might be deposited, the solution, before emerging at the surface, came in contact with a siliceous limestone under conditions such that a transfer of materials was effected. The more soluble carbonate was taken up and the less soluble phosphate was deposited in its place. These conditions gave rise to the stony variety, in which the phosphate is clearly seen occupying the place originally held by the carbonate.

If this explanation of the origin of these phosphates is the correct one, some important economic conclusions follow as to the extent of the deposits. So long as the waters were percolating slowly and at considerable depths they would take up rather than deposit phosphate. They would find conditions favorable for the latter process only comparatively near the surface, where the excess of carbonic acid might readily escape. Hence the deposits must not be expected to extend to any considerable depth. They are essentially superficial pocket deposits, and in most cases their depth will be limited by the depth of the residual mantle of chert and clay with which they are so intimately associated. It seems probable that the stony variety may extend to greater depths than any of the others, since the process to which it is attributed is one which does not depend directly on surface conditions—the escape of carbonic acid and the evaporation of the solution—but upon some conditions, not fully understood, favoring replacement.

The deposits were probably much more extensive than now. The deepening of the valleys has removed the greater portion of

the original deposits, and those which remain are merely the remnants which have accidentally escaped erosion.

41. Utilization of the White Phosphate.—From the foregoing description of the several varieties of white phosphate it will be readily understood that this rock is not available for shipment without undergoing some process of concentration. That a high-grade product can be obtained by the proper concentration is shown from the numerous analyses of selected hand specimens, which sometimes show as much as 80 per cent. of lime phosphate. Evidently the method of treatment should differ with the different varieties. The analyses already given show that the stony variety contains less than 50 per cent. of lime phosphate, and in it the phosphate is so intimately associated with the silica that no ready means of separating the two elements suggest themselves. In case of the other two varieties, however, the problem of concentration is a much simpler one. In case of the breccia, the properties which may be taken advantage of in separating the chert and the phosphate are, first, differences in specific gravity, and, second, differences in hardness. It has been suggested that the two constituents of the rock may be cheaply separated by some form of jigging apparatus. Determinations of their specific gravity, however, do not offer much encouragement for this view. The chert is found to have a specific gravity varying from 2.61 to 2.69. The matrix of lime phosphate with which it is associated has a gravity of 2.83 to 3.07. This difference of 0.3 or 0.4 is probably not sufficient for any simple and cheap device. The specific gravity of the lamellar variety is somewhat higher than that of the structureless breccia matrix.

The difference in hardness between the chert and the matrix suggests the possibility of making a high-grade concentrate, though not of making a complete separation of the two constituents of the rock. As already stated, when long exposed to the atmosphere the matrix becomes considerably indurated, so that it is separated from the chert with great difficulty. Below the surface, however, it seems probable that the phosphate will generally be found soft and granular, so that it can be easily pulverized and separated from the chert. The chert, on the other hand, shows

little if any change of hardness from that at the surface. If this softer breccia, therefore, were passed through a suitable crusher, most of the phosphate would be pulverized, while the chert would remain in much larger blocks. If the material thus treated were passed over a screen with a proper mesh, which could be determined only by experiments, it seems altogether probable that a fairly complete separation would be effected. The process suggested above would be a simple and cheap one, and, considering the ease with which the rock can be raised, it seems probable that a cheap and merchantable product could be obtained in this manner.

A part of the lamellar variety would require no further treatment than hand picking at the bank. The quantity of such rock, however, is probably not large, and the greater part of this variety will have to be separated from the clay through which it is found disseminated. This would probably necessitate, first, screening in the bank, to separate it from the greater part of the clay; second, washing, to remove the remainder of the clay; and, third, hand-picking, to remove the free chert with which it is associated. None of these processes are expensive, and if careful prospecting shall show this variety to exist in considerable quantities, it can doubtless be prepared for market at slight expense. It is important, however, for the successful development of these deposits that thorough prospecting should precede the erection of a plant for treating the rock. The prospecting should be done in a systematic manner and by a competent engineer.

STATISTICS AND COMPOSITION

42. Tennessee Phosphates.—Tennessee produced during the year 1903, 460,530 pounds of phosphate rock containing from 77 to 80 per cent. of lime phosphate. It is well known that almost all of the rich phosphates produced in Florida are exported to Europe.²² Of the rich phosphates produced in Tennessee, however, only about one-fourth are sent to Europe. The other three-fourths are consumed in this country. The Tennessee phosphates are not looked upon with very great favor in Europe because of their content of iron and alumina. Five samples of

²² *Annales de Chimie analytique*, 1906, 11 : 256.

Tennessee phosphate were found to have the following composition :

	1	2	3	4	5
Insoluble (silica, etc.).....	1.31	2.56	1.85	2.16	5.87
Phosphoric acid.....	36.55	36.55	35.47	35.50	32.85
Phosphate of lime.....	79.80	79.80	77.45	77.50	71.73
Oxid of iron and alumina	2.00	2.48	3.16	3.88	4.52
Carbonate of lime	13.27	12.05	11.46	14.29	9.93
Organic matters and water	3.62	3.11	6.08	3.17	7.95

The above samples belong to what is known as the Brown Rock and come chiefly from the vicinity of Mt. Pleasant in Maury County.

43. Blue Phosphate.—In Hickman County, which is adjacent to Maury County, large quantities of phosphate rock are found of a bluish gray tint and less rich in phosphate of lime than the deposits above mentioned. These rocks are found to contain from 60 to 70 per cent. of phosphate of lime, and from 2.5 to 5 per cent. of oxids of iron and alumina and from 1.5 to 5 per cent. of silica. The iron exists in these rocks partly in the form of pyrite. In Perry County another variety of phosphate of a reddish or white color is found with a still lower content of phosphate of lime, ranging from 30 to 50 per cent. These samples come from the surface. The interior deposits, on the contrary, are quite rich, containing from 70 to 75 per cent. of phosphate of lime. Still other deposits are found in Tennessee containing from 77 to 80 per cent. of phosphate of lime and from two to three per cent. of oxids of iron and alumina.

44. Phosphates from South Carolina Deposits.—It has been estimated that up to the present time there have been furnished to the markets from the South Carolina deposits about 11,000,000 tons of rock, of which about one-third has gone to Europe. The discovery of the Florida phosphates was a severe blow to the industry in South Carolina, the annual exports from South Carolina having fallen to about 30,000 tons. The reason of this is that the South Carolina rocks are somewhat low in their content of phosphate of lime, ranging between 55 and 60 per cent. They contain from seven to 11 per cent. of carbonate

of lime, from eight to 12 per cent. of silica, and from two to four per cent. of oxids of iron and alumina.

Small deposits of phosphates occur in other parts of the United States; namely, in North Carolina, in Pennsylvania, in Arkansas, and in Alabama. Lately deposits have also been found in Wyoming, in the county of Uinta, near the village of Cokeville, which are made up of grayish black phosphates in the form of heavy and very durable rocks. These deposits are found in the upper carboniferous rocks of the central Cordilleran region in a series of oolitic beds.

Considerable quantities of phosphates are also produced in Canada. The smallness of the deposits and the difficulties of quarrying, however, have kept the Canada production down to a small amount, the production not exceeding 30,000 tons per year. It is estimated that only about 850,000 tons of phosphate rock are exported to Europe from the United States, principally from Florida and Tennessee, Florida leading with about 85 per cent. of the total exportations.

45. Magnitude of Product.—In 1904 the production of phosphates in the United States, principally in Florida, Tennessee and South Carolina, amounted to approximately 1,782,503 long tons, valued at \$5,703,582. This is an increase compared to 1903 of 212,275 tons in quantity, and \$709,670 in value. Exports in 1904, chiefly to Germany, France, Italy and Great Britain, totaled about 880,000 tons as against 785,259 tons in 1903, showing an increase of 94,741 tons, or 12 per cent. The ocean freight was \$2.64 to \$3.72, equivalent to from one-third to one-half of the c. i. f. prices paid for the phosphates, which were \$9.84 to \$12.09 for Florida high-grade rock; \$6.39 to \$8.40 for land pebble; \$9.54 to \$11.40 for Tennessee rock; \$5.61 to \$6.88 for South Carolina rock. In competition with the American phosphates were exports of 775,000 tons from Africa, paying an ocean freight of \$1.44 to \$2.22, and selling in Europe at \$6 to \$7.60 for Algerian, and \$5.75 to \$6.60 for Tunis rock. There were also sent to Europe in 1904 some 125,000 tons high-grade phosphate from the Christmas and Ocean islands, paying a freight of about \$6.48, and marketed at \$11.75 to \$14.45 per ton,

delivered. Summed up, Europe imported from the countries named a total of 1,780,000 tons valued at approximately \$10,375,-683, of which \$5,105,650, or over 50 per cent., represented cost of freight.

The domestic trade, which takes little over half the production, showed some improvement in 1904, and prices ranged from \$6.50 to \$7.50 per ton for high-grade rock, f. o. b. Florida ports; \$3.75 to \$4 for Florida land pebble; \$4 to \$4.25 for Tennessee export rock, f. o. b. Mount Pleasant, and \$2.95 to \$4 for the various domestic grades; \$2.75 to \$3.50 for South Carolina rock, f. o. b. Ashley River.

The industry in Florida is gradually coming under control of a few large miners, and the affiliation of important concerns has greatly lessened competition in the export trade. It is proposed to erect superphosphate plants, to utilize the large stocks of 70 to 77 per cent. rock in Florida. In Tennessee new capital has been invested in mining, and in South Carolina, because of the decadence of the river industry, work will be begun on the marsh lands on Morgan, Coosaw and Buzzard islands.

Undoubtedly the most gratifying feature of the phosphate industry to-day is the gradual elimination of speculative buying, and the introduction of economic management, which promises better profits for the future.

46. Later Statistics.—The latest tabulated statistics relating to the phosphate industry in the United States are those found in the reports of the Geological Survey. The following tables taken from those documents show the rate of growth and the magnitude of the industry.

47. Production in the United States.—The following table gives the production of phosphate rock in the United States in 1905 and 1906, inclusive, based on the marketed product, classified by kinds or grades:²³

²³ Geological Survey, Mineral Resources of the United States, 1906: 1080.

PRODUCTION OF PHOSPHATE ROCK IN THE UNITED STATES, 1905-1906,
BASED ON THE QUANTITY MARKETED.

State	1905		Average value per ton	1906		Average value per ton
	Quantity (long tons)	Value		Quantity (long tons)	Value	
Florida :						
Hard rock	577,672	\$2,993,732	\$5.18	587,598	\$3,440,276	\$5.85
Land pebble . . .	528,587	1,045,113	1.98	675,444	2,029,202	3.00
River pebble . . .	87,847	213,000	2.42	41,463	116,100	2.80
Total	1,194,106	4,251,845	3.56	1,304,505	5,585,578	4.28
South Carolina :						
Land rock	234,676	774,447	3.30	190,180	711,447	3.74
River rock	35,549	103,722	2.92	33,495	105,621	3.15
Total	270,225	878,169	3.25	223,675	817,068	3.65
Tennessee :						
Brown rock	438,139	1,509,748	3.45	510,705	2,027,917	3.97
Blue rock	44,031	121,486	2.76	35,669	114,997	3.22
White rock	689	2,155	3.13	1,303	5,077	3.90
Total	482,859	1,633,389	3.38	547,677	2,147,991	3.92
Other States ¹	5,100	28,800	5.65
Grand total.	1,947,190	6,763,403	3.47	2,080,957	8,579,437	4.12

¹ Includes Arkansas and Idaho.

48. **Marketed Production.**—Since 1880 the quantity and the value of the phosphate rock produced (marketed) in the United States have been as follows :

MARKETED PRODUCTION (LONG TONS) OF PHOSPHATE ROCK IN THE
UNITED STATES, 1880-1906.

Year	Quantity	Value	Year	Quantity	Value
1880	211,377	\$1,123,823	1894	996,949	\$3,479,547
1881	266,734	1,980,259	1895	1,038,551	3,006,094
1882	332,077	1,992,462	1896	930,779	2,803,372
1883	378,380	2,270,280	1897	1,039,345	2,673,202
1884	431,779	2,374,784	1898	1,308,885	3,453,460
1885	437,856	2,846,064	1899	1,515,702	5,084,076
1886	430,549	1,872,936	1900	1,491,216	5,359,248
1887	480,558	1,836,818	1901	1,483,723	5,316,403
1888	448,567	2,018,552	1902	1,490,314	4,693,444
1889	550,245	2,937,776	1903	1,581,576	5,319,294
1890	510,499	3,213,795	1904	1,874,428	6,580,875
1891	587,988	3,651,150	1905	1,947,190	6,763,403
1892	681,571	3,296,227	1906	2,080,957	8,579,437
1893	941,368	4,136,070			

49. **Imports.**—The following table shows the imports of fer-

tilizers of all kinds into the United States for the years 1903-1906, inclusive:

FERTILIZERS IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES, 1903-1906, IN LONG TONS.

Year	Guano		Kieserit and Kainit		Apatite, bone dust, crude phosphates, and other substances used only for manure		Total value
	Quantity	Value	Quantity	Value	Quantity	Value	
1903	21,985	\$252,132	158,313	\$ 773,758	246,042	\$2,231,575	\$3,257,465
1904	37,127	498,702	218,957	1,050,082	243,130	2,455,618	4,004,402
1905	27,104	379,667	351,053	1,850,622	197,115	2,450,835	4,681,124
1906	23,222	322,766	334,843	1,790,969	211,274	2,598,451	4,712,186

50. **World's Production.**—In the following table will be found a statement of the world's production of phosphate rock from 1903 to 1905, inclusive.

WORLD'S PRODUCTION OF PHOSPHATE ROCK, 1903-1905, BY COUNTRIES, IN METRIC TONS.

Country	1903		1904		1905	
	Quantity	Value	Quantity	Value	Quantity	Value
Algeria	320,843	\$1,238,454	343,317	\$1,325,104	334,784	\$1,225,126
Aruba (Dutch West Indies)	15,749	(¹)	23,128	(¹)	23,307	(¹)
Belgium	184,120	332,250	202,480	252,263	193,305	332,292
Canada	1,251	8,214	832	4,590	1,179	8,425
Christmas Island (Straits Settlements)	71,218	(¹)	72,905	(¹)	99,519	(¹)
France	475,783	2,115,647	423,521	1,909,859	476,720	2,093,118
French Guiana	7,893	60,023	(²)	(²)
Norway	1,795	24,120	1,456	19,564	2,522	33,768
Redonda (British West Indies)	1,102	7,207	1,729	10,498
Russia	14,635	47,580	(²)	(²)
Spain	1,124	5,968	3,305	19,136	1,370	7,295
Sweden	3,219	8,627	2,929	6,279	(²)
Tunis	352,088	1,260,137	455,197	1,582,165	521,731	1,812,493
United Kingdom	71	423	59	423
United States	1,606,881	5,319,294	1,904,418	6,580,875	1,978,345	6,763,403

¹ Value not reported.

² Statistics not yet available.

51. **General Observations.**—The foregoing data show, as stated in the report, that the output of phosphate rock in the United

States in 1906 was 2,080,957 long tons, valued at \$8,579,437. A comparison of the figures of late years indicates that, although the output has usually increased each year, the demand has made even more rapid strides, and that the tendency of the market price is upwards. The new Western fields will probably help to supply the increasing demand, but as their market is somewhat local they will not materially affect the general conditions throughout the country. The demand will be likely to continue in excess of the supply unless the new Tennessee field proves to be more extensive than is anticipated. The outlook for the newer fields is therefore bright and will soon become even more promising as the older fields become exhausted. It is not impossible that the increasing demand and higher prices will make it possible to operate many low grade deposits which it has hitherto been impracticable to utilize.

52. Quantity of Phosphoric Acid Removed by Crops.—It is estimated that the quantity of phosphoric acid removed from the soil annually in the United States is equivalent to that contained in 7,000,000 tons of 14 per cent. superphosphate.²⁴ This estimate does not include the quantity removed by erosion and leaching. It is evident that in order to maintain the present fertility of our arable soil in respect of phosphoric acid about one million tons of this substance, calculated as P_2O_5 , must be added to the soil each year.

53. General Conclusions.—From the study of the origin of the deposits of mineral phosphates it appears that those which are suitable for economic uses have been derived chiefly from the decay of organic matter—mostly of animal origin. The phosphoric acid was evidently very generally diffused in the mineral matter which first formed the crust of the earth. It began to be utilized by the simplest forms of vegetable growth which first appeared on the earth's surface, and through this intermediary passed into animal organisms. In these it was finally segregated in the bones in large quantities. In the decay of animal bodies the bony structure is attacked by solvents; for instance, the nitric acid produced by the oxidation of the protein of vegetable and

²⁴ Voorhees, *Journal of the Franklin Institute*, 1905, 160 : 211.

animal origin, by the carbonic acid in water and by the humic acids of the soil. The solutions thus produced are carried into the soil where a complex series of actions due to unstable chemical equilibria takes place. The phosphoric acid which in the bones is combined with lime as tricalcium phosphate, and which in solution is in the form of free acid or as monocalcium phosphate, tends again to form more stable compounds and is finally deposited chiefly in the form in which it existed in the bones, viz., tricalcium phosphate. All these changes take place strictly in harmony with the laws of physical chemistry. The deposits of phosphates, therefore, are due to chemical rather than geological phenomena.

54. The Value of Bone Meal from which the Nitrogen Constituents Have Been Extracted, as a Fertilizing Reagent.—When fresh, finely ground bones are applied to use as a fertilizer and valuable results are obtained they may be ascribed either to the nitrogen constituent in bone or to its content of phosphoric acid. In general, the bone phosphate has not been regarded as being of great value, and the chief utility of ground bone has been ascribed to its nitrogen constituent. If the value of a phosphate as a fertilizer be governed by its solubility in ammonium citrate or citric acid, it has been shown that considerable portions of phosphoric acid in finely ground bone are soluble in these reagents.

Since the original observations of Huston have shown that the phosphoric acid of finely ground bone is soluble in ammonium citrate, this problem has been studied by many other observers. Reitmair has made investigations on this subject with the results which follow.²⁵ The observations were carried on at the same time with degelatinized bone meal and basic slags, and the quantity of rye produced per hectare when these bodies were used for the fertilizing reagents was determined. As a result of these investigations Reitmair concluded that the solubility of a phosphate in citric acid is no criterion for its value as a fertilizer or as a measure of its solubility in the soil. The solubility in citric acid of phosphate is no measure for the quantities of the active forms of phosphoric acid which are given. It is

²⁵ Wiener landwirtschaftliche Zeitung, 1905, 55 : 879-881 and 889-891.

not even a measure, as has often been supposed, of the favorable mechanic properties of phosphatic manure. The larger particles of bone phosphate and of basic slags were brought into solution both by the usual and by the modified digestion methods practiced. Various samples of the bone meal from different sources were treated with citric acid, according to the usual method, to determine the percentage of solubility therein, and the quantity of fine particles, passed through a sieve with fine mesh, was determined. A bone meal containing 86.5 per cent. of fine particles showed a solubility of 92.3 per cent. in citric acid, while the degelatinized sample of bone meal containing only 12.6 per cent. of fine particles showed a solubility of 87.6 per cent. Thus, while it is generally true that the solubility in citric acid varies inversely with the size of the particles, it does not vary proportionately thereto. The period of digestion in each case was one-half hour.

It is evident from the above that the agricultural chemist has yet much to learn concerning the character and speed of the solution of phosphate in a soil. The changes which take place in the ordinary digestion in citric acid in the laboratory are evidently of a very different degree of magnitude and are carried on with a very different degree of speed from that which takes place during the growing period in the soil itself.

All the experiments conducted by Reitmair indicate that the degelatinized phosphoric acid has a distinct value as a phosphatic fertilizer and this depends primarily upon the state of subdivision and is indicated only approximately by its solubility in citric acid. Attention, however, must be called to the fact that in the manufacture of degelatinized bone meal it has not yet been possible to produce a product entirely free from nitrogen on a commercial scale. The last traces of nitrogen are not removed and there usually remains in the degelatinized bone about 0.5 per cent. of nitrogen. This residue must be regarded as an unavoidable contamination of the bone meal for experimental purposes, but it is of a magnitude so small as to be practically ignored in the experimental work. It is evident, therefore, that any attempt to determine the fertilizing value either of degelatinized bone or of basic slag by its solubility

in citric acid solutions is likely to lead to erroneous conclusions. Moreover, the fertilizing value of any material of this kind is not a constant quantity, but varies always with the character of the soil to which it is applied and of the seasonal environment to which it is subjected. The chemist has done all that could be reasonably expected of him when he has determined the fineness of the subdivisions of the material and its relative solubility in certain reagents which indicate the relative amount of acid present which readily passes into solution under the ordinary conditions to which it is likely to be subjected. It must be remembered, however, that in the field the processes of solution go on constantly for a period of three or four months; in fact, as long as the plant continues feeding. A very feeble solubility in the soil, therefore, would render the phosphoric acid constantly available in the proportion in which it is used. If a reagent of the same feeble power was used in the laboratory it would necessarily have to be kept in activity over a long period of time to yield results which are comparable to those found in the soil. Therefore, it seems only reasonable to use a stronger reagent for a limited period of time such as can be used practicably by the analyst for his determinations.

While the use of the various reagents which have been proposed for the valuation of these materials may not lead to results directly comparable to those that take place in the growing season, they do, undoubtedly, give an idea of the availability, which is of great practical importance.

ANALYTICAL PROCESSES

55. Constituents to be Determined.—The most important point in the analysis of mineral phosphates is to determine their content of phosphoric acid. Of equal scientific interest, however, and often of great commercial importance is the determination of the percentage of other acids and bases present. The analyst is often called on, in the examination of these bodies, to make known the content of water both free and combined, of organic and volatile matter, of carbon dioxid, sulfur, chlorin, fluorin, silica, iron, alumina, calcium, manganese, magnesia, and the alkalies. The estimation of some of these bodies presents problems

of considerable difficulty, and it would be vain to suppose that the best possible methods are now known. Especially is this the case with the processes which relate to the estimation of the fluorin, silica, iron, alumina, and lime. The phosphoric acid, however, which is the chief constituent from a commercial point of view, it is believed, can now be determined with a high degree of precision. Often the estimation of some of the less important constituents is of great interest in determining the origin of the deposits, especially in the case of fluorin. While the merchant is content with knowing the percentage of phosphoric acid and the manufacturer asks in addition only some knowledge of the quantity of iron, alumina, and lime, the analyst in most cases is only content with a complete knowledge of the constitution of the sample at his disposal.

56. Dissolving the Phosphoric Acid.—It often happens, in the case of a mineral phosphate, that the only determination desired is of the phosphoric acid. In such a case the analyst may proceed as follows: If the qualitative test shows the usual amount of phosphoric acid, two grams of the sample passed through a sieve, with a millimeter, or, better, a half millimeter mesh, are placed in a beaker and thoroughly moistened with water. The addition of water is to secure an even action of the hydrochloric acid on the carbonates present. The beaker is covered with a watch-glass and a little hydrochloric acid is added from time to time until all effervescence has ceased. There are then added about 30 cubic centimeters of aqua regia and the mixture is raised to the boiling-point on a sand-bath or over a lamp. The heating is continued until chlorine is no longer given off and solution is complete. The volume of the solution is then made up to 200 cubic centimeters without filtering, filtered, and an aliquot part of the filtrate, usually 50 cubic centimeters, representing half a gram of the original sample, used for the determination of the phosphoric acid according to some one of the accredited methods. The small quantity of insoluble material from phosphates of the usual composition does not introduce any appreciable error into the process when the volume is made up to 200 or 250 cubic centimeters.

INCINERATION IN A MIXTURE OF SULFURIC AND NITRIC ACIDS

57. Destruction of Organic Matter.—The preliminary destruction of the organic matter for the purpose of determining the phosphoric acid and other mineral matters, save sulfur and nitrogen, may be conveniently conducted as follows:

Neumann has proposed incineration in a mixture of sulfuric and nitric acids as a convenient method of preventing the formation of free carbon, which is destroyed very slowly by subsequent burning.²⁶ The acid mixture is prepared by pouring slowly and with constant shaking, one-half liter of concentrated sulfuric acid into one-half liter of concentrated nitric acid of a specific gravity of 1.4.

58. Apparatus.—The incineration is carried on in a deep, round flask of Jena glass which has the normal length of neck of about 10 centimeters and a capacity of from one-half to three-fourths of a liter. Over this is placed in a glass or porcelain ring a funnel provided with a stop-cock, which is conveniently provided with a capillary dropping-tube, and the whole apparatus is fixed to an appropriate stand. In the preparation of the sample different processes are employed, according to the condition of the sample. Dry, powdery substances are placed in small glass tubes (weighing tubes) which can be easily passed into the neck of the incineration flask. Sticky substances can be placed in a piece of a broken test-tube. Liquids can be placed in thin, weighed, small tubes which are easily broken after placing in the flask. Dry or moist substances can be used for the incineration, and even liquids in not too large quantities, without any previous preparation. In the case of blood it is better to evaporate it before incineration. Fats or materials rich in carbohydrates, such as milk, should be treated before incineration with one per cent. of pure potash lye and evaporated to a sirupy consistence in order to avoid foaming or bumping in the flask. For instance, for 25 cubic centimeters of milk about 15 cubic centimeters of one per cent. potash lye are used.

59. Conduct of the Incineration.—The substance which has been

²⁶ *Zeitschrift für physiologische Chemie*, 1902-3, **37** : 115.

prepared in some of the ways described is placed in the flask and a measured quantity of the acid mixture, from five to 10 cubic centimeters, poured over it and warmed with a moderate flame. As soon as the evolution of brown nitroso-vapors becomes slow a further addition of the acid mixture, drop by drop, from the funnel furnished with a stop-cock, is added and this addition continued until the reaction ceases and the intensity of the brown vapors evolved is diminished. In order to determine whether the destruction of the material has been completed, the addition of the acid mixture is discontinued for a short time and the mass further heated until the brown vapors formed disappear and it is noticed whether the liquid in the flask is still dark or black. If this is the case the acid mixture is again added and the test above described, after a few minutes, is repeated. If on standing and after the expulsion of the brown vapors the bright yellow or colorless liquid is not again darkened by further heating, and also no evolution of gas is observed, the incineration may be regarded as complete. If the liquid is colored slightly yellow it generally becomes completely clear on cooling. Three times as much water is now added as the quantity of acid mixture which has been used, the mixture heated and boiled from five to 10 minutes. By this process brown vapors are evolved which are derived from the decomposition of the nitrosyl sulfuric acid which has been formed.

It must be remembered that in the above operation the nitrogen of the protein matter is not converted into ammonia. In fact, no trace of ammonia can be found in the resulting liquid. The ash constituents, however, of the organic matter are found in a completely inorganic state dissolved in the mixture, and this mixture can be used for the determination of these constituents in the ordinary way.

The above method for freeing the phosphorus and converting it into inorganic forms has given good results in the laboratory of the Bureau of Chemistry.

60. Loss of Phosphoric Acid by Incineration.—It is well known that in certain substances used for fertilizing purposes, such as

oil cakes and other organic compounds, the large quantity of phosphoric acid which they contain is in organic combination and unless special precautions are exercised a portion of the phosphorus is lost in burning. The loss of phosphoric acid which takes place in cereals has lately been carefully studied by Leavitt and LeClerc.²⁷ In the case of wheat it is shown that the principal part of the organic phosphorus is in a water-soluble form, known as phytin. This substance has a relatively high molecular weight compared to the phosphorus molecule. A comparatively large percentage of the phosphorus may be lost in ashing without changing very greatly the apparent weight of the ash.

As is well known, the addition of calcium acetate previous to burning prevents the volatilization of phosphoric acid. The proportion of phosphorus lost by the ordinary incineration as compared with the amount obtained with the previous addition of calcium acetate has been found in the extreme cases to be 50 per cent. of the total quantity present. The ordinary incineration was conducted at redness. If, however, the incineration is accomplished without any treatment whatever at incipient redness just sufficient to show a faint radiation of light from the dishes, there is no appreciable loss of phosphoric acid. The results show that the ashing below the point of fusion of the mineral portions of the ash is not a very important factor where only the percentage of ash is desired. But in order to determine the quantity of the phosphorus as phosphoric acid the greatest caution must be observed to keep the temperature below the volatilization point of the combined phosphorus. This is to be accomplished either by incineration at an extremely low temperature or by previous treatment with calcium acetate.

Later investigations show that in reality there is no appreciable loss of phosphoric acid even at bright redness. The phosphoric acid is simply changed into a form which is not precipitable by ammonium molybdate until the ash has been boiled a long time with nitric acid, or has been treated according to Neumann's method of digesting with nitric and sulfuric acid.

²⁷ *Journal of the American Chemical Society*, 1908, **30** : 391, 617.

61. Official Method.—The official chemists recommend seven methods of solution for mineral phosphates, phosphatic materials and preparations thereof; viz.,²⁸

1. Ignite and dissolve in hydrochloric acid.

2. Evaporate with five cubic centimeters of magnesium nitrate solution and dissolve in hydrochloric acid. This method is applicable in the presence of organic matter.

3. Boil with from 20 to 30 cubic centimeters of strong sulfuric acid, adding from two to four grams of sodium or potassium nitrate at the beginning of the digestion and a small quantity after the solution has become nearly colorless. Or the nitrate in small quantities may be added at regular intervals during the whole time of the digestion, which is conducted in a kjeldahl flask marked at 250 cubic centimeters. When the solution is colorless add 150 cubic centimeters of water, boil for a few minutes, cool and make up to the mark with water.

4. Digest with strong sulfuric acid and such other reagents as are used in the processes for converting nitrogen in nitrogenous compounds into sulfate of ammonia as described in the second part of this volume. Do not add any potassium permanganate but after the solution has become colorless add about 100 cubic centimeters of water, boil for a few minutes, cool and make up to a convenient volume (250 cubic centimeters). The operation should be conducted on about 2.5 grams of substance.

Processes 3 and 4 are especially applicable to organic substances such as oil cakes, which contain considerable quantities of phosphorus.

5. Dissolve in 30 cubic centimeters of concentrated nitric and a small quantity of hydrochloric acid and boil until organic matter is destroyed.

6. Add to the substance 30 cubic centimeters of concentrated hydrochloric acid, heat and add cautiously in small quantities at a time about 0.5 gram of finely pulverized potassium chlorate to destroy organic matter.

7. Dissolve the substance in from 15 to 30 cubic centimeters of strong hydrochloric acid and from three to 10 cubic centimeters

²⁸ Bureau of Chemistry, Bulletin 107, 1907 : 2.

of nitric acid. This method is particularly suited to samples containing much iron or aluminum phosphate.

From the above directions it is seen that in a purely mineral phosphate a single strong acid or a mixture of acids is sufficient to bring all the phosphoric acid into solution. Where organic matter is present the use of strongly oxidizing solvents as in 4 and 5 is necessary. In substances containing phosphorus in organic forms such as blood, tankage, oil cakes, seeds, etc., especial care is required to complete the oxidation and secure all the phosphorus in the form of phosphoric acid.

GENERAL METHODS FOR ESTIMATING PHOSPHORIC ACID IN FERTILIZERS

62. Preliminary Considerations.—The chief sources of the phosphoric acid in commercial fertilizers are the mineral phosphates and bones. In respect of the general analyses of mineral phosphates detailed directions have been given in the preceding volume. Bones are valuable for fertilizing materials, both because of their content of phosphoric acid and of their organic nitrogen. The method of treating bones for their phosphoric acid will be found in the general methods for fertilizing materials, and their nitrogen content can be determined by the processes to be described hereafter. Other fertilizing materials also contain phosphorus, as ashes, tankage, oil cakes, and other organic products. In general, the methods for determining the phosphoric acid is the same in all cases, but the means of destroying the organic matter precedent to the analysis vary in different cases. In most cases a simple ignition is sufficient, while, if the phosphorus be found in certain organic products, the oxidation must be accomplished by one of the methods described in the processes adopted by the official chemists. In all cases of acid phosphates and superphosphates, the water and ammonium citrate-soluble phosphoric acid is to be determined as well as the total. In basic slags the amount soluble in ammonium citrate or dilute citric acid is also to be ascertained.

In all cases where soluble or so-called reverted acid is to be considered, the analysis must be performed without previous desiccation or ignition. If water content or loss on ignition is

to be considered, the operation to determine them must be conducted on a separate part of the sample.

The methods of analysis which have been adopted by associations of chemists should be given the preference in the conduct of the work, although it must be admitted that they may contain sources of error, and may be in no respect superior to processes employed by chemists in their private capacity. In this country the methods adopted by the Association of Official Agricultural Chemists should be followed as closely as possible. The great merit of other methods, however, must not be denied. Especially those methods which shorten the time required or diminish the labor and expense of the analysis are worthy of careful consideration. In factory work, for instance, it is often far more important for the chemist to be able to rapidly determine the phosphoric acid in a great number of samples with approximate accuracy than to confine his work to one with absolute precision. Some of the shorter methods, moreover, notably the citrate or titration process, appear to be quite, if not altogether, as reliable as the molybdate method, while in the case of the uranium volumetric process, it must not be forgotten that it has been largely practiced in France. Other volumetric processes are given in full, as, for instance, the one perfected by Pemberton and Kilgore, and data are at hand to justify their strong recommendation. It should be remembered that this manual is not written for the beginner, but rather for the chemist already acquainted with the principles and practice of general chemical analysis, and it is, therefore, expected that each analyst will make intelligent use of the data placed at his disposal.

63. Preparation of Reagents.—*Ammonium Citrate Solution.*—

(a) Mix 370 grams of commercial citric acid with 1500 cubic centimeters of water, nearly neutralize with commercial ammonia, cool, add ammonia until exactly neutral (testing with saturated alcoholic solution of corallin) and bring to a volume of two liters. Determine the specific gravity, which should be 1.09 at 20°, before using.

(b) *Optional Method.*—To 370 grams of commercial citric acid add commercial ammonia, of 0.96 specific gravity, until near-

ly neutral; reduce the specific gravity to nearly 1.09 and proceed as follows: Prepare a solution of fused calcium chlorid 200 grams to the liter, and add four volumes of strong alcohol. Make the mixture exactly neutral, using a small amount of freshly prepared corallin solution as a preliminary indicator, withdrawing a portion, diluting with an equal volume of water, and testing with cochineal solution. Fifty cubic centimeters of this solution will precipitate the citric acid from 10 cubic centimeters of the citrate solution. To 10 cubic centimeters of the nearly neutral citrate solution add 50 cubic centimeters of the alcoholic calcium chlorid solution, stir well, filter at once through a folded filter, dilute with an equal volume of water and test the reaction with neutral solution of cochineal. If acid or alkaline, add ammonia or citric acid, as the case may be, to the citrate solution, mix, and test again as before. Repeat this process until a neutral reaction of the citrate solution is obtained. The specific gravity must be 1.09 at 20°.

The reagents employed in the separation of the phosphoric acid are prepared according to the following formulas:

Molybdate Solution.—Dissolve 100 grams of molybdic acid in 144 cubic centimeters of ammonia, specific gravity 0.90, and 271 cubic centimeters of water; pour the solution thus obtained, slowly and with constant stirring, into 489 cubic centimeters of nitric acid, specific gravity 1.42, and 1148 cubic centimeters of water. Keep the mixture in a warm place for several days, or until a portion heated to 40° deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve it in glass-stoppered vessels.

Ammonium Nitrate Solution.—Dissolve 200 grams of commercial ammonium nitrate in water and dilute with water to two liters.

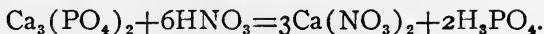
Magnesia Mixture.—Dissolve 22 grams of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding an excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter; add 280 grams of ammonium chlorid, 700 cubic centimeters of ammonia of specific gravity 0.96, and water enough to

make a volume of two liters. Instead of the solution of 22 grams of calcined magnesia, 110 grams of crystallized magnesium chlorid ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) may be used.

Dilute Ammonia for Washing.—This solution is prepared so as to contain 2.5 per cent. NH_3 .

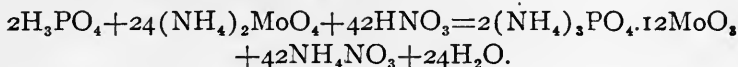
Magnesium Nitrate Solution.—Dissolve 320 grams of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess; boil; filter from the excess of magnesia, ferric oxid, etc., and dilute with water to two liters.

Formulas for the Reactions.—The reactions which take place when a mineral acid, for instance, nitric, dissolves tricalcium phosphate, may be represented as follows: $\text{Ca}_3(\text{PO}_4)_2 + 4\text{HNO}_3 = \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{Ca}(\text{NO}_3)_2$. In the case of a large excess of acid, free phosphoric acid may be formed thus:

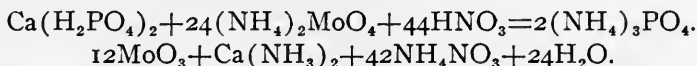


Assuming that the phosphoric acid is in a soluble state in the solutions prepared with the strong hot acids, the reactions which take place in the process of separating it are as follows:

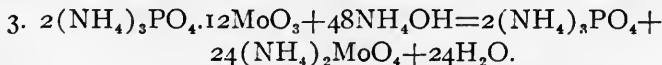
1. (For free phosphoric acid):



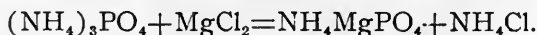
2. (For monocalcium phosphate):



The yellow precipitate $2(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ is dissolved in ammonia with regeneration of ammonium molybdate as follows:



4. Precipitation of the phosphoric acid with magnesia salts:



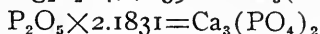
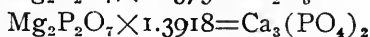
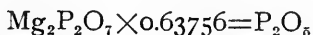
5. Conversion of the ammonia-magnesium phosphate into magnesium pyrophosphate by heat:



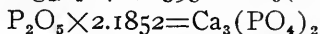
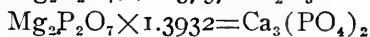
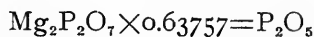
The factors for calculating the phosphorus pentoxid and tri-

calcium phosphate from the weight of pyrophosphate are given below on the two bases, viz., hydrogen equals 1, and oxygen equals 16.

$$H=1.$$



$$O=16.$$



64. Official Method for Total Phosphoric Acid.—Having now described the approved methods of bringing into solution all the phosphorus in the form of phosphoric acid, the next step is to separate this acid and bring it into a homogeneous compound in which it may be titrated or weighed. The usual method of separation depends on the property possessed by phosphoric acid of forming in a strongly acid solution, which prevents the precipitation of the associated bodies, an insoluble compound with molybdc acid. The separation is accomplished as follows:²⁹

Determination.—Neutralize an aliquot portion of the solution prepared as above, corresponding to 0.25 gram, 0.50 gram, or one gram, with ammonia, and clear with a few drops of nitric acid. In case hydrochloric or sulfuric acid has been used as solvent, add about 15 grams of dry ammonium nitrate or a solution containing that amount. To the hot solution add 50 cubic centimeters of molybdc solution for every decigram of P_2O_5 that is present. Digest at about 65° for an hour, filter, and wash with cold water, or preferably ammonium nitrate solution. Test the filtrate for phosphoric acid by renewed digestion and addition of more molybdc solution. Dissolve the precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 cubic centimeters. Nearly neutralize with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (about one drop per second), stirring vigorously. After 15 minutes add 12 cubic centimeters of ammonia solu-

²⁹ Bureau of Chemistry, Bulletin 107, 1907: 3.

tion of density 0.90. Let stand for some time; two hours is usually enough. Filter, wash with 2.5 per cent. NH_3 until practically free from chlorids, ignite to whiteness or to a grayish white, and weigh.

65. Influence of Insoluble Silica.—It is assumed in the above methods that there is no more than a mere trace of soluble silica in the solutions of the phosphate with which the operations are conducted. Silica in solution (silicic acid) has also the property of forming yellow compounds with molybdate of ammonia and thus when present in any quantity would contaminate the precipitate produced. This trouble is avoided if the acid solution of the phosphate is evaporated to dryness, rubbed to a fine powder before becoming perfectly dry, moistened with hydrochloric acid and taken up with water. The pasty state of the phosphoric acid and large quantities of soluble salts present in these cases make this a tedious process to be practiced only when necessary.

66. Use of Tartaric Acid in Phosphoric Acid Estimation.—In the presence of iron the molybdate mixture is likely to carry down some ferric oxid with the yellow precipitate. To prevent this, and also hinder the separation of molybdic acid in the solution on long standing, tartaric acid has been recommended.

Jüptner has found that the presence of tartaric acid does not interfere with the separation of the yellow precipitate, as some authorities assert.³⁰ Even 100 grams of the acid in one liter of molybdate solution produce no disturbing effect. Molybdate solution treated with tartaric acid does not show any separation of molybdic acid when kept for a year at room temperatures. The presence of tartaric acid, therefore, is highly useful in preventing the danger of obtaining both ferric oxid and molybdic acid with the yellow precipitate.

67. Water-Soluble Phosphoric Acid.—The method of procedure recommended by the Association of Official Agricultural Chemists is as follows:³¹ Place two grams of the sample in a nine centimeter filter; wash with successive small portions of cold water, allowing each portion to pass through before adding more,

³⁰ *Chemisches Central-Blatt*, 1894, 2 : 813.

³¹ *Bureau of Chemistry, Bulletin 107*, 1907 : 3.

until the filtrate measures about 250 cubic centimeters. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume; mix well; take any convenient portion and proceed as under total phosphoric acid.

68. Citrate-Insoluble Phosphoric Acid.—The official method applied to samples previously acidulated is as follows: Heat 100 cubic centimeters of strictly neutral ammonium citrate solution of 1.09 specific gravity to 65° in a flask placed in a bath of warm water, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65°, drop into it the filter containing the washed residue from the water-soluble phosphoric acid determination, close tightly with a smooth rubber stopper; and shake violently until the filter paper is reduced to a pulp. Place the flask again in the bath and maintain the water in the bath at such a temperature that the contents of the flask will stand at exactly 65°. Shake the flask every five minutes. At the expiration of exactly 30 minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter as rapidly as possible. It has been shown by Sanborn in his investigations, that the filtration is greatly facilitated by adding asbestos pulp. Wash thoroughly with water at 65°. Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 cubic centimeters of strong hydrochloric acid, and digest until all phosphate is dissolved; or return the filter with contents to the digestion flask, add from 30 to 35 cubic centimeters of strong nitric, and from five to 10 cubic centimeters of strong hydrochloric acid, and boil until all the phosphate is dissolved. Dilute the solution to 200 cubic centimeters. If desired, the filter and its contents can be treated according to methods 1, 2, or 3, paragraph 61, under preliminary treatment of samples containing organic matter. Mix well; filter through a dry filter; take a definite portion of the filtrate and proceed as under total phosphoric acid, paragraph 64.

In case a determination of citrate-insoluble phosphoric acid be required in non-acidulated goods it is to be made by treating two grams of the phosphatic material, without previous washing

with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.), the residue insoluble in ammonium citrate is to be treated by one of the processes described under 1, 2, or 3, paragraph 61.

69. Citrate-Soluble Phosphoric Acid.—The sum of the water-soluble and citrate-insoluble subtracted from the total gives the citrate-soluble phosphoric acid.

70. Time Required for the Precipitation of Phosphoric Acid.—The length of time required for the complete precipitation of the phosphoric acid by molybdate mixture is perhaps much less than generally supposed. At 65° the precipitation, as shown by de Roode, is complete in five minutes.³² In a given case the weight of pyrophosphate obtained after five minutes was 0.0676 gram, and exactly the same weight was found after 24 hours. In view of these facts analysts would often be able to save time by omitting the delay usually demanded by the setting aside of the yellow precipitate for a few hours in order to secure a complete separation of the phosphoric acid. In the method of the official chemists it is directed that the digestion at 65° be continued for one hour, and this time may possibly be shortened with advantage. In all cases, however, where there is any doubt in regard to the complete separation, some of the molybdate solution should be added to the filtrate and, with renewed digestion, it should be noted whether any additional precipitate be formed.

71. Examination of the Pyrophosphate.—In fertilizer control it is not usually thought necessary to examine the magnesium pyrophosphate for impurities. Among those most likely to be found is silica. It is proper, in all cases where accuracy is required, to dissolve the precipitate in nitric acid, boil for some time to convert the pyro- into orthophosphate, and reprecipitate with molybdate and magnesia mixture. This treatment will separate the silica, which remains practically insoluble after the first ignition. It has been observed by some analysts that the results obtained by the official method are a trifle too high and also that on re-resolution the second precipitate of pyrophosphate weighs.

³² Journal of the American Chemical Society, 1895, 17 : 43.

less than the first.³³ The difference in most cases is very little, but it may become a quantity of considerable magnitude in samples where soluble silica is found in notable quantities. The danger of contamination with iron, alumina, and arsenic has already been mentioned and the precautions suggested should be carefully observed.

72. Insolubility of Silica.—It is evident that many of the errors which are incident to the methods of separating phosphoric acid by ammonia phosphomolybdate are due to the presence of silica. The fact has been repeatedly pointed out by analysts. Pellet proposes to render the silica insoluble and thus prevent the error by the following procedure:³⁴ The weighed phosphate is placed in a platinum capsule and moistened with free hydrochloric acid. The moistened mass is evaporated to dryness after which the silica is no longer soluble in hot hydrochloric acid. Pellet claims that this method, which saves the time of a previous solution and evaporation to dryness, is quite as effective as the longer method.

73. Direct Determination of Available Phosphoric Acid.—The direct determination of available phosphoric acid is not new, being official in several of the European countries. In this country, however, it has not met with favor, probably because the citrate method is not official here. The necessity of destroying the organic matter before precipitating with molybdate solution precludes the use of the molybdate method.³⁵

In 1893 Ross presented a method for the direct determination of the reverted phosphoric acid.³⁶ While the aim of this method met with hearty approval from the official chemists, the method itself did not, owing to some difficulties met with in the manipulation, and more particularly to the fact that it did not give results agreeing with the official method.³⁷ Agreement could hardly be expected, because the method did not account for the phosphoric acid removed in the water used in washing the citrate-insoluble. The estimation of the available phosphoric acid

³³ Journal of the American Chemical Society, 1895, 17 : 43.

³⁴ Annales de Chimie analytique, 1906, 11 : 331.

³⁵ Veitch, Journal of the American Chemical Society, 1899, 21 : 1090.

³⁶ Division of Chemistry, Bulletin, 38, 1893 : 17.

³⁷ Division of Chemistry, Bulletin 43, 1894 : 72 and Bulletin 47, 1896 : 81.

consisted in the determination of the water-soluble phosphoric acid by the volumetric method, as modified and carried out by Veitch;³⁸ the direct determination of the citrate-soluble by the citrate method in 50 cubic centimeters of the citrate filtrate, and the determination of that removed by washing the citrate-insoluble residue, using the modified volumetric method. The sum of these three results should equal the available phosphoric acid by the official method.

It is perhaps sufficient to say that the citrate method at that time and later gave satisfactory results.³⁹

The two methods gave practically the same results on availables and on totals. The work also shows very plainly why the Ross method differs from the official, from 0.09 per cent. to 1.48 per cent. being removed and accounted for in the wash water of the official method that could not be accounted for by the Ross method. Of course, the amount removed by the wash water will vary somewhat in the hands of different analysts, according as they wash the citrate-insoluble much or little. It is the practice of Veitch to wash until the filtrate and washings amount to about 250 cubic centimeters.

A comparison of the official method with the citrate and the molybdate methods, precipitating with magnesia mixture and with molybdate solution, respectively, in the mixed filtrates containing the water-soluble and the citrate-soluble, was undertaken.

The method finally adopted is as follows: The water-soluble extracted as usual, is received in a 500 cubic centimeter flask, graduated roughly at 250 cubic centimeters and containing from five to 10 cubic centimeters nitric acid. The citrate-soluble is then extracted as usual and the filtrate and washings received in the flask with the water-soluble. After cooling, the volume is completed, shaken, filtered, and in aliquots of 100 cubic centimeters the phosphoric acid is determined by one of two methods, the molybdate or citrate, the precipitants being added directly to the solution without destroying the organic matter, and the precipi-

³⁸ Journal of the American Chemical Society, 1896, 18 : 389.

³⁹ Division of Chemistry, Bulletin 49, 1897 : 61.

tates are allowed to stand over night before filtering. The determinations are completed as usual.

The results by the citrate method were unexpectedly low. In Veitch's hands this method has always given satisfactory results, even on low percentages. It is probable the low results are due to an excess of citrate. This addition is unnecessary, and better results obtained when more citrate is not added, lead to the belief that this additional citrate is the cause of the low results.

The results by the molybdate method are good. It was feared that the organic matter present would prevent the complete precipitation of the ammonium phosphomolybdate. To insure complete precipitation the samples were allowed to stand over night before filtering.

Notwithstanding the oft-repeated statement that salts of organic acids and organic matter generally prevent the complete precipitation of ammonium phosphomolybdate, the molybdate method is used to determine soluble phosphoric acid in the presence of what organic matter may be dissolved by the water used in the extraction. In the Wagner method for basic slag, the precipitation is accomplished with molybdate solution in the presence of three grams of citric acid. Lorenz precipitates in the presence of two per cent. of citric acid to prevent contamination with magnesia. Jüptner uses as much as 100 grams of tartaric acid per liter of molybdate solution to prevent the precipitation of iron and the separation of molybdic acid.⁴⁰ The successful use of the molybdate method in these cases seems to warrant the conclusion that we are needlessly alarmed at the presence of, at least, some forms of organic matter in phosphate solutions.

The direct determination of the available phosphoric acid possesses several advantages. Only one determination is required instead of two as by the present method. The probable error is reduced one-half. The soluble, reverted, insoluble, and total phosphoric acid can also be determined in one sample and with one weighing, where it now takes two samples and two weighings.

The saving of time effected by this method is of considerable

⁴⁰ Abstract, Experiment Station Record, 1894-5, 6: 610.

importance in control and in factory laboratories, whether the citrate or the molybdate method is used.

74. International Methods.—The international commission for the analysis of artificial fertilizers presented a report to the Fifth International Congress of Applied Chemistry embracing certain processes of analysis which are recommended for international adoption.⁴¹ The methods suggested for phosphoric acid are as follows:

1. *Determination of Moisture.*—Ten grams of the substance are used; the drying is conducted at 100° to constant weight; substances containing gypsum are dried three hours.

For potash salts the regulations of the Kali syndicate at Leopoldshall-Stassfurt hold good.

2. *Determination of Insoluble Matter.*—Ten grams of the substance are used.

A. When the substance is dissolved in mineral acids, the silica is rendered insoluble and the total residue ignited.

B. When the substance is dissolved in water, the residue is dried at 100° to constant weight.

3. *Determination of Phosphoric Acid.*—A. Method of making the solutions.

1. In the case of water-soluble P_2O_5 , 20 grams substance are to be agitated for 30 minutes with about 800 cubic centimeters water in a liter bottle and then filled up to 1000 cubic centimeters. The solution of so-called double superphosphates must be boiled with HNO_3 previous to precipitation of the P_2O_5 , whereby any pyrophosphoric acid which may be present is converted into orthophosphoric acid.

For every 25 cubic centimeters of solution of double superphosphate, 10 cubic centimeters concentrated HNO_3 must be used.

When the amount of citrate-soluble phosphoric acid in superphosphates is required, the determination must be made according to Petermann.

2. For total phosphoric acid five grams of the substance are boiled with aqua regia or 20 cubic centimeters HNO_3 and 50

⁴¹ Proceedings of the Fifth International Congress of Applied Chemistry, Berlin, 1903, 1 : 228.

grams concentrated H_2SO_4 for 30 minutes and filled up to 500 cubic centimeters.

3. To determine P_2O_5 in slag phosphates, the meal, which appears to contain coarse particles, is passed through a two millimeter sieve; the portion which remains behind is slightly crushed. The determination of P_2O_5 is made in the portion which passes through the sieve, the result being calculated so as to include the portion which remains behind.

(a) Citric acid soluble P_2O_5 .

Five grams of the substance are placed in a 500 cubic centimeter flask with five cubic centimeters of alcohol to prevent baking and shaken with two per cent. citric acid solution for one half hour at $17^\circ.5$ in a rotary apparatus which makes 30-40 revolutions per minute.

(b) Total P_2O_5 .⁴²

Ten grams of the substance are placed in a 500 cubic centimeter flask, thoroughly mixed with a few cubic centimeters of water and boiled for 30 minutes with 50 cubic centimeters concentrated H_2SO_4 , the flask being frequently shaken.

B. Analysis of the Solutions.

1. Molybdate method according to Fresenius and P. Wagner.
2. Citrate method.
3. Free acid.

(a) Total free acid: The aqueous solution A 1 is titrated with a solution of NaOH , using methyl orange as an indicator.

(b) Free phosphoric acid: An alcoholic solution is used for making a gravimetric determination.

4. *Determination of Ferric Oxid and Alumina.*

This determination must be made either according to the method of Eugen Glaser⁴³ as improved by R. Jones⁴⁴ or, in the case of the determination of alumina, according to Henri Lasne.⁴⁵ The method adopted must be mentioned.

⁴² When a determination of the fine dust is to be made, a sieve of 0.17 millimeter mesh must be used.

⁴³ Zeitschrift für angewandte Chemie, 1889, 2 : 636; Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 284.

⁴⁴ Zeitschrift für angewandte Chemie, 1891, 4 : 3; Zeitschrift für analytische Chemie, 1891, 30 : 743.

⁴⁵ Bulletin de la Société chimique de Paris, 1896, [3], 15 : 146, 237; Chemiker-Zeitung Repertorium, 1896, 20 : 47, 65.

75. Methods of the German Experiment Stations.—The processes adopted by the union of the German agricultural experiment stations are based on the general methods of procedure already outlined as is seen from the following resumé.⁴⁶ The sample containing the phosphoric acid is dissolved in aqua regia in the proportion of five grams of the sample to 50 cubic centimeters of the acid, made by mixing three parts of hydrochloric acid of 1.12 specific gravity with one part of nitric acid of 1.25 specific gravity or 20 cubic centimeters of nitric acid of 1.42 specific gravity with 50 cubic centimeters of sulfuric acid of 1.8 specific gravity. With the latter reagent the boiling is continued for 30 minutes. The phosphoric acid is then determined by the direct (Böttcher) method.⁴⁷

76. Water-Soluble Phosphoric Acid.—The soluble acid in acid phosphates is extracted by treating 20 grams of the sample in a liter flask with 800 cubic centimeters of water for 30 minutes with vigorous shaking, filling the flask to the mark, shaking and filling. A mechanical shaker is recommended with a vibration or rotation of 150 turns a minute. The acid is determined in an aliquot part of the filtrate by the magnesia citrate method. Solutions of double acid phosphates are boiled with nitric acid before treatment in order to bring all the phosphoric acid in the ortho form. When required the content in water-soluble and citrate-soluble acid must be returned separately and not in one figure as citrate-soluble acid. It was decided that the new Wagner method for determining citrate-soluble acid in basic slag should be adopted. This method is given in another paragraph, and it is not to be applied to other phosphatic materials such as bone-meal.

77. Official Norwegian Methods.—The Director of the Chemical Control Station of Norway, expresses the opinion, that for Norwegian, Swedish, Danish and German conditions, the quantities of material required by the American methods for the determination of phosphoric acid, notwithstanding their analytical exact-

⁴⁶ Die landwirtschaftlichen Versuchs-Stationen, 1904, 60 : 371.

⁴⁷ Die landwirtschaftlichen Versuchs-Stationen, 1903-4, 59 : 313; 1904, 60 : 221.

ness, are insufficient.⁴⁸ In those countries are found many, in part, poorly pulverized, and badly mixed manures, such as ammonium-superphosphate, potassium-superphosphate, and potassium-ammonium-superphosphate, and these can not usually be so well pulverized and mixed that one can secure a true average sample of from two to two and five-tenths grams. Care in the analysis is useless when the material employed does not represent the average conditions of the materials investigated. Therefore, in the countries named, often from 10 to 20 grams, and almost never less than five grams of substance are used in the preparation of the solutions, except, for instance, in the determination of nitrogen and reverted phosphoric acid.

78. Methods for Phosphoric Acid Used in the Norway Stations.⁴⁹

—1. *Description of the Method for Total Phosphoric Acid.*—For determining the phosphoric acid in bone-meal, fish-guano, and superphosphates, five grams of the substance, with 20 cubic centimeters of nitric acid of 1.42 specific gravity, and 50 cubic centimeters of sulfuric acid of 1.8 specific gravity, are boiled half an hour in a half liter flask, diluted with water, and after cooling, made up to the mark. Fifty cubic centimeters of the filtrate are made alkaline with ammonia, then acid with nitric acid, precipitated with 50 cubic centimeters of molybdic solution for every one-tenth gram of phosphorus pentoxid present, heated over the water bath for one hour, and allowed to stand 12 hours, when the supernatant liquid is separated by decantation, the precipitate washed thoroughly with dilute molybdate solution (1:4), dissolved in warm dilute ammonia, and the filter washed with hot water. The ammoniacal solution is neutralized with hydrochloric acid, cooled, mixed, drop by drop, with constant stirring, with from 10 to 20 cubic centimeters of magnesia mixture, and after a quarter of an hour one-third the volume of 10 per cent. ammonia is added. This, after standing two hours, is filtered, washed with five per cent. ammonia until the disappearance of the chlorin reaction, dried, burned in an open crucible over a bunsen, and finally, for a quarter of an hour, in a covered crucible over the blast.

⁴⁸ Division of Chemistry, Bulletin 47, 1896 : 85.

⁴⁹ Solberg, Division of Chemistry, Bulletin 47, 1896 : 83.

2. *Water-Soluble Phosphoric Acid.*—To 20 grams of the substance in a liter flask, are added 800 cubic centimeters of water, shaken every 15 minutes for two hours; the volume is made up to the mark and the phosphoric acid in 50 cubic centimeters of the filtrate, equalling one gram substance, is determined as under total.

3. *Reverted Citrate-Soluble Phosphoric Acid.*—Two and five-tenths grams substance are rubbed up with water, washed upon the filter with about 100 cubic centimeters of water, the residue on the filter washed into a flask with a part of the measured citrate solution, and digested one hour at from 35° to 40° with 200 cubic centimeters of Petermann's citrate solution. The water and citrate extracts are made up to a quarter of a liter each, and the phosphoric acid determined in from 25 to 50 cubic centimeters, according to the quantity present.

Solutions. 1. *Molybdate Solution.*—Three hundred and seventy-five grams of ammonium molybdate are dissolved in two and five-tenths liters of water, and the solution poured into two and five-tenths liters of nitric acid of 1.20 specific gravity.

2. *Magnesia Mixture.*—Two hundred and seventy-five grams of crystallized magnesium chlorid and 350 grams of ammonium chlorid are dissolved in 3250 cubic centimeters of water and filled up to five liters with ammonia of 0.96 specific gravity.

3. *Petermann's Solution.*—One kilogram of citric acid is dissolved in about two liters of water and 1350 cubic centimeters of ammonia of 0.925 specific gravity and filled up with water to 5750 cubic centimeters. The solution then has a specific gravity of 1.09; 300 cubic centimeters of ammonia of 0.925 specific gravity are added.

79. **The Molybdic Acid Method as Practiced by Members of the Union of the German Experiment Stations.**—The method adopted by the German experiment stations is essentially that used at Halle.⁵⁰ The samples are brought into solution in the following way: For the estimation of phosphoric acid in bone-meal, fish-guano, flesh preparations and raw phosphates, and the total phosphoric acid in superphosphates, five grams of the sample

⁵⁰ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 306.

are dissolved in 50 cubic centimeters of aqua regia, made of three parts of hydrochloric acid of 1.12 specific gravity and one part of nitric acid of 1.25 specific gravity, or the solvent may be made of a mixture of 20 cubic centimeters of nitric acid of 1.42 specific gravity and 50 cubic centimeters of sulfuric acid of 1.8 specific gravity. The boiling should continue for half an hour. The solution is made up to half a liter and filtered. Fifty cubic centimeters of the filtrate containing the phosphoric acid, (with double superphosphates, 25 cubic centimeters), are digested with 200 cubic centimeters of ammonium molybdate solution for three hours at 50° in a water bath and, after cooling, filtered, so that as little as possible of the precipitate is collected upon the filter, which is made of strong paper.

The yellow precipitate is washed by decantation in the flask nine times with 20 cubic centimeters of molybdic solution diluted with one volume of water and the filter washed out once with the same quantity of liquid. The funnel, with the filter, is immediately placed upon the flask and the portion of the precipitate collected in the filter dissolved in five per cent. ammonia, which is easily accomplished by throwing ammonia upon it from a wash bottle. Afterwards the filter is washed with a sufficient quantity of hot water and finally removed. The contents of the flask are neutralized while warm with hydrochloric acid, the acid being added until the precipitate first formed, after continued shaking, is again dissolved in the liquid. The solution is then cooled and treated, drop by drop, with constant stirring, with 20 cubic centimeters of magnesia mixture. Finally 25 cubic centimeters of dilute ammonia solution are added, the precipitate is not shaken, and after two hours is filtered through a gooch.

For the filtering of the ammonium magnesium phosphate by the molybdic method, freshly prepared felts are always employed since the remarkably fine crystalline precipitates will pass through a filter which has once been used. It is necessary also that special precautions be taken in the ignition. The crucible should be heated in a platinum cap, which has the purpose of protecting the contents of the crucible from the access of reducing gases during the ignition. After redness has been reached

the cap can be removed and the crucible transferred to a blast where it is strongly ignited for 10 minutes before weighing. The precipitate should be pure white.

The molybdic solution is prepared as follows: One hundred and fifty grams of ammonium molybdate are dissolved in a liter of water, and after the solution is completely cooled, poured into a liter of nitric acid of 1.2 specific gravity.

80. Estimation of Soluble Phosphoric Acid.—1. The extraction of the superphosphates is made as follows: Twenty grams of the superphosphates are placed in a liter flask with 800 cubic centimeters of water and shaken continuously for 30 minutes. The flask is then filled with water to the mark and the whole again thoroughly shaken and filtered. For shaking, a machine is recommended, driven by hand or water power. The normal rate of the machine is fixed at 150 turns per minute.

2. The solution of double superphosphates, obtained as above, must be boiled with nitric acid before the precipitation of the phosphoric acid in order to convert any phosphoric acid present as pyrophosphoric into tribasic phosphoric acid. For each 25 cubic centimeters of the superphosphate solution 10 cubic centimeters of concentrated nitric acid are added and the mixture boiled.

3. The precipitation of the phosphoric acid is conducted by the molybdate method as usually practiced.

4. For the estimation of iron and alumina in each of the superphosphates the Glaser alcohol method is recommended provisionally. A description of this method is given further on.

81. The French Official Method.—For the purpose of securing the most appropriate method of analysis the materials to be examined are divided by the French authorities into the following classes:⁵¹

These groups are:

1. Mineral phosphates, consisting of tricalcium phosphate more or less mixed with carbonate of lime, silicious matters, oxids of iron and alumina, etc.

2. Bone phosphates and bone black.

3. Phosphates in manures, poudrettes and guanos.

⁵¹ Sidersky, *Analyse des Engrais*, 1901 : 54 ; *La Sucrierie indigène et coloniale*, 1897, 50 : 382.

4. Superphosphates, precipitated (reverted) phosphates, ammonia-magnesium phosphates.

5. Phosphatic slags.

In the first class the phosphoric acid is determined by direct precipitation by the citrate method.

In the second and third classes previous to the separation of the phosphoric acid the organic matter is destroyed after treating with some slaked lime to prevent the organic matter from reducing any phosphate. After the reduction of the organic matter the process is continued as in the first class.

In the fourth class the precipitated (reverted) phosphoric acid is dissolved in ammonium citrate. About 0.75 gram of the sample is rubbed in a mortar with a few drops of the citrate solution and the paste washed into a flask of 150 cubic centimeters capacity with 60 cubic centimeters of the citrate of ammonia solution and digested with frequent shaking for 12 hours. The flask is subsequently filled to the mark and, after shaking, the contents are poured on a filter, and in 100 cubic centimeters of the filtrate, representing 0.5 gram of the sample, the phosphoric acid is separated as above.

The total phosphoric acid is determined as in the first instance.

In the fifth class the phosphoric acid is separated as usual after solution in hydrochloric acid and not nitric. When the slags are very rich in lime it is advisable to dissolve first in acetic acid and separate the greater part of the lime as oxalate before dissolving the phosphoric portion of the slag in hydrochloric acid.

The molybdate method is also used officially by the French chemists in harmony with the usual directions.

The methods employed are so nearly like those already described that their repetition is not deemed necessary. The determination of the degree of fineness of the sample is properly regarded by the French chemists as of great importance.

In the case of natural phosphates and slags it is advised that the sample be separated by a sieve of 0.17 millimeter mesh. At least 90 per cent. of the sample should pass such a sieve.

82. Swedish Official Method for Determination of Phosphoric Acid.⁵²—The Swedish chemists determine phosphoric acid in fertilizers both by the molybdate and the citrate methods. These methods carefully conducted according to the directions given below, give very concordant results. In doubtful cases the former method is taken as the deciding one, it having proved by long practice to give very satisfactory results.

Reagents for the Molybdate Method.—1. *Molybdic Solution.*—Prepared by dissolving 100 grams of finely powdered molybdic acid with heat in 400 grams of eight per cent. ammonia of 0.967 specific gravity and pouring the solution into 1500 grams of nitric acid of one and two-tenths specific gravity; or else by dissolving 150 grams ammonium molybdate in one liter of hot water, and pouring the solution into one liter of nitric acid of 1.2 specific gravity. Prepared in this way, the molybdic solution will contain, in the former case, five per cent., in the latter case, from five to six per cent. of molybdic acid, and 100 cubic centimeters of it are required for precipitating one-tenth gram of phosphorus pentoxid.

2. *Magnesia Mixture.*—Prepared with 110 grams of crystallized magnesium chlorid, 140 grams of ammonium chlorid, 700 grams of eight per cent. ammonia of 0.967 specific gravity and 1300 grams of distilled water. The mixture is filtered after a few days, if necessary; 10 cubic centimeters are required for precipitating one-tenth gram of phosphorus pentoxid.

3. *Ten per cent. ammonia* of 0.959 specific gravity.

Determinations: (a) *Water-Soluble Phosphoric Acid.*—1. *Preparation of the Aqueous Solution.*—Of superphosphates and other fertilizers containing water-soluble phosphoric acid, 20 grams are treated with water in a mortar; lumps are crushed lightly but completely with the pestle without pulverizing finer; the whole mass is then washed into a graduated flask holding one liter, which at once is filled up to the mark. The volume taken up by the residue insoluble in water is left out of consideration in the calculation. After standing in the flask (which is

⁵² Official Swedish Methods Translated for the Author by F. W. Woll.

occasionally shaken) at the ordinary temperature of the room for two hours, the mixture is filtered.

2. *The Determination.*—To 25 cubic centimeters of the superphosphate solution thus prepared (or a quantity of the sample equal to one-tenth gram phosphorus pentoxid) add a quantity of molybdic solution sufficient for complete precipitation, leave standing for four hours in a beaker covered with a watch-glass; decant the solution through a small filter, wash the precipitate first by decantation, then on the filter, with a mixture containing 100 parts molybdic solution, 20 parts nitric acid of 1.2 specific gravity, and 80 parts water, until a few drops put into alcohol, to which some dilute sulfuric acid has been added, do not any longer cause turbidity. The molybdic precipitate is now washed with a little water from the filter into a beaker and particles adhering to the filter are dissolved by a hot mixture of one part ammonia and three parts water, which is allowed to flow into the beaker till the precipitate is finally completely dissolved in it. To the clear solution add dilute hydrochloric acid while stirring till the yellow precipitate formed by the acid is no longer immediately dissolved; then add from six to eight cubic centimeters of ammonia through the filter. The volume of the solution is not to exceed 75 cubic centimeters. It is cooled completely and one cubic centimeter of magnesia mixture is added from a burette for every centigram of phosphorus pentoxid which it is expected to contain, and finally one-quarter of its volume of ammonia is added. The precipitate may be filtered after four hours, and washed on the filter, preferably by means of suction, with a mixture of one part ammonia and three parts water till the filtrate is entirely free from chlorine. After drying, heat the precipitate, first gently, then stronger, and finally with a blast for a few minutes and then weigh it.

Treated with hydrochloric acid it must leave no insoluble residue (SiO_2), nor should hydrogen sulfid cause any precipitation in the solution thus formed (MoO_3).

(b) *Total Phosphoric Acid.*—1. *In Superphosphates.*—For the determination of total phosphoric acid, treat a weighed quantity of the superphosphate with nitric acid, if necessary to bring a dif-

difficultly soluble residue into solution, with addition of hydrochloric acid, or of potassium chlorate, to destroy organic matter present. Dilute the solution to a definite volume and determine the phosphoric acid in a measured quantity thereof, as directed under (a) 2; if hydrochloric acid or potassium chlorate be applied in the preparation of the solution, however, the determination of the phosphoric acid must not be made till the measured quantity has been repeatedly evaporated to dryness with concentrated nitric acid.

2. *In Bone-meal*.—Destroy organic matter in five grams of the sample by ignition, dissolve the residue in nitric acid, filter from the insoluble residue, dilute the filtrate to half a liter, and determine the phosphoric acid as directed under (a) 2 in an aliquot part containing about one-tenth gram phosphoric pentoxid.

3. *In Fish-guano* (and other fertilizing materials of organic origin).—The organic matter cannot here be removed by simple ignition, as in this way a loss of phosphorus may take place; it is therefore destroyed either in the wet way by nitric acid and potassium chlorate, or in the dry way by fusion with a mixture of potassium nitrate and sodium carbonate, otherwise the procedure is as in (b) 1.

4. *In Mineral Phosphates*.—Determine the phosphoric acid in a solution obtained by nitric acid; organic matter if present is destroyed preferably in the wet way.

5. *In Basic Slag*.—Dissolve 10 grams of powdered slag by treating it with 100 cubic centimeters of hot fuming hydrochloric acid; wash the solution into a graduated half liter flask, fill to the mark, shake well, and filter. Determine the phosphoric acid in 25 cubic centimeters of the clear filtrate, according to (a) 2, after having first, however, evaporated the solution to dryness and then at least three times evaporated the residue to dryness with concentrated nitric acid.

83. Method Employed by the Royal Experiment Station of Holland.—*A. Soluble Phosphoric Acid.*⁵³—The necessary reagents are:

(1) Molybdate solution, made by dissolving 150 grams of am-

⁵³ Methoden van Onderzoek aan de Rijkslandbouwproefstationen, 1893: 4.

monium molybdate in a liter of water and pouring the solution into a liter of nitric acid of 1.20 specific gravity.

(2) A 10 per cent. solution of ammonium nitrate.

(3) Strong and dilute ammonia, the latter being between two and five-tenths and three per cent. and of 0.988 specific gravity.

(4) Magnesia mixture made by dissolving 110 grams of crystallized magnesium chlorid, 140 grams of ammonium chlorid, and 700 cubic centimeters of ammonia of 0.96 specific gravity in water and bringing the solution to two liters.

(5) Ammoniacal citrate solution, made by dissolving 500 grams of citric acid in a liter of water, and mixing with four liters of 10 per cent. ammonia of 0.96 specific gravity.

Manipulation.—Place 20 grams of the substance in a mortar together with some cold distilled water or pure rain water, stir, and decant the water and suspended matters into a liter flask. After this has been repeated several times, rub up the residual mass and wash it all into the flask. Fill up to about 900 cubic centimeters and allow to stand two hours (24 hours in the case of double phosphates with more than 22 per cent. of soluble phosphoric acid); shaking repeatedly, or shaking continuously, for half an hour. Fill up to the liter mark and filter through a dry filter. Add 100 cubic centimeters of molybdate solution for each 100 milligrams of phosphorus pentoxid present, to portions of 25 or 50 cubic centimeters for each determination, warm to about 80° for an hour, filter, and wash the precipitate with the ammonium nitrate solution. Add a little molybdate solution to the filtrate, warm, and, if a fresh precipitate be observed, it is to be added to the first. The precipitate is dissolved in ammonia and hydrochloric acid carefully added until the precipitate caused by it only slowly redissolves on stirring. The phosphoric acid is precipitated from the clear liquid, which is still ammoniacal, with magnesia mixture, using 10 cubic centimeters for each 100 milligrams of phosphorus pentoxid present. This is added, drop by drop, and the liquid kept stirred during the addition. Allow to stand at least two hours, filter, wash with dilute ammonia, dry, and ignite, at first with a very small flame, and finally with the blast-lamp or in a Rössler furnace. To insure burning to white-

ness, nitric acid may be used, but not more than one or two drops.

B. Total Phosphoric Acid.—(1) For bone and flesh-meal, fish-guano, and similar fertilizers the reagents necessary are the same as before.

Carefully burn five grams to ash, boil the ash for half an hour with nitric acid of 1.32 specific gravity, dilute with water, and, after cooling, dilute to 500 cubic centimeters. Filter through a dry filter and add 100 cubic centimeters of the molybdate solution for each 100 milligrams of phosphorus pentoxid present to 50 cubic centimeters of the filtrate. Treat further as before described.

(2) Phosphates, guanos, bone-black, etc.

One gram of substance, after powdering, and, if necessary, igniting, is covered with four cubic centimeters of hydrochloric acid of 1.13 specific gravity and a little water and heated for an hour and a half. Evaporate to dryness without filtration, making repeated additions of nitric acid until no more vapors of hydrochloric acid are evolved. Boil the residue with nitric acid, cool, make up to 100 cubic centimeters with water, and shake. Filter and treat 50 cubic centimeters of the resulting solution by the molybdate method and proceed further as before described.

84. Sources of Error in the Molybdate Method.—When conducted with proper care, the gravimetric molybdate method is one of the most exact processes known to analytical chemistry.

There are, however, some sources of error in the process which should be avoided as carefully as possible or taken into account.

1. *Error Due to Occluded Silica.*—When silica passes into solution in the original sample, and this may be the case especially with mineral phosphates, it may appear both in the yellow precipitate and in the final magnesium pyrophosphate. In all such cases the residue, after ignition, should be dissolved in hydrochloric acid and any insoluble residue weighed as silica and deducted from the first weight. If the silica be removed by evaporating the solution of the original material to dryness, and igniting to destroy organic matter, care must be taken to reconvert all phosphoric acid into the ortho form by long boiling with nitric acid before precipitation.

Another method of avoiding any trouble from silica consists in using sulfuric and a little nitric acid as the solvent for the original substance. Silica is not soluble in hot concentrated sulfuric acid. The volume of the sulfuric should be about ten times that of the nitric acid used, and the boiling be continued until sulfuric vapors are evolved.

2. *Error Due to Arsenic.*—Only in rare cases will arsenic be found in phosphatic fertilizing materials. In case of pyritic phosphates, the iron disulfid may carry arsenic. The solution in such a case is best accomplished in hydrochloric acid. If aqua regia be used, all nitric acid should be removed by repeated evaporation with hydrochloric acid. The arsenic can then be precipitated in the hot dilute hydrochloric acid solution by hydrogen sulfid.

3. *Error Due to Occluded Magnesia.*—The danger of contamination of the final precipitate with magnesium oxid has been pointed out by some authors. The re-solution of the precipitate followed by a second precipitation is the usual remedy proposed. Lorenz states that this source of error may be entirely avoided by the addition of two per cent. of citric acid to the solution.⁵⁴ Without the addition of citric acid the precipitation of some magnesia with the phosphate, at least in strongly ammoniacal solutions, cannot be avoided even by the slowest and most careful addition of the magnesia mixture. The citric acid is used in the common form of ammonium citrate solution.

4. *Error Due to Volatility of Phosphoric Acid.*—This source of error has been made the subject of a special study by Neubauer.⁵⁵ From the results a table has been constructed, the use of which is recommended for phosphoric acid determinations. The source of error in the method where neutralization is omitted lies exclusively in the loss of phosphoric acid by volatilization. The magnesia-covered crucible lid offers a very good control of this error, and its use is recommended to the analyst. Of course, the presence of sulfur in the gas used for ignition is liable to disturb this check.

⁵⁴ Zeitschrift für analytische Chemie, 1893, 32 : 64.

⁵⁵ Journal of the American Chemical Society, 1894, 16 : 289. Translated and Abridged by K. P. McElroy.

The following course of procedure in the determination of phosphoric acid can be recommended to avoid or correct this error:

Separate the phosphoric acid in the form of the yellow precipitate and wash this latter in the usual way. Too high a heat should not be employed, nor should the solutions be allowed to stand too long, lest excess of molybdic acid separate. Dissolve the phosphomolybdate in 100 cubic centimeters of cold two and five-tenths per cent. ammonia and add as many cubic centimeters of the usual magnesia mixture (55 grams magnesium chlorid and 70 grams ammonium chlorid dissolved in a liter of two and five-tenths per cent. ammonia) as there are centigrams of phosphorus pentoxid present. Addition should not be made faster than 10 cubic centimeters per minute. Stir during the addition. After the precipitation stir briskly once more and allow to stand at least three hours. Wash with two and five-tenths per cent. ammonia till the chlorin reaction disappears, dry the filter, and introduce into a well cleaned crucible which has been thoroughly ignited. Place the lid at an angle, carbonize the filter, and gradually raise the heat, though not higher than a medium red heat, till the pyrophosphate becomes completely white. When this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. For example, if the weight be 250 milligrams, the correction to be added is four and two-tenths milligrams, and the correct weight is then 254.2 milligrams. Multiplication of the sum by sixty-four gives the amount of phosphorus pentoxid in the weight taken for analysis.

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contains no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

Found, Mg ₂ P ₂ O ₇ in grams.	Lost, milligrams Mg ₂ P ₂ O ₇ .	Found, Mg ₂ P ₂ O ₇ in grams.	Lost, milligrams Mg ₂ P ₂ O ₇ .
0.10	0.6	0.24	4.0
0.12	0.8	0.25	4.2
0.14	1.2	0.26	4.6
0.15	1.4	0.27	5.0
0.16	1.6	0.28	5.5
0.17	2.4	0.29	6.1
0.18	2.6	0.30	6.8
0.19	3.2	0.31	7.6
0.20	3.5	0.32	8.6
0.21	3.6	0.33	9.6
0.22	3.8	0.34	10.6

85. Modification of Jörgensen.—Jörgensen has submitted to a renewed detailed study the standard methods of precipitation of phosphoric acid as magnesium ammonium phosphate for the purpose of determining whether any errors have crept into the usual methods.⁵⁶ He used as the basis of his test for accuracy by preference a preparation of sodium ammonium phosphate in a crystalline state, $\text{NaNH}_4\text{HPO}_4\text{H}_2\text{O}$. He selected this salt as the one best suited for testing the accuracy of the method and the purity of reagent because it can be prepared easily in a state of purity by recrystallization out of ammoniated water. The crystals are subsequently exposed in the air until dry. It is also a salt which has little tendency to efflorescence, and its purity can be determined without reference to its phosphoric acid content by determining the loss of weight upon ignition and by determining its content of ammonia. If these two determinations show a pure salt the content of phosphoric acid may be left out of consideration, since this is the material upon which methods and solutions are to be tried.

Aside from the variation in the standard of comparison, there is little new in Jörgensen's work. He makes a few changes in the composition of preparations which he uses, but the change in no case is great enough to introduce any appreciable difference in the manipulation.

⁵⁶ Zeitschrift für analytische Chemie, 1906, 45 : 273.

Jørgensen calls especial attention to the tests which he has made on the influence of impurities in the phosphatic materials which are to be determined, and especially of the maximum quantities of silica, iron, calcium, aluminum, or salts thereof, which may be present without interfering with the accuracy of the process. He also uses a concentrated molybdate solution of which about 61 cubic centimeters are necessary for the precipitation of 0.2 gram (P_2O_5) on the supposition that one part of phosphorus is best precipitated in the presence of about 12 parts of molybdenum.

In the application of the method for fertilizing materials Jørgensen prefers that they should be brought into solution either with hydrochloric or sulfuric acids, hydrochloric preferred. For the conversion of the pyrophosphates into phosphates, however, nitric acid is necessary. If the solution contains about 0.2 of pyrophosphoric acid in 50 cubic centimeters, it should be boiled with 10 cubic centimeters of nitric acid of a specific gravity of 1.4 for a quarter of an hour, or 2.5 of nitric acid of the same strength for half an hour, or 1.25 cubic centimeters for an hour. In the precipitation of the phosphoric acid in the fertilizers, if ferric oxid is present not exceeding in quantity 0.22 gram, aluminic oxid in quantity not exceeding 0.11 gram, calcium oxid in quantity not exceeding 0.42 gram, and silica in quantities not exceeding 0.17 gram, these bodies do not exert any injurious effect. The molybdate precipitate is washed about 10 times by decantation with from 20 to 25 cubic centimeters of a nitric acid solution of ammonium nitrate consisting of about one per cent. of nitric acid to about five per cent. of ammonium nitrate in 100 parts of the solution, and afterwards the precipitate is dissolved in a measured quantity of 2.5 per cent. of ammonia in such a way that about 100 cubic centimeters of the solution are used for each 0.2 gram phosphoric anhydrid, with similar quantities of phosphoric acid and correspondingly less quantities of the sulphate. If the filter is not considered well washed, a small quantity of water may be used afterwards for this purpose. The solution is then heated in a covered beaker until bubbles of steam begin to escape, and drop by drop treated with a neutral mag-

nesium solution of which from 15 to 20 cubic centimeters are required for each 0.2 gram of phosphoric anhydrid present. After the addition of the magnesium solution and during the cooling it is desirable to frequently shake the vessel containing the precipitate, especially if the precipitate has changed into the dense, crystalline form, which is apt to be the case, for the addition of the magnesium mixture has been slow and there is not a sufficient excess of ammonia. The ordinary stirring apparatus which is used can give valuable service at this point. The filtration of the precipitated phosphoric acid should not take place until after four hours' standing. A longer time than four hours does not have any influence upon the results. After the collection of the material in the filter it is washed with 2.5 per cent. of ammonia. It is very convenient to have the bottom of the crystal covered with precipitated platinum, since in this case the heating over a blast-lamp is unnecessary, the ordinary heating over a common burner being sufficient. For conversion the factor 0.63757 is used. (Log. $0.80453 \div 1$).

86. Influence of Aluminium, Magnesium and Calcium upon the Phosphoric Acid Determination.—In solutions containing aluminium, iron, magnesium and calcium in which phosphoric acid is to be determined, the influence of these bases upon the determination must not be neglected. Neubauer has called attention to this point, especially in connection with the determination of phosphoric acid in the hydrochloric acid solutions of soils.⁵⁷

The well known fact that the chlorid of lime and aluminium at moderate heating in the air and in water produce insoluble oxids with which the phosphoric acid as an insoluble sulfate is entangled is well known. The chlorids of alkalies, however, are not changed by this heating, and this difference in deportment is the principle upon which Neubauer bases his observations. Where only potassium and phosphoric acid are to be determined in a hydrochloric acid solution, for instance, of a soil, Neubauer uses the following process:

A volume of the solution corresponding to 25 grams of the original substance (soil) is evaporated to dryness in a platinum

⁵⁷ Die landwirtschaftlichen Versuchs-Stationen, 1905-6, 63 : 141.

dish. If no chlorid of lime is contained in the original soil before the evaporation takes place a half gram of calcium carbonate is added to the solution. The residue from drying is heated carefully and in order to avoid too rapid evaporation a platinum or nickel plate is placed between the source of the heat and the dish. After complete dryness has been secured, the flame is so regulated that the bottom of the dish containing the residue is heated almost to a low red heat, but even in this case the volatilization of the aluminium chlorid is not to be feared. After the vigorous evaporation of the vapors of hydrochloric acid has diminished somewhat the platinum or nickel plate is laid upon the top of the dish. The mass within the dish soon reaches a condition in which it can be rubbed into a fine powder by a glass rod, after which it is heated a while longer and stirred continually until all parts of the material are reduced to a fine powder. After about an hour of treatment of this kind the organic substances which the solution may contain are completely destroyed and the residue is ready for further investigation.

The contents of the dish are washed in a 125 cubic centimeter flask with a sufficient quantity of water to fill the flask half full and the contents of the flask are boiled over a low flame for about half an hour; after cooling, the flask is filled to the mark, thoroughly mixed and filtered through a very small dry filter into a dry vessel. The filtrate must be completely colorless and at most only slightly alkaline, and if the operation above indicated has been properly carried out, it is entirely free from iron, phosphoric acid and silicic acid. One hundred cubic centimeters of the filtrate, corresponding to 20 grams of the original soil, is the quantity used, if the volume of insoluble material is not taken into consideration.

If a correction is desired for this, the ignited residue is weighed and its volume approximately calculated by taking into consideration its specific gravity and weight.

In a porcelain dish 100 cubic centimeters of filtrate are evaporated to dryness, a few drops of hydrochloric acid added and a sufficient quantity of platinum chlorid for the determination of potassium salts in the usual manner. Inasmuch as other salts

may be found in this operation, their separation is recommended by the method described by Neubauer.⁵⁸

For the estimation of phosphoric acid the insoluble residue obtained in the estimation of potash above described is used. After the whole of the filtrate has run through a small filter upon which the reddish brown precipitate has been collected, replace in the flask and treat with a dilute sulphuric acid corresponding to five cubic centimeters of the concentrated acid; then boil the half-filled flask for about half an hour. A small quantity of oxid sometimes remains very firmly attached to the platinum dish, and for this reason the acid is conveniently used for washing out the dish. It is then certain that no trace of phosphoric acid is lost. If any stains remain upon the platinum dish due to the iron they are easily removed by treatment with zinc and hydrochloric acid.

The phosphoric acid which has passed into solution corresponds to 20 grams of the original solution (soil) which has been extracted and is conveniently determined by the molybdate method. This molybdate method is recommended because, even with all the care which has been exercised, the solution usually still contains a little salicylic acid. Neubauer, however, highly recommends in this case, for the estimation of small quantities of phosphoric acid, the direct weighing of the yellow precipitate. In this case only 25 cubic centimeters of the solution are employed, corresponding to five grams of the soil, and this is treated with 25 cubic centimeters of nitric acid of 1.2 specific gravity, and the rest of the process is carried out as described in the volumetric method.

For the estimation of calcium and magnesium another portion of the solution, corresponding to 25 grams of soil, except in the case of marly soil, where a smaller quantity is used, is treated as above described, except, of course, without the addition of calcium carbonate. The residue is treated with water and the liquid should give no trace of an acid reaction. Otherwise it is evident that the deposition of the chlorid has not been sufficiently secured.

According to the estimated quantity of calcium from about two

⁵⁸ *Zeitschrift für analytische Chemie*, 1904, **43**: 14.

to five grams of ammonium chlorid are added and the mixture heated upon the water bath until no further evaporation of ammonia takes place. The mixture is washed in a 125 cubic centimeter flask and treated with a few drops of ammonia, boiled a few minutes, cooled, filled to the mark, filtered through a small dry filter and 100 cubic centimeters of the filtrate, corresponding to 20 grams of the soil, used for the estimation of lime and magnesium by the usual methods.

Neubauer claims that the method described is recommended particularly by reason of its speediness. According to him, it also has other advantages. For instance, the precipitation by ammonia and ammonium carbonate is avoided in which a slimy, difficultly filterable precipitate is often produced which can easily intertangle notable quantities of phosphoric acid and potash. The filtrate from the iron and aluminium precipitate must, on account of its ammonia and ammonium carbonate, be very carefully evaporated to dryness in order to avoid loss by spurting.

Finally, one of the especial advantages of the process appears to be that the disturbing influences of organic substances is completely eliminated and no impure potassium platinum chlorid or brown colored phosphoric acid precipitate is any longer possible.

This method, which is originally designed for application to soils, may be used, apparently, with advantage in the examination of slags containing small quantities of potash and phosphoric acid to determine their value as fertilizing material. A quantity of phosphoric acid and potash, especially the latter, which is directly soluble in hydrochloric acid, may prove to be an index of the comparative availability of these two plant foods contained in slag.

87. The Color of the Magnesium Pyrophosphate.—After the final ignition of the magnesium pyrophosphate, whether secured by the citrate or the molybdate method, a black or grayish tint is often noticed. This may be due to traces of organic matter brought down by the precipitate and especially to a lack of care in the initial ignition. Many devices have been proposed for the purpose of avoiding this coloration, although general experi-

ments have shown that there is no appreciable increase in the weight of the precipitate when colored in this way.

When the precipitation is carried on according to the citrate method, Neubauer proposes to eliminate this coloration by the use of ammonium sulfate.⁵⁹ About seven cubic centimeters of a saturated solution of ammonium sulfate should be added to the solution before the precipitation by the magnesium mixture. With this precaution it is possible to obtain a perfectly white precipitate after five minutes of ignition. The lively glowing of the precipitate throughout the whole mass at the time of changing into pyrophosphate is much more easily observed by this treatment than when the mass is gray or black. Even should the addition of the ammonium sulfate solution to one containing a large amount of lime produce a precipitate of crystalline calcium sulfate, it is of no importance, inasmuch as the ammonium citrate immediately dissolves large quantities of the calcium salt.

A white pyrophosphate is easily obtained by treating the precipitate on the gouch after washing free from chlorids with a drop or two of ammonium nitrate. The ignition is commenced very gently at first and afterwards, when the mass is white, the blast is used.

If the ignited residue be gray it may sometimes be whitened by moistening with a drop or two of nitric acid, burning at a very low temperature, followed by the blast. There is no appreciable difference in weight between a gray and white pyrophosphate.

88. Determination of Phosphoric Acid and Nitrogen in the Same Solution by Treatment with Sulfuric Acid and Mercury.—Fertilizing materials which contain organic nitrogen and phosphoric acid, such as bones, are of such a nature that it is often difficult to obtain a fair sample of them in quantities suited to the direct determination; viz., about one gram. Thus it often becomes important to take a much larger quantity of the material, to bring it into solution and to take an aliquot part thereof. It may also often happen that it is important to determine the phosphoric acid in the same sample which has been used for the determination of the nitrogen by moist combustion with sulfuric acid and mercury.

⁵⁹ *Zeitschrift für angewandte Chemie*, 1894, 7 : 678.

In this connection, however, it is somewhat difficult to avoid the precipitation of some of the mercury with the phosphoric acid.

The mercuric sulfate which is produced by the Kjeldahl method is not precipitated in the presence of ammoniacal solution of ammonium citrate, but there may be small quantities of mercurous salts present or some finely divided metallic mercury which may contaminate mechanically the phosphate precipitate. These disturbing influences may be removed by previous treatment with sodium chlorid. If from 50 to 60 cubic centimeters of sulfuric acid have been used for the solution and oxidation and this be made up to half a liter, it will be sufficiently dilute to permit an almost quantitative separation of the mercurous chlorid produced by treatment with sodium chlorid.

Neubauer, who has proposed this method, finds that when sodium chlorid is used previous to the precipitation of the phosphoric acid, a precipitate of ordinary size contains, at most, only one milligram of mercury, while without the use of sodium chlorid as much as four milligrams may be found. The details of the method employed by Neubauer are as follows:⁶⁰

Ten grams of the fertilizing material are placed in a half liter flask with from 50 to 60 cubic centimeters of strong sulfuric acid, two grams of mercury, and a little paraffin to prevent foaming. The oxidation is carried on as usual in the Kjeldahl method. The liquid, after cooling, is diluted with water and one cubic centimeter of a citrate solution of sodium chlorid added, cooled, filled to the mark, filtered, and 50 cubic centimeters taken for the determination of the phosphoric acid, according to the citrate method, and the same quantity for the determination of the ammonia by distillation. The methods of digestion of soils with sulfuric acid described in Volume I, are also applicable to fertilizing materials.

THE CITRATE METHOD

89. General Principles.—It has been seen that in the molybdate method there is introduced a process at considerable cost, both of reagents and time, having for its object the separation of the phosphoric acid from all the other acids and bases which may

⁶⁰ Zeitschrift für angewandte Chemie, 1894, 7 : 678.

have been present in the original sample. The phosphorus is thus obtained in composition with molybdenum and ammonium in a form easily soluble in ammonia, from which it can be accurately separated by means of a soluble salt of magnesia.

The citrate method has for its object the suppression of this intermediate step and the determination of the phosphoric acid by direct precipitation in presence of iron, lime, and alumina. The principle in which it is based rests on the well known power of an alkaline ammonium citrate to hold in solution the salts of iron, alumina, and lime, while at the same time it permits of the separation of phosphoric acid, as ammonium magnesium phosphate. In no case can the citrate method be regarded as a rigidly exact analytical process, but large experience has shown that the errors of the method are compensatory and that it affords a good and ready method for fertilizer control.

When phosphoric acid solutions which contain no iron, lime, alumina, or manganese, are precipitated in presence of ammonium citrate the results obtained vary markedly with the quantity of magnesia mixture employed. Grupe and Tollens were the first to point out that a portion of the phosphoric acid might remain in solution, but that the precipitate might contain a sufficient excess of magnesia to compensate for the loss.⁶¹ If lime, iron and alumina, moreover, are present, the precipitate obtained is not wholly free from these bodies. It is true that the quantities of these bodies found in the precipitate are quite small, but they may at times influence the accuracy of the results. The presence of lime and magnesia in the precipitate, as already mentioned, is indicated by the yellow color produced by moistening the white ignited precipitate with silver nitrate.⁶² It has been further shown by Glaser, as well as by Neubauer, that a portion of the phosphoric acid may be lost by volatilization in the citrate method.⁶³ When the ignition is carried on in a crucible where the cover is coated with magnesia to intercept the volatilized acid, a considerable quantity of it can be recovered by the molybdate method.

⁶¹ Journal für Landwirtschaft, 1882, 30 : 23.

⁶² Tollens, Journal für Landwirtschaft, 1882, 30 : 48.

⁶³ Zeitschrift für angewandte Chemie, 1894, 7 : 544.

Where too little magnesia mixture is employed, therefore, two sources of loss are to be guarded against; viz., a part of the phosphoric acid may remain in solution and another part be volatilized on ignition. The explanation of the volatilization is as follows: In the presence of ammonium citrate, magnesium chlorid may be partly converted into magnesium citrate and ammonium chlorid. There may be a time, therefore, in the precipitation with not too great excess of magnesia mixture, when proportionally there is little magnesium chlorid and much ammonium chlorid present. The formation of a salt represented by the formula $2\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$ may take place which, upon ignition, breaks up into $2\text{Mg}(\text{PO}_3)_2$ and finally passes into $\text{Mg}_2\text{P}_2\text{O}_7$ with loss of P_2O_5 . This theoretical condition has but little weight, however, practically in the analysis of fertilizers, since in these cases a large quantity of lime is always present. But even in these cases traces of volatile P_2O_5 may be discovered.

Wells has shown that the citrate method gives good results in certain conditions, but that this accuracy is reached by a fortunate compensation of errors.⁶⁴ The ammonium magnesium salt does not precipitate all the phosphoric acid in this process, but contains enough impurities to make up for this loss.

Johnson in conjunction with Osborne has shown that the results by the citrate method practiced in accordance with the details laid down by Vögel, are too low, but that this difficulty could be overcome by using more and stronger magnesia mixture and a larger quantity of strong ammonia solution.⁶⁴ The citrate method was found to give unsatisfactory results when iron and alumina were present in any considerable quantity. In the examination of the final ignited precipitate, which should be pure magnesium pyrophosphate, it was found to consist of only from 94.98 to 97.83 per cent. of that salt. The chief impurity found was calcium oxid, the percentage of which varied from 2.05 to 3.95 in six cases. There was also a considerable percentage of loss due, probably, to magnesia and pyrophosphoric acid.

The presence of large quantities of iron and alumina also impairs the accuracy of the molybdate method when the precipita-

⁶⁴ Journal of the American Chemical Society, 1894, 16 : 462.

tion of the yellow salt takes place at too high a temperature. When the temperature of precipitation in the method is above 50° the results are likely to be too high, while a great excess of nitric acid in the reagent may produce a contrary effect. In the latter case the filtrate from the yellow salt should be mixed with additional quantities of molybdate solution until no further precipitate takes place.

Many methods of conducting the citrate method have been proposed, but the best of them are based on the one elaborated at the experiment station of Halle by Bühring, and which will be given in the next paragraph, followed by some other methods in use in other localities.

90. Method of Halle Agricultural Experiment Station.⁶⁵—

The citrate method elaborated by Bühring, as described by Morgen, is the one employed.⁶⁶ The principle depends upon the direct precipitation of the phosphoric acid by magnesia mixture. By the addition of a solution of ammonium citrate the precipitation of lime, iron, alumina and other bases is practically prevented. The precipitate of ammonium magnesium phosphate is converted by ignition into magnesium pyrophosphate and weighed as such. By the use of this method a part of the phosphoric acid sometimes escapes precipitation and a portion of the other bases is sometimes thrown down with the precipitate. Experience has shown that by adhering to certain precautions the weight of impurities in the precipitate may be made to correspond very nearly to the weight of the phosphoric acid which escapes precipitation.

(1) *Soluble Acid.*—The soluble phosphates are first brought into solution in such a way that one liter of water contains the soluble phosphoric acid from 20 grams of the substance. Twenty grams are rubbed in a porcelain mortar with water and through a wide-necked funnel washed into a bottle-shaped flask in which a little water has been previously placed. The flasks employed are made of thick glass in order to withstand shaking. After the substance is washed in, the flasks are filled to the mark

⁶⁵ Bieler und Schneidewind, Die agrikultur-chemische Versuchsstation, Halle a/S, ihre Einrichtung und Thätigkeit, 1892 : 56.

⁶⁶ Die chemische Industrie, 1890, 13 : 135, 139.

and closed with rubber stoppers. They are placed upon a shaking rack, as indicated in Fig. 3, which is also furnished with an apparatus for separating the fine meal from the basic slag.

On a table, as shown in the figure, is fastened a movable horizontal board by means of hinges. On one side of this movable board is placed an open wooden box in which is a perforated shelf for the purpose of holding the flasks, so as to prevent their striking together during the shaking. On the other side is placed the sifting apparatus above mentioned. The to and fro movement of the shaker is imparted by any convenient mechanism.

Good results are obtained by placing the substance to be exam-

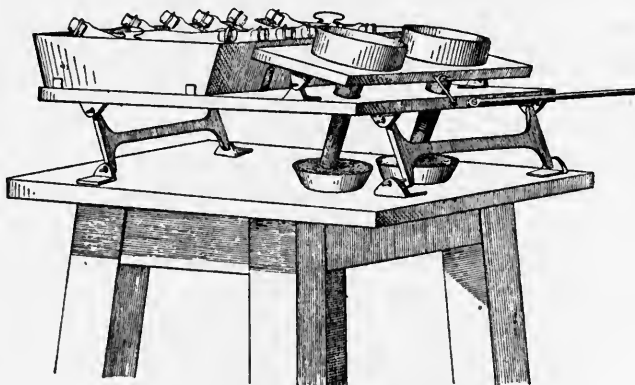


Fig. 3. Shaking Apparatus for Superphosphates.

ined in the flask in a dry state, adding 800 cubic centimeters of water and shaking by means of the machine indicated for half an hour. Afterwards the flasks are filled up to the mark, well shaken and their contents filtered through double folded filters into ordinary flasks of about 400 cubic centimeters capacity. Before any of the filtrate is collected the first that runs through should be well shaken in the receiving flasks and rejected. Fifty cubic centimeters of the filtrate thus collected, corresponding to one gram of the substance, should be used for the determination.

(2) *Total Acid*.—For total phosphoric acid, including the insoluble portions, except in the case of basic slags, the material is treated as follows: Five grams of the substance are placed in a

500 cubic centimeter flask with 20 cubic centimeters of nitric acid of 1.42 specific gravity, and 50 cubic centimeters of pure concentrated sulfuric acid, and boiled briskly for half an hour. With substances which contain much organic material, a little paraffin is added to avoid frothing. Such substances also require a larger quantity of nitric acid than that above specified. The flasks are allowed to cool, water added, again allowed to cool, and filled up to the mark at 17°.5. If hydrochloric instead of sulfuric acid be used in making the above solution, when the citrate method is employed, the results are always too high, because the precipitate contains lime and alumina in such quantities as to render any compensation for them inaccurate. In addition to this the sulfuric has this great advantage over the hydrochloric acid; viz., it does not separate the silicic acid, inasmuch as silicic acid is insoluble in boiling sulfuric acid.

(3) *Citrate-Soluble Acid*.—As is well known, in acidulated phosphate a part of the phosphoric acid at first soluble in water becomes insoluble, or, as usually expressed, reverted. This portion, however, is still soluble in ammonium citrate. By the Halle method it is determined as follows: Two grams of the sample are digested with 100 cubic centimeters of ammonium citrate solution, 1.09 specific gravity, for half an hour at 50° in a beaker. Afterwards the soluble matter is separated by filtration with the aid of a filter-pump and the residue washed with a solution of one part water and one part citrate solution until all the dissolved phosphoric acid is removed from the filter. Generally three or four washings are sufficient. The residue on the filter is dried, ignited and dissolved in a mixture of two cubic centimeters of nitric and 20 cubic centimeters of sulfuric acid, the solution made up to a volume of 200 cubic centimeters, filtered, and 100 cubic centimeters of the filtrate used for the determination. The acid in the filtrate is nearly neutralized and 50 cubic centimeters of the citrate solution used in the determination of total acid are added, and afterwards 25 cubic centimeters of magnesia mixture and 20 cubic centimeters of 24 per cent. ammonia. After standing for 48 hours, the precipitate is separated by filtration, ignited, and weighed in the usual way. The difference be-

tween the total phosphoric acid and that in the insoluble residue, after treatment with ammonium citrate, as above, gives the quantity of phosphoric acid soluble in citrate solution. The difference between the total citrate-soluble and the water-soluble gives the quantity of the reverted phosphoric acid.

The ammonium citrate solution (Petermann's) used for the digestion is made as follows: Two hundred and fifty grams of crystallized citric is dissolved in half a liter of hot water, diluted with 550 cubic centimeters of water, 275 cubic centimeters of 24 per cent. ammonia added, and finally, exactly neutralized by adding, little by little, 50 per cent. citric acid solution.

The Halle methods of separating the water and citrate-soluble acids appear to be less complete and reliable than those in use by the Official Agricultural Chemists of this country. The precipitation of basic phosphates, when large quantities of water are used at once in separating soluble acid, must tend to diminish the quantity obtained, while the lack of care in assuring the neutrality of the citrate solution might lead to varying results.

(4) *Double Superphosphates.*—In the case of double superphosphates, which sometimes contain large quantities of pyrophosphate, the solution is made in the usual way so that in 100 cubic centimeters there will be contained two grams of the substance. Usually 10 grams are used and the volume made up to half a liter. Twenty-five cubic centimeters of the filtrate are diluted with 75 cubic centimeters of water and the pyroconverted to orthophosphoric acid by heating with 10 cubic centimeters of strong nitric acid on a sand-bath. The heating should be continued until the volume is reduced to 25 cubic centimeters. The strongly acid liquid is made alkaline with ammonia and afterwards slightly acid with nitric acid, and the rest of the process is carried on in the usual way.

(5) *Phosphoric Acid in the Residue of Superphosphate Manufacture.*—In the mixture of superphosphates and gypsum, the residue of the manufacture of double superphosphates, the phosphoric acid is estimated in the following manner: Five grams of the substance are placed in a dish, rubbed up with absolute alcohol, and washed into a 250 cubic centimeter flask. The flask is

filled with absolute alcohol to the mark, closed with a stopper, and, with frequent shaking, allowed to stand for two hours; it is thereupon filtered as quickly as possible; 50 cubic centimeters of the filtrate, corresponding to one gram of the substance, is used for the estimation. This is evaporated on a sand-bath to a sirupy consistence, diluted with water and treated as in the case of the soluble phosphates above mentioned. In all cases, as described above, after the solutions are obtained they are treated with the ammonium citrate solution and the phosphoric acid estimated as in the method for soluble acid.

(6) *Solutions Employed.*—

(a) The citrate solution is made as follows: Fifteen hundred grams of citric acid are dissolved in water, treated with five liters of 24 per cent. ammonia, and made up to 15 liters.

(b) The magnesia mixture is made as follows: Five hundred grams of magnesium chlorid, 1050 grams of ammonium chlorid, three and five-tenths liters of 24 per cent. ammonia, and six and five-tenths liters of distilled water are used.

In the case of the superphosphates 50 cubic centimeters of the citrate solution are employed and with the basic slags 100 cubic centimeters; and in both cases 25 cubic centimeters of the magnesia mixture.

(7) *Details of the Manipulation.*—On the addition of the citrate solution there should be no permanent troubling of the liquid, but any precipitate at first formed should entirely disappear after the addition of the whole quantity of the reagent. In order to facilitate this, after the addition of the citrate solution the flasks should be gently shaken so as to distribute the solution throughout the mass. Solutions from bone-black superphosphates show sometimes, after the addition of the citrate solution, a more or less strong opalescence, but this opalescence does not influence the results. Should it happen that with superphosphates which are made from raw material containing large excesses of iron or clay 50 cubic centimeters of the citrate solution are not sufficient to prevent the other bases from being precipitated, an additional quantity up to 25 cubic centimeters may be added. The addition of the magnesia mixture must follow as quickly as

possible after the addition of the citrate solution to avoid a separation of crystalline calcium phosphate. On the addition of the citrate solution there is always a rise in temperature. Inasmuch as the precipitation of the phosphoric acid with magnesia must take place in the cold, the liquid must be cooled after the addition of the citrate, and the cooling should take place as quickly as possible.

The above method was adopted by the chemical section of the International Agricultural Congress held at Vienna, September, 1890.⁶⁷

In order to hasten the precipitation of the ammonium magnesium phosphate and to prevent the fixation of the precipitate on the walls of the erlenmeyer, the flask should be shaken for half an hour. For this purpose the flasks should be closed with smooth well-fitting rubber stoppers and placed in a shaking machine. The shaking machine of the form given in Fig. 4, recommended by the Halle station, is very conveniently used for this purpose.

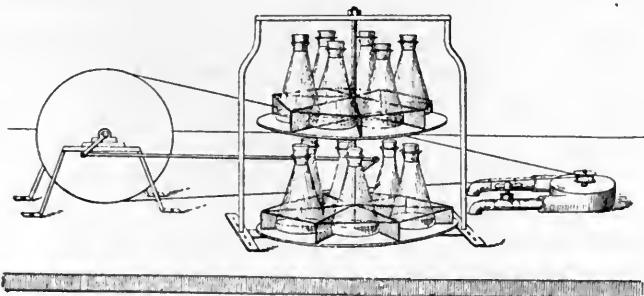


Fig. 4. Shaking Machine for Ammonium Magnesium Phosphate.

On a vertical axis are carried two platforms for holding the flasks. The flasks are prevented from striking each other by means of the partitions shown. The apparatus is conveniently driven by a small water-motor, as indicated, which imparts to the platforms a partial back and forth revolution.

After shaking for half an hour, any precipitate adhering to the rubber stoppers is carefully washed off with ammonia water into the flask. The filtration can be made immediately after the shaking or after two or three days; the results are the same.

⁶⁷ Chemiker-Zeitung, 1890, 14 : 1246.

The filtration of the ammonium magnesium phosphate is made through gooches. The asbestos felt is prepared in the following way: The coarse fibers of asbestos are chopped up with a sharp knife on a glass plate and boiled for two hours with strong hydrochloric acid; afterwards, by repeated washing with distilled water,

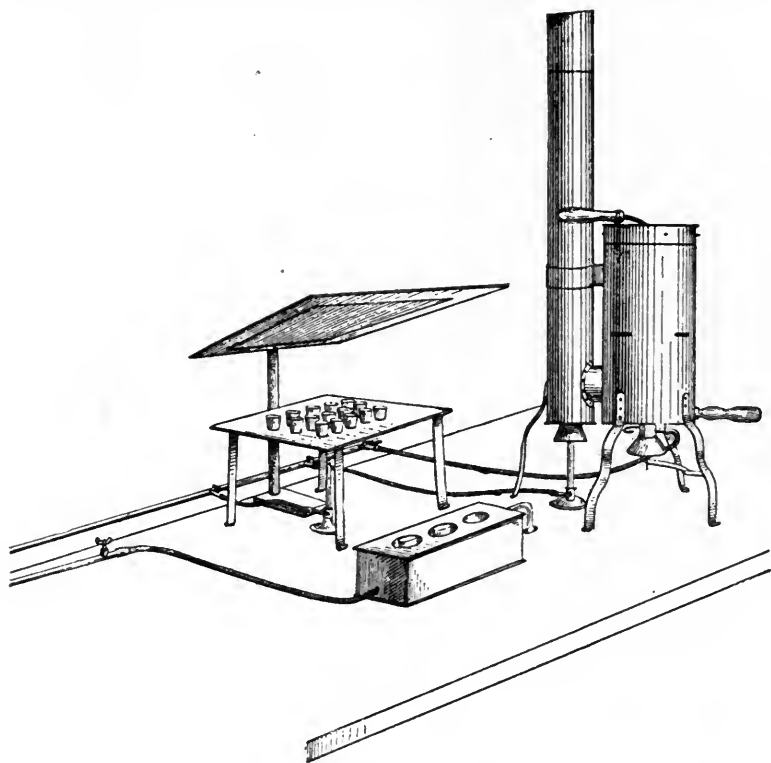


Fig. 5. Rössler Ignition Furnace.

they are freed from acid and the fine particles of asbestos which would tend to make the filter too impervious. After the last wash-water is poured off, the asbestos is suspended in water and used for making the felt on the filter. The preparation of the crucible and the filtration under pressure are accomplished in the usual way.

The ignition of the precipitate is accomplished in a Rössler ig-

nitron oven, Fig. 5. When the muffle of the furnace shows a white heat or a white-red heat, it is at the proper temperature for the estimation. At higher temperatures, the filtering property of the asbestos felt is easily injured. Generally, an ignition of five minutes is sufficient, but with double superphosphates, 10 minutes are required.

91. The Swedish Citrate Method.⁶⁸—This method of determination is a modification of the citrate method already described and is founded on the observation that phosphoric acid in the presence of calcium salts, without the necessity of previously converting into phosphomolybdate, is precipitated directly by magnesia mixture from a solution to which ammonium citrate has been added, provided first, that the solution contain a sufficient quantity of sulfuric acid to convert all the calcium compounds into sulfates, and second, that only as much citrate be added as is required to keep the calcium salts in alkaline solution. In other words, it is the method of separation devised by C. Glaser and others.⁶⁹

Reagents. (1) *Citric Acid Solution.*—Prepared by dissolving 500 grams of citric acid in water and completing to a volume of one liter.

(2) *Ammonia* of 0.959 specific gravity.

(3) *Magnesia Mixture*, composed of 140 grams of magnesium sulfate, 150 grams ammonium sulfate, and 30 grams of chlorid of ammonium dissolved in 350 cubic centimeters of 16 per cent. ammonia and 1650 cubic centimeters of water. The ammonium chlorid is added to prevent the precipitation of basic magnesium sulfate.

The various processes are conducted as follows:

(a) *Water-Soluble Phosphoric Acid.*—Add 20 cubic centimeters of citric acid solution to 50 cubic centimeters of the water-soluble solution obtained according to the Swedish molybdate method, and then add 33 cubic centimeters of ammonia.

⁶⁸ Official Swedish Methods Translated for the Author by F. W. Woll.

⁶⁹ Zeitschrift für analytische Chemie, 1885, 24 : 178; 1886, 25 : 416.

Chemiker-Zeitung, 1888, 12 : 85, 492.

Zeitschrift für angewandte Chemie, 1888, 1 : 354.

Die landwirtschaftlichen Versuchs-Stationen, 1888, 35 : 439.

When the mixture has cooled, add slowly 25 cubic centimeters of the magnesia mixture, and then 42 cubic centimeters of the ammonia. Keep the solution stirred by means of a closely clipped feather which is pressed tightly against the sides of the beaker; by this process the phosphate is precipitated after half an hour in pure condition and completely without in the least sticking to the wall of the beaker; filter, wash, and ignite, as usually directed.

(b) *Insoluble Phosphoric Acid*.—Moisten, in a porcelain dish, 10 grams of the powdered sample with water; add 50 cubic centimeters of concentrated sulfuric acid, and heat for 15 minutes so that fumes of sulfuric acid will escape. When the mass has cooled, wash it into a half-liter graduated flask, fill to the mark, and shake well. After filtration, the clear filtrate may, after some time, turn turbid by separation of calcium sulfate, but as the ammonium citrate, which is afterwards added, again brings the precipitate into solution, it is of no importance. Add to 50 cubic centimeters of the solution, corresponding to one gram of the powdered sample, 20 cubic centimeters of the citric acid solution, neutralize the mixture approximately, but not exactly, by ammonia; after cooling, add 25 cubic centimeters of magnesia mixture; stir the fluid by means of a feather, as described, till no more precipitate is formed, and finally add 33 cubic centimeters of ammonia while stirring for several minutes longer; after half an hour the precipitate may be separated by filtration, washed, and ignited, as usually directed.

The above process is essentially the one used with basic slags. When much organic matter is present, by continuing the heating with sulfuric acid for some time it may be destroyed.

92. Methods Adopted by the Brussels Congress, 1894.—The report of the committee on methods of analysis of phosphoric acid requires the molybdate method to be used in all cases where the quantity to be determined is very small. In other cases the citrate method may be employed.⁷⁰

(1) *Soluble Phosphoric Acid*.—The soluble phosphoric acid is determined by the method adopted at Brussels in the following

⁷⁰ L'Engrais, 1894, 9 : 928.

manner: Five grams of the sample are rubbed to a powder in a mortar, and then from 50 to 60 cubic centimeters of water added. After allowing to settle for a few minutes the liquid portion is decanted upon a filter. This operation is repeated three or four times. Finally, the solid portions are washed upon the filter, and the washing with water is continued until the filtrate amounts to about three-quarters of a liter. A few drops of hydrochloric acid are added until the filtrate is perfectly clear, and the volume is then made up to one liter. Fifty cubic centimeters of the solution are then treated with 30 cubic centimeters of ammonium citrate solution and one-third as much ammonia. Afterwards 30 cubic centimeters of magnesia mixture are added, drop by drop, with constant stirring.

For superphosphates containing more than 18 per cent. of phosphoric acid only one gram of the sample is used, for ordinary superphosphates two grams, and for compound fertilizers four grams. The sample is first treated as above for soluble acid until the filtrate amounts to 200 cubic centimeters, then clarified with a drop of nitric acid, and made up to a quarter of a liter.

(2) *Reverted Phosphoric Acid*.—The filter containing the residue is then introduced into a quarter liter flask and treated with 100 cubic centimeters of Petermann's alkaline ammonium citrate solution, vigorously shaken, and left at room temperature for 15 hours. It is digested for an hour at 40° and filtered. Fifty cubic centimeters of the filtrate are placed in a flask and, with constant shaking, 35 cubic centimeters of magnesia mixture added. The aqueous solution is treated in the same way. The precipitate is collected, washed with two and one-half per cent. ammonia until the chlorin disappears, ignited, weighed, and the number obtained multiplied by 0.64 for phosphoric acid. The total acid is determined in the usual way.

93. Dutch Method for Citrate-Soluble Phosphoric Acid.—The reagents necessary are:

(1) *Citrate solution*. Dissolve 165 grams of citric acid in 700 cubic centimeters of water, mix with 250 cubic centimeters of ammonia of 0.92 specific gravity, and, after cooling, bring to the volume of one liter.

(2) *Magnesia mixture*. Dissolve 400 grams of crystallized magnesium chlorid, 800 grams of ammonium chlorid, and 1600 cubic centimeters of ammonia of 0.96 specific gravity in water, and dilute to five liters.

The quantity used for the analysis is five grams where the fertilizer contains less than six per cent. of phosphoric acid (mixed fertilizers); two grams where it contains more than six and less than 15 per cent. (common superphosphates); and one gram where it contains more than 15 per cent. (double superphosphates). Place the weighed substance in a mortar and cover with 100 cubic centimeters of citrate solution. Gently rub up, wash into a half liter flask, and heat on a water bath for an hour to a temperature between 35° and 38°. Allow to cool, fill up to 500 cubic centimeters, and filter through a dry double filter. If the liquid is not clear at the first titration, pour through the filter again, repeating this till clearness is attained. To 100 cubic centimeters of the filtrate add 75 cubic centimeters of magnesia mixture, allowing the latter to flow into the former very slowly, and constantly stirring during the influx. Allow to stand 15 hours, filter, wash with ammonia of 0.96 specific gravity, dry, ignite, and weigh.

The per cent. of phosphoric acid, except where otherwise indicated, is always to be given as per cent. of phosphorus pentoxid (P_2O_5).

94. Method of Lasne.—Lasne recalls some previous observations which are confirmed by later ones, as follows:⁷¹

(1) The precipitation of ammonio-magnesium phosphate takes place without loss when conducted in the presence of citrate of ammonia, and with a sufficient excess of magnesia.

(2) Lime, oxid of iron, alumina and manganese are carried down by the precipitate.

(3) The presence of silica and of fluo-silicates causes an excess of weight in the precipitate over the probable amount due to phosphorus.

(4) Without the addition of an excess of magnesia the precipi-

⁷¹ Bulletin de la Société chimique de Paris, 1897, [3], 17:823 and following.

tation is incomplete and the separated liquid is precipitated alike by magnesia and phosphoric acid.

The results of the work show that when stirred with ammonio-magnesium phosphate the final result is obtained without any loss, and that on calcination the identical weight with which the experiment commenced is obtained. The conclusions obtained by Lasne from a large mass of analytical data are summarized as follows:

(1) The formation of phosphoric acid in the state of pyrophosphate without any other precaution than previous elimination of silica gives results which are not affected by any systematic error.

(2) Rapid precipitations cause an excess of weight in the precipitate due to a partial formation of tri-magnesium phosphate, which is only transformed into ammonio-magnesium phosphate by contact for 16 hours with a sufficiently concentrated solution of ammonium citrate, namely, containing ten grams of citric acid in 150 cubic centimeters of the solution. It is necessary, therefore, in order to obtain rigorous results, to allow the precipitate to stand before filtering for at least 16 hours. Nevertheless, it must be admitted that this excess of weight is so small as not to warrant the complete rejection of the rapid methods for all industrial purposes when proper precautions are employed.

(3) The transformation of tri-magnesium phosphate into ammonio-magnesium phosphate takes place very slowly in the presence of ammonium chlorid alone, and there should always, therefore, in these precipitations, be added the quantity of citrate of ammonia indicated above.

The precipitation of magnesia in the presence of an excess of ammoniacal phosphate gives, in addition to ammonio-magnesium phosphate, a phosphate poorer in magnesium, and as much poorer as the excess of phosphoric acid is larger. The determination of magnesia by this classical method is always erroneous.

95. Comparative Accuracy of the Citrate and Molybdate Methods.—The general use of the citrate method of determining phosphoric acid by the German chemists has led Johnson to review some trials of that method in his laboratory made as early as 1880.⁷² These determinations have lately been repeated in com-

⁷² Journal of the American Chemical Society, 1894, 16 : 462.

parison with the ordinary molybdate methods, with the result that in 67 determinations on bone-dust, superphosphate, cotton-hull ashes, cottonseed-meal, tankage, bone-char, phosphatic guano, and phosphate rock, only three citrate results differed from those obtained by the molybdate method by more than three-tenths of one per cent. The greatest discrepancy between the two methods was 0.41 per cent., and the average difference was 0.09 per cent.

Attention has already been called to the fact that the citrate method was found to give poor results when iron and alumina were present in considerable quantity. Ignited precipitates by the citrate method were found to contain as high as four per cent. of lime, and iron and alumina in small quantities when these bodies were abundant in the original substance.

In the molybdate method the rapid precipitation from solutions at 65° was found to give unsatisfactory results and it was found necessary to conduct the process at temperatures between 40° and 50°. With a relative excess of nitric or a relative deficiency of molybdic acid some phosphoric acid may easily escape precipitation. The chief objection to precipitating at 65° is found in the fact that in presence of considerable iron and alumina some of these bodies may be found in the yellow precipitate, whence they pass to the final ammonium magnesium phosphate.

The citrate method, therefore, only gives safe results by compensating errors which in every class of phosphates must be empirically determined.

The molybdate method gives results too high when iron and alumina are present in considerable quantity and the yellow precipitate is obtained at temperatures above 50°. On the other hand, if there be a great relative excess of nitric acid the results may be too low unless the filtrates from the yellow precipitate be mixed with additional molybdic solution and digested until no further precipitate is formed.

Comparative determinations made by both methods by Maercker for the Association of German Experiment Stations have led to the conclusion that both give practically the same results when

each one is conducted with the proper precautions peculiar to it.⁷³ In the latter part of 1892, at the general meeting of the association, it was declared that the citrate method, after having been subjected to repeated tests, was found to be satisfactory, changing the composition of the solution so that it might have 1100 instead of 1000 grams of citric acid and four liters of 24 per cent. ammonia to each 10 liters. The data afforded by the citrate method, when applied to an artificial mixture of known composition, were more satisfactory than those obtained by the molybdic process.

In the laboratory of the Bureau of Chemistry the citrate method has been found to give nearly agreeing results with the old process. It is much shorter and less expensive, and is recommended most favorably for practical use, with the suggestion, however, that, with every new kind of phosphate or phosphatic fertilizer varying notably in composition from the standard, the work should be checked at first by comparison with the molybdate method. The later investigations carried on by the Association of Official Agricultural Chemists have served only to confirm the superiority of the molybdate gravimetric method for all purposes where great accuracy is demanded and have shown that for speed and convenience the volumetric method already outlined and later to be described in full, is to be preferred to all other quick processes.

96. The Citrate Precipitate Purity.—Jørgensen recommends the following as the safest form of citrate precipitation. The phosphoric acid solution is treated with 25 cubic centimeters of neutral ammonium citrate solution or, in case it contains a large quantity of calcium salts, with 30 cubic centimeters, and then 25 cubic centimeters of a 10 per cent. ammonia solution is added, and the mixture, in a covered dish, heated to the boiling point, and, according to the quantity of the phosphate precipitate, treated with 30 or 40 cubic centimeters of the neutral magnesium chlorid solution. By vigorous stirring or shaking the precipitate crystallizes, and after standing at least four hours is filtered. If very small quantities of phosphoric acid are present the mixture should be left at least 24 hours

⁷³ Die landwirtschaftlichen Versuchs-Stationen, 1892, 41 : 329.

before filtering. In the practice of this method the presence of aluminum oxid not exceeding 0.6 gram, or ferric oxid not exceeding 0.11 gram, may be present, but not in greater quantities than these. Calcium oxid should also not be present in quantities exceeding 0.03 gram.

Detailed data are given by Jörgensen in connection with the general determinations of all forms of phosphoric acid, but they do not differ sufficiently from those already cited to warrant their insertion in full in this manual. The student who desires to study in complete detail this latest contribution to the methods of determining phosphoric acid should consult the original article.⁷⁴

97. The Citrate Method Applied to Samples with Small Content of Phosphoric Acid.—It is well established that the citrate method does not give satisfactory results when applied to samples containing small percentages of phosphoric acid, especially when these are of an organic nature, as, for instance, cottonseed cake-meal. An attempt has been made to remedy this defect in the process so as to render the use of the method possible even in such cases.⁷⁵ Satisfactory results have been obtained by adding to the solution of the cake-meal a definite volume of a phosphate solution of known strength. Solutions of ordinary mineral phosphates are preferred for this purpose. The following example will show the application of the modified method:

In a sample of cake-meal (cottonseed cake and castor pomace) the content of phosphoric acid obtained by the molybdate method was 2.52 per cent.

Determined directly by the citrate method, the following data were obtained:

Allowing to stand 30 hours after adding magnesia mixture, 1.08 and 1.53 per cent. in duplicates.

Allowing to stand 72 hours after adding magnesia mixture, 2.17 and 2.30 per cent. in duplicates.

In each case 50 cubic centimeters of the solution were used, representing half a gram of the sample.

In another series of determinations 25 cubic centimeters

⁷⁴ Zeitschrift für analytische Chemie, 1906, **45** : 273.

⁷⁵ Journal of the American Chemical Society, 1895, **17** : 513.

of the sample were mixed with an equal volume of a mineral phosphate solution, the value of which had been previously determined by both the molybdate and citrate methods. The 50 cubic centimeters thus obtained represented a quarter of a gram each of the cake-meal and mineral phosphates. The filtration followed 18 hours after adding the magnesia mixture. The following data show the results of the determinations:

	Per cent. P ₂ O ₅ in mineral phosphate.	Per cent. P ₂ O ₅ in organic sample.	Per cent. P ₂ O ₅ found in mixture.	Per cent. P ₂ O ₅ in organic sample.
1.....	15.37	2.52	17.90	2.53
2.....	29.16	2.52	31.68	2.52
3.....	31.37	2.52	33.83	2.45
4.....	31.58	2.52	34.20	2.62
				2.53
				Mean content of P ₂ O ₅ in organic sample.....

It is thus demonstrated that the citrate method can be applied with safety even to the determination of the phosphoric acid in organic compounds where the quantity present is less than three per cent. It is further shown that solutions of mineral phosphates varying in content of phosphoric acid from 15 to 32 per cent. may be safely used for increasing the content of that acid to the proper degree for complete precipitation. In cases where organic matters are present they should be destroyed by moist combustion with sulfuric acid, as in the determination of nitrogen to be described in the next part.

98. Direct Precipitation of the Citrate-Soluble Phosphoric Acid.

—The direct determination of the citrate-soluble phosphoric acid by effecting the precipitation by means of magnesia mixture in the solution obtained from the ammonium citrate digestion, has been practiced for many years by numbers of European chemists, and the process has even obtained a place in the official methods of some European countries. Various objections have been urged, however, against the general employment of this method in fertilizer analysis on account of the inaccuracies in the results obtained in certain cases, and it has, therefore, been used to but a very limited extent in this country. Since it is impracticable to effect the precipitation with ammonium molybdate in the presence of citric acid the previous elimination or destruction of this sub-

stance has been recognized as essential to the execution of a process involving the separation of the phosphoric acid as phosphomolybdate.

It is evident from the data cited in the preceding paragraph, that great accuracy may be secured in this process by adding a sufficient quantity of a solution of a mineral phosphate and proceeding by the citrate method.

Ross has also proposed to estimate the acid soluble in ammonium citrate directly by first destroying the organic matter by moist combustion with sulfuric acid.⁷⁶ He recommends the following process:

After completion of the 30 minutes' digestion of the sample with citrate solution, 25 cubic centimeters are filtered at once into a dry vessel. If the liquid be filtered directly into a dry burette, 25 cubic centimeters can be readily transferred to another vessel without dilution. After cooling, run 25 cubic centimeters of the solution into a digestion flask of 250-300 cubic centimeters capacity, add about 15 cubic centimeters of concentrated sulfuric acid and place the flask on a piece of wire gauze over a moderately brisk flame; in about eight minutes the contents of the flask commence to darken and foaming begins; but this will occasion no trouble, if an extremely high or a very low flame be avoided. In about 12 minutes the foaming ceases and the liquid in the flask appears quite black; about one gram of mercuric oxid is now added and the digestion is continued over a brisk flame. The operation can be completed in less than half an hour with ease, and in many cases, 25 minutes. After cooling, the contents of the flask are washed into a beaker, ammonia is added in slight excess, the solution is acidified with nitric acid, and after the addition of 15 grams of ammonium nitrate, the process is conducted as usual.

In case as large an aliquot as 50 cubic centimeters of the original filtrate be used, 10 cubic centimeters of sulfuric acid are added, and the digestion is conducted in a flask of 300-500 cubic centimeters capacity; after the liquid has blackened and foaming has progressed to a considerable extent, the flask is removed

⁷⁶ Division of Chemistry, Bulletin 38, 1893 : 16.

from the flame, 15 cubic centimeters more of sulfuric acid are added, and the flask and contents are heated at a moderate temperature for two or three minutes; the mercuric oxid is then added and the operation completed as before described.

Following are some of the advantages offered by the method described:

(1) It dispenses with the necessity of the frequently tedious operation of bringing upon the filter and washing the residue from the ammonium citrate digestion, while the ignition of this residue together with the subsequent digestion with acid and filtration are also avoided.

(2) It affords a means for the direct estimation of that form of phosphoric acid which, together with the water-soluble, constitutes the available phosphoric acid, thus enabling the latter to be determined by making only two estimations.

(3) In connection with the advantages above mentioned it permits of a considerable saving of time as well as of labor required in manipulation.

In addition to the tests with mercuric oxid, both potassium nitrate and potassium sulfate are used in the digestion to facilitate oxidation. With the former, several additions of the salt are necessary to secure a satisfactory digestion, and even then the time required is longer than with the mercury or mercuric oxid digestion. With potassium sulfate, the excessive foaming which takes place interferes greatly with the execution of the digestion process.

99. Determination of Phosphoric Acid with Preliminary Precipitation as Stannic Phosphate.—This method once much in use and highly recommended, is now almost unknown among the processes of fertilizer control. It was first proposed by Reynoso and modified by Girard, and rests on the precipitation of the phosphoric acid in a nitric acid solution by means of metallic tin.⁷⁷ The stannic acid formed by the oxidation of the tin unites with the phosphoric acid held in a free state by the nitric acid. The precipitation of the phosphoric acid is said to be complete, and considerable quantities of any iron or alumina which may be pre-

⁷⁷ Comptes rendus, 1862, 54 : 468.

sent are carried down with it. A trace of phosphoric acid has been found in the iron and alumina subsequently separated from the solution. The precipitate obtained is dissolved in aqua regia, made strongly ammoniacal and an excess of ammonium hydrosulfid added. The iron and the alumina are thrown out by this treatment. After standing for an hour the precipitate is separated by filtration, washed with the ammonium sulfid to remove the last traces of tin and the phosphoric acid is separated from its filtrate as ammonio-magnesium salt. Following is the second method of conducting the analysis as described by Crookes:⁷⁸

The phosphate should be dissolved in nitric acid, and any chlorine present be expelled by repeated evaporations with the solvent. Finally, to the evaporated mass the strongest nitric acid is added. Pure tin foil is added and heat applied. The phosphoric acid is precipitated by the stannic acid formed. The quantity of tin used should be from four to five times as great as that of the phosphoric acid present. The preliminary heating is indispensable, since in the cold the metal is apt to become passive in which state it resists the action of the acid.

The precipitate is collected on a filter, washed and dissolved in caustic potash. The solution is saturated with hydrogen sulfid, and on adding acetic acid in slight excess the tin sulfid is separated and removed by filtration. The whole of the phosphoric acid, supposed to be almost free of tin, is now found in the filtrate. The filtrate is concentrated to small bulk and any tin sulfid present separated by filtering, and the phosphoric acid finally removed from the ammoniacal filtrate by precipitation with magnesia mixture. The chief difficulties of this method are to be found, on the one hand, in the retention of some of the phosphoric acid by the iron and alumina which may be present, and on the other, in the presence of some tin in the final magnesium pyrophosphate. If the tin be all removed as sulfid, the latter source of error will be avoided. It is difficult to secure pure metallic tin, and this is another disturbing element in the process.

⁷⁸ *Select Methods in Chemical Analysis*, 4th Edition, 1905 : 497.

It can not be recommended for the work which agricultural analysts are usually called on to perform.⁷⁹

100. Phosphoric Acid Soluble in Ammonium Citrate.—There is no other point connected with the determination of phosphoric acid which has excited so much discussion and about which there is such difference of opinion as the solubility of phosphates in ammonium citrate. It was clearly established by Huston, in 1882, that the ammonium citrate, as used in fertilizer analysis, would attack normal tricalcium phosphate as it exists in bones.⁸⁰

In a raw bone, finely ground, containing 20.28 per cent. of phosphoric acid, the following quantities are found to be soluble in a neutral ammonium citrate solution of 1.09 specific gravity:—

Temperature	Time of digestion, thirty minutes.			
	30°	40°	50°	60°
Per cent. P ₂ O ₅ dissolved.....	2.76	4.01	3.39	5.88

From this it appears that the quantity of acid dissolved increases with the temperature of digestion with the exception of the number obtained at 50°. When the time of digestion is increased there is also found a progressive increase in the amount of acid passing into solution. At 40° for 45 minutes the per cent. dissolved is 4.97, and 40° for one hour, 5.92. These early determinations had the effect of calling attention to the thoroughly empirical process which was in use, in many modified forms, by agricultural chemists the world over for determining so-called reverted phosphoric acid in fertilizers. Since the publication of the paper above named many investigations have been undertaken by Huston and others relating to this matter.⁸¹

The conditions of solution studied embraced the influence of time, temperature, kind and quantity of material, and acidity and

⁷⁹ Fresenius, Quantitative Analysis, Cohn's Translation of Sixth German Edition, 1904, 1 : 450.

⁸⁰ Wiley, 32nd Annual Report of the Indiana State Board of Agriculture, 1882 : 225.

⁸¹ American Chemical Journal, 1884-5, 6 : 1.

Proceedings of the Convention of Agricultural Chemists, Atlanta Meeting, 1884, Edited by C. W. Dabney, Secretary : 23, 28, 38, 45.

Division of Chemistry, Bulletin 7, 1885 : 18.

Division of Chemistry, Bulletin 28, 1890 : 171.

Division of Chemistry, Bulletin 31, 1891 : 99.

alkalinity of the solvent on the amount of phosphoric acid dissolved. The materials subjected to experiment represented a wide range of substances used as, or entering into the composition of, phosphatic fertilizers such as bone meal, steamed bone, orchilla guano, navassa rock, navassa superphosphate, Florida soft rock, precipitated calcium phosphate, Pamunky phosphate, calcined redonda, South Carolina rock, apatite, grand connetable, acid navassa, South Carolina phosphate, dissolved bone-black, and cottonseed meal.

The time of digestion extended from half an hour to 10 hours, and in general the quantity of phosphoric acid dissolved by the ammonium citrate solution increased as the time of digestion was prolonged.

The digestions were made at temperatures ranging from 30° to 85°. In general, the quantity of phosphoric acid dissolved increased with the temperature.

The quantity of sample used in its relations to the volume of the solvent was also studied. The percentage of the total acid dissolved increases very rapidly as the weight of the sample diminishes.

The addition of citric acid to the neutral ammonium citrate increases its solvent power. On the other hand, the addition of ammonia to the neutral solution of ammonium citrate diminishes its solvent power.

The finer the state of subdivision of the sample the more efficiently the solvent acts.

An examination of the original paper of Fresenius, Neubauer, and Luck, on whose researches the citrate method is based, shows that the temperature conditions are not carefully controlled.⁸² An attempt has been made to summarize in the above conclusions, work made under well defined conditions which illustrate the various points under consideration. While each authority of value upon the subject is represented, no attempt has been made to discuss all the work done by any of them. One element that seems to have been generally overlooked in discussing the problem is that nearly all results have been obtained from a one-half hour treat-

⁸² *Zeitschrift für analytische Chemie*, 1871, 10 : 133.

ment of the material. This means simply the study of an incomplete reaction, and one which is interrupted while the solution is very rapidly going on. This, of course, is only clearly brought out by comparison of long-time and short-time work in the various tables. In the opinion of Huston, much more work will have to be done before it can be assumed that we have any very clear knowledge of this subject, and probably the conclusion will be that all kinds of materials can not be examined by the same method. The fact that half a gram of dicalcium phosphate is instantly soluble in 100 cubic centimeters of citrate solution, at ordinary temperatures, while an equal amount of iron and aluminum phosphate is acted upon very slowly at ordinary temperatures will probably have to be taken into consideration, as well as the fact that dicalcium phosphate is less soluble in hot solutions of ammonium citrate than it is in cold solutions, while the reverse is true of the precipitated iron and aluminum phosphate.

At present the only conclusion that can be safely drawn from the work is that it would be unsafe to make any generalization upon the subject until more facts are at hand, except that the methods generally in use are unscientific and unsatisfactory. As the work progresses, new features present themselves, and in such a way as to show that they must be given careful consideration before drawing any final conclusions in the matter. At best, it must be confessed that the action of a neutral ammonium citrate solution on the various forms of phosphates entering into the composition of commercial fertilizers is a practically continuous process, varying in speed with changing conditions of temperature, time, relation of quantity of sample to volume of substance, and the fineness of subdivision of the sample. Concordant results can therefore only be obtained by observing fixed conditions of work.

101. Arbitrary Determination of Reverted Phosphoric Acid.—

The so-called reverted phosphoric acid, that is, the acid insoluble in water and soluble in a solution of ammonium citrate, is the most annoying constituent of commercial fertilizers from the point of view of the scientific analyst. A review of all the standard

methods, which have been given in the preceding pages, for its determination must convince every careful observer that, as a rule, each process is based on arbitrary standards, and can give only concordant results when carried out under strictly unvarying conditions. For this reason there can be no just comparison between the results obtained by different methods, which vary from each other only in slight particulars. When, on the other hand, the processes are radically different, the deviations in data become more pronounced.

In such a condition of affairs the analyst is left to choose between methods. He must be guided in his choice not only by what seems to be the most scientific and accurate process, but also, to a certain extent, by the general practice of his professional brethren. For this country, therefore, it is strongly urged that the methods adopted by the Association of Official Agricultural Chemists be followed in every detail.

By the phrase "reverted phosphoric acid" was originally meant an acid once soluble in water, as $\text{CaH}_4(\text{PO}_4)_2$, and afterwards changed to a form insoluble in water, but soluble in ammonium citrate as $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$. But in practice this has never been the true signification of the term. In the manufacture of acid- and superphosphates there is formed, more or less of the dicalcium phosphate, either directly or after a time, and this salt which, in no sense can be called reverted, is entirely soluble in ammonium citrate. The iron and aluminum phosphates are also, to a certain degree, soluble in the same reagent. When an acid phosphate, containing various forms of calcium phosphate, is applied to a soil containing iron and alumina, the soluble parts of the compound tend to become fixed by union with those bases, or by precipitation as $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$. But it is not alone reverted phosphate formed in this way, which the analyst is called on to determine in a fertilizer, although he may have occasion to treat it in soil analysis.

The expression "reverted phosphoric acid," therefore, in practice not only includes a dicalcium phosphate, which once may have been the monocalcium salt, but also all of that salt originally existing in the superphosphate, and formed directly during

its manufacture, as well as any iron and aluminum phosphates present which are soluble in ammonium citrate. It also includes any tricalcium phosphate, such as that existing in bones, which may pass into solution under the influence of ammonium citrate. The expression "citrate-soluble" is, therefore, to be preferred to "reverted" phosphoric acid.

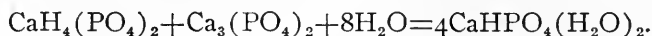
102. Theory of Reversion.—In the reversion of the phosphoric acid in superphosphates the iron plays a far more important role than the aluminum sulfate. It was formerly supposed that the reversion took place as indicated in the following formula: $2\text{CaH}_4(\text{PO}_4)_2 + \text{Fe}_2\text{O}_3 = 2(\text{CaHPO}_4 \cdot \text{FePO}_4) + 3\text{H}_2\text{O}$, while Wagner affirms that the reverted acid compounds consist of varying quantities of ferric oxid, aluminum oxid, phosphorus pentoxid, and calcium oxid, in various states of combination.⁸³ The more probable reaction is the following: $3\text{CaH}_4(\text{PO}_4)_2 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} = 2(\text{FePO}_4 \cdot 2\text{H}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}) + 3\text{CaSO}_4$. This reaction can be demonstrated by adding to a superphosphate solution one of a ferric salt. In addition to free phosphoric acid, iron phosphate is separated, which gradually passes into an insoluble form by the abstraction of water due to the crystallization of the gypsum. The alumina present in a superphosphate seems to have no direct influence on the process of reversion. Its phosphate salt is not acted on by the acid calcium phosphate. Even when a superphosphate solution is treated with alum no precipitation is produced, except on warming, and this disappears when the mass is again cold.

It is therefore not necessary in the process of manufacture to separate the alumina by digestion with a hot soda-lye before treating the mass with sulfuric acid.

In order to avoid the reversion of the phosphoric acid several plans have been proposed. One of the best is to use a little excess of sulfuric acid in the manufacture. This tends to hold the phosphoric acid in soluble form, but is objectionable on account of drying, handling, and shipping the fertilizer. During the digestion, moreover, it is important that the temperature do not rise above 120° . Another method consists in adding to the

⁸³ Lehrbuch der Düngerfabrikation.

dissolved rock a quantity of common salt chemically equivalent to its iron content. Ammonium sulfate also helps to hold the phosphoric acid water-soluble. Reversion of the phosphoric acid is quite certain to take place in those products where the solvent action of the sulfuric acid has not been complete.⁸⁴ Especially is this the case when there are still substances present which can be attacked by the acid calcium phosphate. This action is illustrated by the following equation:



In this case the undissolved tricalcium phosphate is attacked by the acid monocalcium phosphate with the production of a compound insoluble in water.

103. Influence of Movement.—The influence of time and temperature of digestion, and of variations in the composition of the ammonium citrate on the quantity of phosphoric acid dissolved by that reagent, has been pointed out. Of great importance also in the process is the character of the movement to which the materials are subjected during the digestion. For this reason various mechanical devices have been constructed to secure uniformity of solution. Inasmuch as the temperature factor must also be faithfully observed, the best of these devices are so arranged as to admit of a uniform motion within a bath of water kept at the desired temperature which, by the association method, is 65°.

104. Digestion Apparatus for Reverted Phosphates.—The digestion apparatus used by Huston consists of two wheels 25 centimeters in diameter, mounted on the same axis, having a clear space of four and one-half centimeters between them.⁸⁵ In the periphery of each wheel are cut 12 notches, which are to receive the posts bearing the rings through which the necks of the flasks pass. The posts are held in place by nuts which are screwed down on the faces of the wheel. Should it become necessary to

⁸⁴ Rümpler, *Käufliche Düngestoffe und ihre Anwendung*, 4th Edition, 1897 : 85.

⁸⁵ *Indiana Agricultural Experiment Station, Bulletin 54, 1895 : 4.*

take the apparatus apart, it is only necessary to loosen the nuts and the set screw holding one wheel to the shaft and all the parts can at once be removed. The posts extend 10 centimeters beyond the face of the wheels, and the rings are four centimeters in internal diameter. Perforated plates, bearing a cross-bar, and held in place by strong spiral springs attached to the plate and the base of the posts serve to hold the flasks in place. Each plate has a number stenciled through it for convenience in identifying the flasks when it is time to remove them. Attached to the outside of each post, close to the outer end, is a heavy wire which passes entirely around the apparatus, serving to keep the plates in place after they are removed from the flasks.

The apparatus is mounted on a substantial framework, 36 centimeters high and 30 centimeters wide at the base. The space in which the wheel revolves is 14 centimeters wide. The base bars connecting the two sides are extended seven centimeters beyond one side, and serve for the attachment of lateral bracing. At the top of the framework, at one side, is attached a heavy bar 45 centimeters long, which serves to carry the cog gearing which transmits the power. The upright shaft carries a cone pulley to provide for varying the speed. The usual speed is two revolutions a minute for the wheel carrying the flasks. The entire apparatus is made of brass. The details of construction are shown in Fig. 6. Round-bottomed flasks are used, and the rubber stoppers are held in place by tying or a special clamp shown at the lower right-hand corner of the figure.

When high temperatures are used, the plates and flasks are handled by the hooks shown at the left and right-hand upper corners of the figure.

When any other than room temperature is desired, the whole apparatus is immersed in water contained in the large galvanized tank forming the back-ground of the figure. The tank is 75 centimeters long, 75 centimeters high, and 30 centimeters wide. At one end, near the top, is an extension to provide space for heating the fluid in the flasks before introducing the solid, in such cases as may be desired.

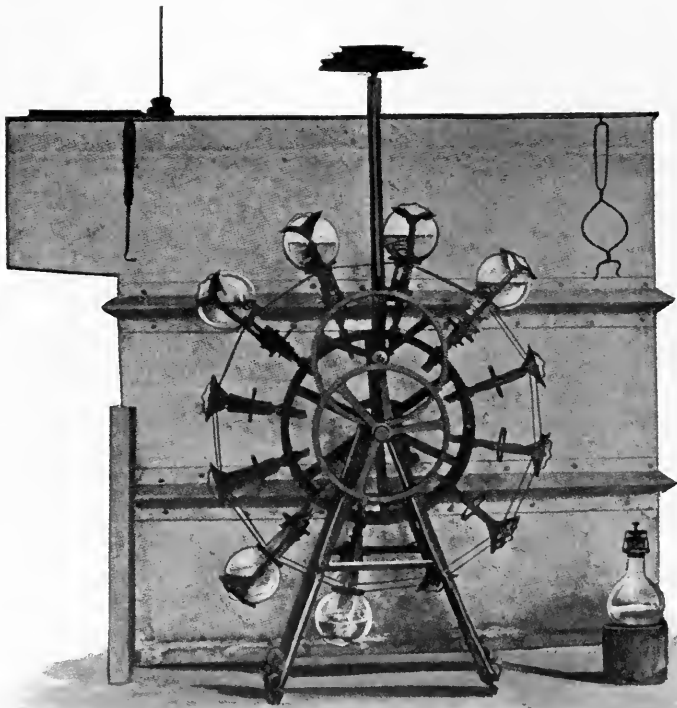


Fig. 6. Huston's Agitating Machine.

The apparatus is held in place by angle irons soldered to the bottom of the tank and a brace resting against the upright bar bearing the gear-wheels.

The water in the tank is heated by injecting steam, or by burners under the tank. As the tank holds about 300 pounds of water it is not subject to sudden changes of temperature, and little trouble has been experienced in raising and lowering the temperature of the water and maintaining it at any desired temperature.

An electric motor, or a small water-motor with only a very moderate head of water, will furnish ample power.

105. Comparison of Results.—The following data show the results obtained by the digester as compared with those furnished by the official method, temperature and time of digestion being the same in each instance.

AMMONIUM CITRATE SOLUTION ON PHOSPHATES.

Substance.	Time of treatment.	Total phosphoric acid. Per cent.	Removed by official method. Per cent.	Removed by digester. Per cent.
Steamed bone,	½ hour	27.67	10.59	14.52
	1 " "	" "	12.21	14.82
	2 hours	" "	14.61	17.56
	3½ " "	" "	16.48	18.53
	5 " "	" "	17.94	20.22
	7½ " "	" "	18.99	20.25
Marl,	10 " "	" "	19.73	21.18
	½ hour	13.86	4.43	4.11
	1 " "	" "	8.28	6.82
	2 hours	" "	10.34	9.76
	3½ " "	" "	11.00	11.31
	5 " "	" "	11.80	11.83
Acidulated bone,	8 " "	" "	12.51	12.64
	10 " "	" "	12.58	13.00
	½ hour	19.38	12.09	12.28
	1 " "	" "	12.47	12.40
	2 hours	" "	12.20	12.43
	3½ " "	" "	12.40	12.24
Bone,	5 " "	" "	12.43	12.26
	½ hour	21.40	6.97	8.48
	½ " "	18.22	9.28	10.63
	½ " "	2.52	0.23	0.25
Ammoniated dissolved bone,	½ " "	16.55	7.06	7.21
Cottonseed-meal and castor pomace,	¼ " "	" "	" "	" "
Phospho bone,	" "	" "	" "	" "

In comparing duplicates, the results from the use of the digester are found to be subject to less variation than those from the usual method. It is seen that in many, in fact, the majority

of cases, the quantity of phosphoric acid dissolved is markedly greater than by the methods where no mechanical stirring is employed.

106. Huston's Mechanical Stirrer.—The stirring apparatus shown in Fig. 7 differs from those which have heretofore come into use in requiring but a single belt to drive all the stirring rods, and having all the parts protected from the laboratory fumes.⁸⁶ The details of the belt system are shown in the small diagram in the lower central part of the figure. The apparatus is mounted on a substantial wooden box, 200 centimeters long, 30 centimeters high, and 18 centimeters wide. The driving pulleys, 10 centimeters in diameter, are enclosed in the upper part of the case. The shafts on which these pulleys are mounted extend through

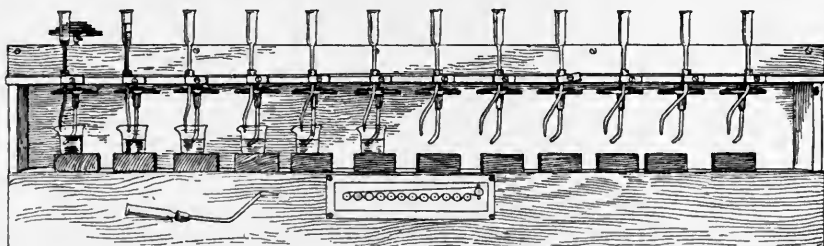


Fig. 7. Huston's Mechanical Stirrer.

the bottom of the enclosing box and carry a wooden disk, 11 centimeters in diameter, to prevent particles of foreign matter from falling into the beakers. The shafts extend two centimeters below these disks, and to the end of the shafts the bent stirring rods are attached by rubber tubing.

The board forming the support of the driving pulleys is extended two centimeters in front of the apparatus, and in this extension 12 notches are cut, in which are held the corks carrying the tubes which contain the solution to be used in precipitating the material in the beakers.

The ends of these tubes are drawn out to a fine point so as to deliver the liquid at the rate of about one drop per second.

The front of the apparatus is hinged and permits the whole to be closed when not in use, or during the precipitation.

⁸⁶ Indiana Agricultural Experiment Station, Bulletin 54, 1895 : 7.

The apparatus has proven extremely satisfactory in the precipitation of ammonium magnesium phosphate. The precipitate is very crystalline, and where the stirring is continued for some minutes, after the magnesia solution has all been added, no amorphous precipitate is observed on longer standing.

107. Precipitation of the Water and Citrate-Soluble Phosphoric Acid.—The importance of rapid precipitation with vigorous stirring when the molybdate solution is employed has also been pointed out by Ledoux and likewise the desirability of keeping the temperature low (16°).⁸⁷

In the use of the aqueous and citrate extract of superphosphates the precipitation is conducted as follows:

The aqueous or citrate extract, or both combined, is made up to a volume of 250 cubic centimeters, or each is made up to that volume. A part of the solution representing 0.2 gram of the sample is boiled with 15 cubic centimeters of strong nitric acid of 1.4 specific gravity for five minutes to convert all phosphoric acid into the ortho type. After cooling, 15 cubic centimeters of ammonia of 0.92 specific gravity is added, leaving the mixture slightly acid, and then 100 cubic centimeters of the molybdic solution, prepared by dissolving 150 grams of molybdic acid in 600 cubic centimeters of ammonia of 0.96 density and pouring the solution into 1070 cubic centimeters of nitric acid of 1.22 density. The precipitation is made with vigorous stirring, best by a mechanical agitator, for 30 minutes at a temperature not exceeding 16° . The precipitate is perfectly pure and the phosphoric acid may be determined by direct weighing, by titration or by the gravimetric process.

Many of the above precautions were previously pointed out by Pellet who especially called attention in 1889 to the volumetric method of Thilo, afterwards developed by Pemberton and Kilgore.⁸⁸

⁸⁷ Bulletin de l'Association belge des Chimistes, 1901, **15** : 125.

⁸⁸ Annales de Chimie analytique, 1900, **5** : 244; 1901, **6** : 248.

Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie, 1893-94, **11** : 152; 1896-97, **14** : 423.

Bulletin de l'Association belge des Chimistes, 1888-89, **3** : 51, 73.

108. Veitch's Method for Available Phosphoric Acid.—The general acceptance of the term "available acid" as including both the quantity soluble in water and afterwards the additional quantity soluble in ammonium citrate solution has led to the suggestion that a single determination of the total amount of the dissolved acid is, for practical purposes, fully as valuable as the determination of the two extracts separately. The usual objection to the direct determination of the citrate-soluble acid with the preliminary separation with molybdate solution has been the supposed difficulty of precipitating the phosphoric acid in the presence of a large quantity of organic matter, viz., the excess of the citrate used in extracting the phosphoric acid. Experience has shown that accurate separation can be secured, even in the presence of this form of organic matter. This fact led Veitch to combine the two extracts and determine the so-called available acid in one operation. This process is as follows:⁸⁹

The two extracts, viz., with water and with ammonium citrate, are placed in a 500 cubic centimeter flask with 10 cubic centimeters of nitric acid and the volume completed to the mark. The phosphoric acid is determined in aliquots of 100 cubic centimeters, whether by the molybdate or direct citrate of magnesia method. The precipitates are allowed to stand 18 hours before filtering.

Comparisons with the official method with many varieties of phosphate fertilizers containing from five to 15 per cent. of available acid, show close agreement when the molybdate separation is used, while by direct precipitation with citrate of magnesia, the results are somewhat lower.

The method therefore possesses certain advantages. Only one determination is required instead of two, and the probable error in manipulation is reduced one-half.

109. Availability of Phosphatic Fertilizers.—There is perhaps no one question more frequently put to analysts by practical farmers than the one relating to the availability of fertilizing materials. The object of the manufacturer should be to secure each of the valuable ingredients of his goods in the most useful form. The ideal form in which phosphoric acid should come

⁸⁹ Journal of the American Chemical Society, 1899, 21 : 1090.

to the soil is one soluble in water. Even in localities where heavy rains may abound, there is not much danger of loss of soluble acid by percolation. As has before been indicated, the soluble acid tends to become fixed in all normal soils and to remain in a state accessible to the rootlets of plants and yet free from the danger of exhaustive leaching. For this reason the water-soluble acid is regarded by most agronomists as more available than that portion insoluble in water, yet soluble in ammonium citrate.

In many of the States the statutes, or custom, prescribe that only the water and citrate-soluble acid shall be reckoned as available, the insoluble residue being allowed no place in the estimates of value. In many instances such a custom may lead to considerable error, as in the case of finely ground bones and some forms of soft and easily decomposable tricalcium phosphates. There are also, on the markets, phosphates composed largely of iron and aluminum salts, and these appear to have an available value, often in excess of the quantities thereof soluble in ammonium citrate.

As a rule the apatites, when reduced to a fine powder and applied to the soil are the least available of the natural phosphates. Finely ground bones also tend to give up their phosphoric acid with a considerable degree of readiness in most soils. The soft, finely ground phosphates, especially in soils rich in humus, have an agricultural value, almost if not quite, equal to a similar amount of acid in the acid phosphates. Natural iron and aluminum phosphates, have also, as a rule, a high degree of availability. Next in order come the land rock and pebble phosphates which, in most soils, have only a limited availability. In each case the analyst must consider all the factors of the case before rendering a decision. Not only the relative solubility of the different components of the offered fertilizer in different menstrua must be taken into consideration, but also the character of the soil to which it is to be applied, the time of application and the crop to be grown. By a diligent study of these conditions the analyst may, in the end, reach an accurate judgment of the merits of the sample.

DIRECT WEIGHING OF THE PHOSPHOMOLYBDATE PRECIPITATE

110. **Method of Hanamann.**—It has already been stated that many attempts have been made to determine the phosphoric acid by direct weighing as well as by titration, as in the Pemberton method. The point of prime importance in such a direct determination is to secure an ammonium phosphomolybdate mixture of constant composition. Unless this can be done no direct method, either volumetric or gravimetric, can give reliable results. Hanamann proposes to secure this constant composition by varying somewhat the composition of the molybdate mixture and precipitating the phosphoric acid under definite conditions.⁹⁰ The molybdate solution employed is prepared as follows:

Molybdic acid.....	100 grams.
Ten per cent. ammonia.....	1.0 liter.
Nitric acid (1.246 sp. gr.)	1.5 liters.

The precipitation of the phosphoric acid is conducted in the cold with constant stirring. It is complete in half an hour. The ammonium phosphomolybdate is washed with a solution of ammonium nitrate and then with dilute nitric acid, dried, and ignited at less than a red heat. It should then have a bluish black color throughout. Such a body contains 4.018 per cent. of phosphoric anhydrid.

Twenty-five cubic centimeters of a sodium phosphate solution containing 50 milligrams of phosphoric acid (P_2O_5), treated as above, gave a bluish black precipitate weighing 1.249 grams, which multiplied by 0.04018, equaled 50.018 milligrams of phosphorus pentoxid. The method should be tried on phosphates of various kinds and contents of phosphorus pentoxid before a definite judgment of its merits is formed. The method is applicable to phosphates containing a large percentage of phosphoric acid as well as to compounds having very little. In the former case only a small aliquot of the solution is subjected to precipitation, while in the latter, all or large portions are used. In one mixture 20 grams of superphosphate were dissolved in one liter of water and 10 cubic centimeters of the solution poured into 35 cubic centimeters of the

⁹⁰ Chemiker-Zeitung, 1895, 19 : 553.

molybdate mixture. The precipitate obtained weighed 0.9182 gram, showing a content of 18.44 per cent. of phosphoric acid in the original sample. A gravimetric determination yielded the same figure. On the other hand a sample of soil which showed 0.14 per cent. of phosphoric acid by the gravimetric method, was extracted with HNO_3 and the acid extract after separation of the silica, made up to 100 cubic centimeters and the whole poured into the molybdate mixture, gave a content of 0.14082 per cent. of phosphoric acid.

III. Method of Lorenz.—The various methods which have been proposed for the direct weighing of the ammonium molybdate precipitate of phosphoric acid, have been made the subject of a practical and critical study by Lorenz.⁹¹

The methods of Meineke, Hanamann, Woy and Hundeshagen are compared and the modifications thereof described.

The reagents employed by Lorenz are:

1. *Ammonium Molybdate.*—This reagent is prepared by pouring on 100 grams of pure dry ammonium sulfate in a glass cylinder of two liters capacity, one liter of nitric acid of 1.36 specific gravity at 15° and stirring until the salt is dissolved. In a liter flask 300 grams of purest dry ammonium molybdate are dissolved in hot water, cooled to about 20° and the flask filled to the mark. The contents of the flask are poured in a thin stream with constant stirring into the solution of ammonium sulfate in nitric acid. After standing for at least 48 hours, the solution is filtered and stored in a well stoppered bottle kept in the dark.

2. Nitric acid of 1.20 specific gravity at 15° .

3. A mixture of sulfuric and nitric acids made by pouring 30 cubic centimeters of sulfuric acid of 1.84 specific gravity into a liter of nitric acid of 1.20 specific gravity.

4. A two per cent. aqueous solution of pure ammonium nitrate.

5. Alcohol of from 90 to 95 per cent. strength.

6. Pure ether.

The solution of the phosphate is run into a measuring cylinder in quantities of 10, 15, or 20 cubic centimeters, according to its strength in phosphoric acid and the volume completed to 50 cubic

⁹¹ Die landwirtschaftlichen Versuchs-Stationen, 1901, 55 : 183.

centimeters with the sulfuric-nitric acid mentioned and the mixture placed in a flask of 250 cubic centimeters capacity. The mixture is heated and there is added thereto, 50 cubic centimeters of the ammonium molybdate reagent. After standing five minutes the mixture is stirred vigorously for one minute. The precipitate is allowed to stand for from three to 18 hours and then separated on a gooch under pressure, not through asbestos felt, but as recommended by Kilgore, through a disk of ash-free filter paper. The last traces of the yellow precipitate are brought into the filter and washed several times with the two per cent. ammonia nitrate solution. The precipitate is washed three times with alcohol and as many times with ether, sucking the filter dry after each addition of the washing liquids. When washed and dried as described the crucible with its contents is placed in a partial vacuum desiccator without CaCl_2 or H_2SO_4 for 30 minutes and weighed. The ammonium phosphomolybdate prepared in this way contains 3.295 per cent. of P_2O_5 .

112. Method of Woy.—The direct weighing of the yellow precipitate in the determination of the phosphoric acid in slags extracted by citric acid is accomplished by Woy in the following manner.⁹²

To 50 cubic centimeters of the solution obtained from basic slags by treatment with a two per cent. citric acid solution are added 30 cubic centimeters of nitric acid of 1.153 specific gravity, and 45 cubic centimeters of ammonium nitrate solution containing 340 grams of the salt in one liter of water, the mixture boiled and the phosphoric acid precipitated by the addition of 100 cubic centimeters of a boiling aqueous six per cent. solution of ammonium molybdate. After standing for 15 minutes the supernatant liquid is decanted, the precipitate washed with 50 cubic centimeters of a solution of 50 grams of ammonium nitrate and 40 cubic centimeters of nitric acid in one liter at a lukewarm temperature and then collected on a gooch crucible, dissolved in 10 per cent. ammonia, 20 cubic centimeters of ammonium nitrate, 30 cubic centimeters of water and one cubic centimeter of ammonium molybdate added to the filtrate, boiled and the yellow precipitate re-formed by

⁹² Chemiker-Zeitung, 1903, 27 : 279.

the addition of 10 cubic centimeters of nitric acid. The precipitate is collected in the gooch crucible, washed first with the acid ammonium nitrate above described, then with alcohol and finally with ether. The precipitate is ignited at first gently and then with a medium flame until the surface assumes a brilliant crystalline deep blue-black appearance. The precipitate is represented by the formula $24\text{Mo}_3\text{P}_2\text{O}_5$, and contains 3.946 per cent. of P_2O_5 .

Lorenz regrets that the German experiment stations have persisted in retaining the direct citrate method which is not a strictly scientific proceeding, but asserts that his own method of drying the yellow precipitate with ether without ignition consumes less time and is more accurate than Woy's modification as given above.⁹²

Sherman and Hyde slightly modify the processes of Woy and have been able to obtain results with this method on some 20 samples of fertilizers, embracing all the common sources of phosphoric acid, which agree within two-tenths of one per cent. with results obtained by the molybdate-magnesia method, except in the case of a phosphatic slag, in which the variation was three-tenths per cent.⁹⁴⁻⁹⁵ As the precipitate of magnesium pyrophosphate contained iron, the results by the gravimetric method were probably high. The authors use a three per cent. solution of neutral ammonium molybdate and add from five to eight cubic centimeters of nitric acid to the neutral phosphate solution. The ammonium phosphomolybdate is washed with one per cent. nitric acid until the washings amount to from 250 to 300 cubic centimeters, and ignited at a low heat in the usual way without dissolving and reprecipitating. The weight of the phosphomolybdate multiplied by 0.3949 gives the phosphoric acid.

113. Berju's Modification of P. Neumann's Method.—Berju calls attention to the fact that for at least 10 years it has been well known that phosphoric acid could be determined with great exactness by the direct weighing of the phosphomolybdate precipitate.⁹⁶ During this period the fact has been repeatedly verified. In his

⁹³ *Chemiker-Zeitung*, 1903, **27** : 495.

⁹⁴ *Journal of the American Chemical Society*, 1900, **22** : 652.

⁹⁵ *Chemiker-Zeitung*, 1897, **21** : 441, 469.

⁹⁶ *Journal für Landwirtschaft*, 1906, **54** : 31.

opinion, none of the methods which have heretofore been proposed for this process has been introduced into the experiment stations for the purpose of applying it to the estimation of phosphoric acid in fertilizers, these stations having continued to follow the time-consuming method of the direct precipitation of the phosphoric acid in the citrate solutions, although this method has led to no certain results.

The method of P. Neumann is preferred as the process for securing the phosphoric acid, because it requires less time than the other methods proposed and is equally exact.⁹⁷ Berju, therefore, has applied the principles of this method for general use in the investigation of fertilizers containing phosphoric acid. The accuracy of the method was first ascertained by its application to pure sodium phosphate ($\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$). For the formula of the precipitate he adopts that proposed by Hundeshagen, namely, $12\text{MoO}_3\text{PO}_4(\text{NH}_4)_3$, which contains 3.78 per cent. P_2O_5 .⁹⁸ The method of procedure is the following:

Fifty cubic centimeters of the phosphate solution, corresponding to 0.5 gram of sodium phosphate, are treated with five cubic centimeters of nitric acid of 1.2 specific gravity, and with 75 cubic centimeters of ammonium nitrate-molybdate solution prepared according to the directions of Wagner-Stutzer, for the purpose of precipitating the phosphoric acid. The mixture is stirred for a quarter of an hour, and after three-quarters of an hour, the precipitate is collected upon a gooch after decanting three times with about 30 cubic centimeters of the aqueous solution of a five per cent. ammonium nitrate solution and one per cent. nitric acid. The filtrate is washed six times and the precipitate collected as nearly as possible upon the asbestos felt.

The gooch is placed in a somewhat higher porcelain crucible and the precipitate carefully dried over a free flame, the temperature being gradually raised to about 150° to 180° until the ammonium nitrate is completely removed. This is determined by placing a watch glass upon the top of the crucible for at least half a minute and noticing whether any deposit is found thereon.

⁹⁷ *Zeitschrift für analytische Chemie*, 1898, 37 : 303.

⁹⁸ *Zeitschrift für analytische Chemie*, 1889, 28 : 141.

The dried precipitate is cooled in a desiccator and weighed, covered with a watch glass, replaced upon the burner, converted with a stronger heat into the phosphomolybdate anhydrid, and cooled and weighed as before. The weight of this precipitate multiplied by 0.03946 gives the quantity of phosphoric anhydrid (P_2O_5).

This method was applied to superphosphates and basic slags. In the case of basic slags it was found that the results by the foregoing method were accurate, even without the removal of the silicic acid. In the illustrations given it appears that after the removal of the silicic acid there was found 19.30 per cent. of P_2O_5 by the direct gravimetric method, while by the weighing of the phosphomolybdate precipitate without the separation of the silica in two cases the results were 19.35 per cent. P_2O_5 and 19.26 per cent. P_2O_5 .

In a determination of the phosphoric acid soluble in a citrate solution of basic slag by the direct method, there was found 14.7 per cent. of P_2O_5 . In the estimation of the same acid after the removal of the silicic acid there was found 14.42 per cent. of P_2O_5 by the direct method. Without the removal of the silicic acid by direct weighing of the phosphomolybdate precipitate, there was found 14.43 per cent. of P_2O_5 .

The general conclusions of the investigation are:

1. The methods tried for the estimation of the phosphoric acid in fertilizers, depending upon the simplification of the method of direct precipitation of the phosphoric acid as $MgNH_4PO_4$, give almost constantly too high results.

2. The estimation of phosphoric acid as $24MoO_3P_2O_6$, according to the method of P. Neumann, gives without exception, very exact results, and the use of the different solvents for the phosphoric acid in these fertilizers, as well as the presence of dissolved silicic acid in the hydrochloric acid and citrate solutions, are without influence on the accuracy of the results.

Neumann's method is at least more simple and as readily applicable as the common method for estimating phosphoric acid as $Mg_2P_2O_7$.

114. The Method of Graftiau.—Graftiau has proposed some slight modifications of the method of determining phosphoric

acid by weighing the ammonium phosphomolybdate. His procedure is based upon a solution containing a proper content of nitric acid, of ammonium nitrate, and ammonium citrate. In such a solution in the presence of an excess of nitromolybdate ammonium, the phosphoric acid is precipitated rapidly at a temperature of about 70° . The precipitate which is formed is pure and it is dried upon filter paper without decomposition at from 105° to 110° .

The method is used particularly in Belgium, where by an agreement between Belgium, Holland, and the Grand-Duchy of Luxembourg, only two methods of international examination of phosphates are permitted, *i. e.*, the direct phosphomolybdate method or the citro-magnesium method. The method by the direct weighing of phosphomolybdate ammonium is therefore employed only as a means of control in these countries.

The solutions of phosphates are prepared according to the methods prescribed by Kuss for the analysis of fertilizing materials, cattle feeds, and agricultural products for the Grand-Duchy of Luxembourg.

The acid solutions of the phosphates and basic slags are neutralized by ammonium until precipitation commences. The precipitate is redissolved by a few drops of nitric acid and 10 cubic centimeters of Petermann's citrate of ammonium solution added. The rest of the process is the same as that employed where citric acid or ammonium citrate is originally used for securing a solution of phosphates soluble therein.

The phosphoric acid having been thus obtained in the presence of a solution of citrate of ammonium, the samples are treated as follows:

There is added to each sample containing from 0.1 to 0.4 gram of the original material, according to its richness in phosphoric acid, from two to three cubic centimeters of concentrated citric acid from 10 to 15 cubic centimeters of a saturated solution of ammonium nitrate, and from 50 to 70 cubic centimeters of water. The mixture is brought to the boiling point, the lamp removed, and there is added from 60 to 100 cubic centimeters (according to the richness of the sample) of ammonium nitro-

molybdate, containing 110 grams of molybdic acid dissolved in 400 cubic centimeters of ammonium, 0.96 specific gravity, and the solution poured slowly into 1500 cubic centimeters of nitric acid of 1.20 specific gravity. The solution is cooled to about 70° and allowed to rest for 15 to 30 minutes. The precipitate sinks very rapidly, leaving a perfectly limp liquid. The greater part of the liquid is siphoned off from the precipitate, which is afterwards put on a filter and washed two or three times with water containing one per cent. of nitric acid. The phosphomolybdate of ammonium is then ready to be dried.

All these operations require very little time because the precipitate is already freed from its mother liquors by the liquids which have been used for washing out the flasks.

The precipitate, after removing from the funnel, is first placed on filter paper, with care so as not to break the paper, and is afterwards transferred to the drying oven where it is dried for two hours at a temperature of from 105° to 110°, as above described.

The different factors which should be used for calculating the amount of phosphoric acid from the weight of phosphomolybdate vary among different authors and the factor finally selected is 0.0375, which is only slightly different from that proposed by Boussingault, *i. e.*, 0.0373.⁹⁹

115. The Method of Pellet.—In 1887 Pellet proposed to the French chemists the method of determining phosphoric acid by weighing ammonium phosphomolybdate, and this method has been employed by a certain number of chemists in France since that time.¹ Pellet is led to believe from the results of his investigations that, when precipitated in the presence of a citrate, ammonium phosphomolybdate is of constant composition and can be accurately dried and weighed on tared filter paper. The factor used for calculating the phosphoric anhydrid is 0.0374.²

⁹⁹ Atti del VI Congresso internazionale di Chimica applicata, Roma, 1906, **1** : 64.

¹ Atti del VI Congresso internazionale di Chimica applicata, Roma, 1906, **1** : 321.

² Bulletin de l'Association des Chimistes de Sucrierie et de Distillerie, 1906-07, **24** : 525.

116. Gladding's Modification.—Gladding has proposed the following modified method for the direct determination of phosphoric acid by weighing the yellow precipitate:³ To the solution of phosphoric acid 25 cubic centimeters of strong ammonia, 0.90 specific gravity, is added, and concentrated nitric acid to acidity. The beaker containing the solution is placed in a water bath at 50° and the ordinary molybdate solution added at the rate of three drops per second in excess and with constant stirring. After standing 10 minutes the solution is filtered through a weighed filter paper, washed six times with 1:100 nitric acid, once with water and dried to constant weight at from 105°-108° in a glycerol or salt water oven. Careful analysis of the dried precipitate led to the formula: $24\text{MoO}_3, \text{P}_2\text{O}_5, 3(\text{NH}_4)_2\text{O} + 24\text{MoO}_3, \text{P}_2\text{O}_5, 2(\text{NH}_4)_2\text{O} \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$.

Later Gladding recommended that the yellow precipitate be given two final washings with alcohol to facilitate drying.⁴ This method has been examined by the Association of Official Agricultural Chemists. With slight modifications, such as a gooch crucible with a paper or asbestos felt for the filtrations, and more thorough washing of the precipitate with water (total quantity from 100 to 300 cubic centimeters) it has been found to give very accurate and trustworthy results.⁵

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID.

117. Classification of Methods.—The time required for a gravimetric determination of phosphoric acid has led analysts to try the speedier, if less accurate processes, depending on the use of volumetric methods. The chief difficulty with these methods has been in securing combinations of standard composition and some sharp method of distinguishing the end reaction. In some cases, as, for instance, in the uranium method, it has been found necessary to remove a portion of the titrated solution and prepare it for final testing by subsidence or filtration. As is well known, this method of determining the end reaction is less accurate and more time-consuming than those processes depending on a change

³ Journal of the American Chemical Society, 1896, **18** : 23.

⁴ Division of Chemistry, Bulletin 51, 1898 : 47.

⁵ Division of Chemistry, Bulletin 49, 1897 : 60 ; Bulletin 51, 1898 : 47.

of color in the whole mass. Free tribasic phosphoric acid can not be conveniently titrated directly with a standard alkali, because of the development of an amphoteric action near the point of neutrality. When, for instance, an alkali is added to the acid, a combination is formed of such a character that it will affect an indicator both as an acid and alkali. All the volumetric processes now in general use may be divided into two classes, viz., (1) the direct titration of phosphoric acid and the determination of the end reaction by any appropriate means, and (2) the previous separation of the phosphoric acid, usually by means of a citromagnesium or molybdenum mixture, and in the latter case the subsequent titration of the yellow ammonium phosphomolybdate either directly or after reduction to a lower form of oxidation. In respect of age and extent of application, by far the most important volumetric method is the one depending on titration by a uranium salt after previous separation by ammoniacal magnesium citrate. A promising method, after previous separation by molybdenum, is the one proposed by Thilo and developed by Pemberton, and modified by Kilgore and other members of the Association of Official Agricultural Chemists, and it has now come into quite general use in this country. For small quantities of phosphoric acid or of phosphorus, such as are found in steels and irons, the method of Emmerton either as originally proposed or as modified by Dudley and Noyes, has been frequently used. Where volumetric methods are applied to products separated by molybdic solution, the essential feature of the analytical work is to secure a yellow precipitate of constant composition. If this could be uniformly done in such methods they would rival the gravimetric processes in accuracy. Hence it is highly important in these methods that the yellow precipitate should be secured as far as possible under constant conditions of strength of solution, duration of time, and manner of precipitation. In these cases, and in such only, can the quicker volumetric methods be depended on for accurate results.

The direct volumetric titration of the phosphoric acid by a uranium salt or otherwise is practised only when the acid is combined with the alkalies and when iron and alumina are absent and only small quantities of lime present. This method

has therefore, but little practical value for agricultural purposes. In all volumetric analyses the accuracy of the burettes, pipettes, and other graduated vessels should be proved by careful calibration. Many of the disagreements in laboratories where the analytical work is conducted equally well can be due to no other cause than the inaccuracy of the graduated vessels which are often found in commerce. Burettes should not only be calibrated for the whole volume but for at least every five cubic centimeters of the graduation.

URANIUM METHOD AS PRACTISED BY THE FRENCH CHEMISTS.

118. The Uranium Method.—Since the phosphoric acid of practical use for agricultural purposes is nearly always combined with lime, alumina and iron, its volumetric estimation by means of a standard solution of a uranium salt is to be preceded by a preliminary separation by means of an ammoniacal magnesium citrate solution. The phosphoric acid may also be separated by means of molybdic solution or by tin or bismuth. The principle of the method was almost simultaneously published by Sutton, Neubauer, and Pincus.⁶ In practise, however, it has been found that when the uranium method is to be used, the magnesium citrate separation is the most convenient. Since this is the method until lately practised almost universally in France, it will be given in detail. It is based essentially on the process of Joulie,⁷ as described by Munro.⁸

119. Preparation of Sample.—(1) *Incineration.*—Since the organic matters present in a phosphatic fertilizer often interfere with the employment of uranium as a reagent, it is necessary to incinerate the sample before analysis.⁹

(2) *Solution of the Material.*—All phosphates, with the exception of certain aluminum phosphates, amblygonite for example, are easily dissolved in nitric and hydrochloric acids more or less

⁶ Chemical News, 1860, 1 : 97, 122; Sutton, Volumetric Analysis, 9th Edition, 1904 : 298.

Archive für wissenschaftliche Heilkunde, 1860, 4 : 228.

Journal für praktische Chemie, 1859, 76 : 104.

⁷ Bulletin de la Société des Agriculteurs de France, 1876 : 53; Encyclopédie chimique, 1888, 4 : 10.

⁸ Chemical News, 1885, 52 : 85.

⁹ Manuel agenda des Fabricants de Sucre, 1889 : 307.

dilute, especially on ebullition. The best solvent, however, for calcium phosphates in the uranium method is incontestably hydrochloric acid which also very easily dissolves the iron and aluminum phosphates often found with calcium phosphates.

(3) *Nitric Acid*.—In many laboratories nitric acid is preferred in order to avoid, in part, the solution of ferric oxid which interferes with the determination of phosphoric acid in certain processes. Since it does not act in this way for the citro-magnesium uranium method, it is preferable to employ hydrochloric acid, especially because it dissolves the iron completely and thus permits the operator to judge of the success of the solvent action by the completely white color of the residue.

(4) *Pyritic Phosphates*.—Certain phosphates contain pyrites which hydrochloric acid does not readily dissolve, and there is left, consequently, a residue more or less colored. In this case it is necessary to add some nitric acid and to prolong the boiling until the pyrite has disappeared, since it might retain a small quantity of phosphoric acid in the state of iron phosphate.

(5) *Sulfuric Acid*.—Some chemists decompose the phosphates by means of dilute sulfuric acid. This method, which is certainly able to give good results for certain products and for certain processes, presents numerous inconveniences tending to render its use objectionable for volumetric purposes. The calcium sulfate formed, requires prolonged washings which lead to chances of fatal error.

If an aluminum phosphate be under examination, containing only very little or no lime, sulfuric acid is to be preferred to hydrochloric and nitric acids, since it attacks amblygonite, which, as has been before stated, resists the action of the other two acids. But these are cases which are met with very rarely, and which can always be treated by the general method of previously fusing the material with a mixture of sodium and potassium carbonate.

In the great majority of cases the decomposition by hydrochloric acid is very easily accomplished by simply boiling in a glass vessel, and without effecting the separation of the silica. This operation is only necessary after the substance has been fused with alkaline carbonates, or in case of substances which

contain decomposable silicates giving gelatinous silica with hydrochloric acid.

There are two methods [see (6) and (7)] of securing a solution of the sample which varies from one to five, and even to 10 grams, according to the apparent quantity of phosphoric acid in the material to be analyzed.

(6) *Solution by Filtration and Washing.*—The ordinary method can be employed consisting in decomposing the substance by an acid, filtering, washing the residue upon the filter and combining all the wash-waters to make a determinate volume. Afterwards an aliquot fraction of the whole is used for the precipitation. This method is long, and presents some chances of error when the insoluble residue is voluminous and contains silica which obstructs the pores of the paper and renders the filtration difficult.

(7) *Volumetric Solution.*—It is advisable to substitute volumetric solution for solution by filtration and washing, which is accomplished by decomposing the substance in a graduated flask, the volume being afterwards made up to the mark with distilled water after cooling. The solution is filtered without washing, and by means of a pipette an aliquot part of the original volume is removed for analysis. Thus all retardations in the process are avoided, and likewise the chances of error from washing on the filter. It is true that this method may lead to a certain error due to the volume of the insoluble matter which is left undecomposed, but since this insoluble matter is usually small in quantity, and since it is always possible to diminish the error therefrom by correspondingly increasing the volume of the solution, this cause of error is much less to be feared than those due to the difficulties which may occur in the other method. Let us suppose, in order to illustrate the above, that we are dealing with a phosphate containing 50 per cent. of insoluble sand which may be considered as an extreme limit. In working on four grams of the material in a flask of 100 cubic centimeters capacity, there will be an insoluble residue of two grams occupying a volume of less than one cubic centimeter, the density of the sand being generally above two. The 100 cubic centimeter flask will then contain more than 99 cubic

centimeters of the real solution and the error at the most would be less than 0.01. This error could be reduced to one-half by dissolving only two grams of the material in place of four, or by making the volume up to 200 instead of 100 cubic centimeters.

In general it may be said that the errors which do not exceed 0.01 of the total matter under treatment, are negligible for all industrial products. The method of volumetric solution does not present any further inconvenience. It deserves to be and has been generally adopted by reason of its rapidity in all the laboratories where many analyses are to be made. In the volumetric method great care should be taken not to make up to the volume until after the cooling to room temperature, which may be speedily secured by immersing the flask in cold water. Care should also be exercised in removing the sample for analysis by means of the pipette immediately after filtration, and filtration should take place as soon as the volume is made up to the standard. By operating in this way the possible variations from changes of volume due to changes of temperature are avoided.

(8) *Examination for Arsenic Acid.*—When the sample examined contains pyrites, arsenic is often present. When the decomposition has been effected by means of nitric acid, arsenic acid may be produced. This deports itself in all circumstances like phosphoric acid, and if it is present in the matter under examination, it will be found united with the phosphoric acid and determined therewith afterwards. It is easy to avoid this cause of error by passing first a current of sulfurous acid through the solution, carrying it to the boiling point in order to drive out the excess of sulfurous acid, and afterwards precipitating the arsenic by a current of hydrogen sulfid. After filtration, the rest of the operation can be carried on as already described.

120. Precipitation of the Phosphate in Presence of Citrate.—By means of an accurate pipette a quantity of the solution representing from 0.125 to 0.250 gram or more is measured, according to the presumed richness of the product to be examined. In order that the following operations may go on well, it is advisable that the quantity of phosphoric acid contained in the sample should be about 50 milligrams. The sample being measured is run into a

beaker, and there are added, first, 10 cubic centimeters of magnesium citrate solution, and second, a large excess of ammonia. If the quantity of the magnesium citrate solution be sufficient, the mixture should at first remain perfectly limpid and only become turbid at the end of some moments and especially after the mixture is stirred.

If there should be an immediate turbidity, it is proof that the quantity of magnesium citrate solution employed has been insufficient to hold the iron and aluminum phosphates in solution until the new compounds are formed, and it is necessary to begin again by doubling its amount. Good results can not be obtained by adding a second portion of the magnesium citrate solution to the original, since the iron and aluminum phosphates which are once formed are redissolved with difficulty. Many chemists at the present time abstain from using the magnesium citrate solution and replace it by a solution of citric acid and one of magnesium sulfate, which they pour successively into the sample under examination. This is a cause of grave errors which it is necessary to point out. Joulie has indeed recognized the fact that the precipitation of the phosphoric acid is not completed in presence of ammonium citrate unless it is employed in conjunction with a sufficient excess of magnesia. But the foreign matters which accompany the phosphoric acid require different quantities of ammonium citrate in order to keep them in solution, and it is important to increase the magnesium solution at the time of increasing the citric acid in order to maintain them always in the same proportion. This is easily accomplished by measuring the two solutions, but it is much more easily done by uniting them and adding them together.

121. The Magnesium Citrate Solution.—The formula originally proposed by Joulie, modified by Millot, and adopted by the French Association of Chemists, is as follows: Citric acid, 400 grams; pure magnesium carbonate, 40 grams; caustic magnesia, 20 grams; distilled water, half a liter. After solution, add enough of ammonia to render strongly alkaline, requiring about 600 cubic centimeters. Make the volume up with distilled water to one and a half liters. If the solution be turbid, it is proof that the

magnesia or the carbonate employed contains some phosphoric acid, which is to be separated by filtration, and the solution can then be preserved indefinitely.

This solution is made by the formula given by Sutton as follows: Add 27 grams of pure magnesium carbonate by degrees to a solution of 270 grams of citric acid in 350 cubic centimeters of warm water. When all effervescence has ceased and the liquid is cooled to room temperature, add 400 cubic centimeters of ammonia of about 0.96 specific gravity, containing approximately 10 per cent. of NH_3 . The volume is made up to one liter and kept in a well stoppered bottle.¹⁰

122. Time of Subsidence.—When the phosphoric acid is precipitated by the mixture above mentioned, it is necessary to allow it to subside for a certain time under a bell jar in order to avoid the evaporation of the ammonia. In order to give plenty of time for this subsidence, it is well to make the precipitations in the afternoon and the filtrations the following morning. There are thus secured from 12 to 15 hours of repose, which is time amply sufficient for all cases.

123. Filtration and Washing.—Filtration is performed easily and rapidly upon a small filter without folds placed in a funnel with a long stem of about two millimeters internal diameter. Placed in a series of six or eight, they allow the filtration to take place in regular order without loss of time, the first filter being always empty by the time the last one is filled. The supernatant liquid from the precipitate should first be decanted on the filter, avoiding the throwing of the filtrate on the filter, which would greatly retard the process, especially if it should contain a little silica, as often happens.

When the clear liquid is thus decanted as completely as possible, the rest of the precipitate is treated with water to which one-tenth of its volume of ammonia has been added, and the washing is continued by decantation as at first, and afterwards by washing upon the filter until the filtered solution gives no precipitate with sodium phosphate. Four washings are generally sufficient to attain this result.

¹⁰ Sutton, Volumetric Analysis, 9th Edition, 1904: 299.

If the operations which precede have been well conducted, the total phosphoric acid contained in the material under examination is found upon the filter paper, except the small portion which remains adhering to the beaker in which the precipitation has been made. The determination of the phosphoric acid comprises the following operations: First, solution of the ammonium magnesium phosphate, and second, titration by means of a standard solution of uranium.

124. Solution of the Ammonium Magnesium Phosphate.—The phosphate which has been collected upon the filter is dissolved by a 10 per cent. solution of pure nitric acid. This solution is caused to pass into the beaker in which the precipitation was made in order to dissolve the particles of phosphate which remain adherent to its sides; and this solution is then thrown upon the filter. The filtrate is then received in a flask of about 150 cubic centimeters capacity, marked at 75 cubic centimeters. After two or three washings with the acidulated water, the filter itself is detached from the funnel and introduced into the vessel which contains the solution.

The whole of the filtrate being collected in the flask, it is saturated by one-tenth ammoniacal water until a slight turbidity is produced. One or two drops of dilute nitric acid are now added until the liquor becomes limpid, and the flask is placed upon a sand-bath in order to carry the liquid to the boiling-point. After ebullition there is added five cubic centimeters of acid sodium acetate so as to cause the free nitric acid to disappear, and immediately the titration, by means of a standard solution of uranium, is undertaken.

125. Acid Sodium Acetate.—The acid sodium acetate is prepared as follows: Crystallized sodium acetate, 100 grams; glacial acetic acid, 50 cubic centimeters; distilled water, enough to make one liter.

126. Standard Solution of Uranium Nitrate.—A solution of uranium is to be prepared as follows: Pure uranium nitrate, 40 grams; distilled water, about 800 cubic centimeters. Dissolve the uranium nitrate in the distilled water and add a few drops of ammonia until a slight turbidity is produced, and then a sufficient

amount of acetic acid to cause this turbidity to disappear. The volume is then completed to one liter with distilled water.

The uranium nitrate often contains some uranium phosphate and some ferric nitrate. It is important that it be freed from these foreign substances. This is secured by dissolving it in distilled water and precipitating it by sodium carbonate, which redissolves the uranium oxid and precipitates the iron phosphate and oxid.

The filtered liquor is saturated with nitric acid and the uranium oxid reprecipitated by ammonia. It is washed with distilled water by decantation and redissolved in nitric acid, as exactly as possible, evaporated, and crystallized.

The crystals are taken up with ether, which often leaves behind a little insoluble matter. The solution is filtered, and the ether evaporated. The salt which remains is perfectly pure.

It frequently happens when the uranium nitrate has not been properly purified that the solution, prepared as has been indicated above, deposits a light precipitate of phosphate which alters its strength and affords a cause of error.

Only those solutions should be employed which have been prepared some days in advance and which have remained perfectly limpid. The solution of uranium thus obtained contains uranium nitrate, a little ammonium nitrate, a very small quantity of uranium acetate, some ammonium acetate, and a little free acetic acid. Its sensibility is the more pronounced as the acetates present in it are less in quantity. It is important, therefore, never to prepare the solution with uranium acetate.

127. Typical Solution of Phosphoric Acid.—In order to titrate a solution of uranium, it is necessary to have a standard solution of phosphoric acid; that is to say, a solution containing a precise and known quantity of that acid in a given volume. This solution is prepared by means of acid ammonium phosphate, a salt which is easily obtained pure and dry. Sometimes it may contain a small quantity of neutral phosphate, which modifies the relative proportions of phosphoric acid and ammonia, and it is indispensable to have its strength verified. The titer of the typical solution should be such that it requires for the precipitation of

the phosphoric acid which it contains, a volume of the solution of uranium almost exactly equal to its own, in order that the expansions or contractions which the two liquors undergo, by reason of changes in the temperature of the laboratory, should be without influence upon the results.

The solution of uranium, prepared as has been indicated above, precipitates almost exactly five milligrams of phosphoric acid per cubic centimeter; the typical solution of phosphoric acid is prepared with eight and one-tenth grams of acid ammonium phosphate pure and dry, which is dissolved in a sufficient quantity of distilled water to make one liter.

Since the acid ammonium phosphate contains 61.74 per cent. of anhydrous phosphoric acid, the quantity above gives exactly five grams of that acid in a liter, or five milligrams in a cubic centimeter.

Instead of this solution the following is also recommended: Dissolve 3.087 grams of pure ammonium phosphate in water and make the volume up to one liter. Each 20 cubic centimeters of this solution corresponds to 0.04 gram of phosphoric anhydrid.

128. Salt for Setting the Uranium Solution.—In determining the strength of the uranium solution the crystallized sodium salt, $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$, has been used. This salt easily loses water and for this reason its weight is not constant. Müller proposes to use in its place, the acid sodium-ammonium salt, $\text{NaHNH}_4\text{PO}_4 \cdot 4\text{H}_2\text{O}$. Even better results are secured by using the crystallized dicalcium salt, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, which in the free air or even over phosphoric anhydrid does not vary at ordinary temperatures.¹¹

In the preparation of this salt a solution of disodium phosphate, Na_2HPO_4 , is added little by little to a dilute solution of calcium chlorid until the lime is almost completely precipitated. The gelatinous precipitate at first formed soon becomes crystalline, and it is easy to wash it thoroughly. The washed salt is placed on plates and dried at 70° . Theoretically, the salt thus obtained contains 41.27 per cent. of P_2O_5 .

129. Verification of the Strength of the Standard Solution of Phosphoric Acid.—The strength of the standard solution of phos-

¹¹ Bulletin de la Société chimique de Paris, 1901, [3], 25 : 1000.

phoric acid is verified by evaporating a known volume, 50 cubic centimeters, for example, with a solution of ferric hydroxid containing a known quantity of ferric oxid. The mass having been evaporated to dryness and ignited in a platinum crucible, gives an increase in the weight of the iron oxid exactly equal to the amount of anhydrous phosphoric acid contained therein, both the nitric acid and ammonia being driven off by the heat.

To prepare the solution of ferric hydroxid, dissolve 20 grams of iron filings in hydrochloric acid. The solution is filtered to separate the carbon, and it is converted into ferric nitrate by nitric acid; then the solution is diluted with distilled water and the ferric oxid precipitated by a slight excess of ammonia. The precipitate, washed by decantation with distilled water until the wash-water no longer gives a precipitate with silver nitrate, is redissolved in nitric acid and the solution is concentrated or diluted, as the case may be, to bring the volume to one liter.

In order to determine the quantity of ferric oxid which it contains, 50 cubic centimeters are evaporated to dryness, ignited, and weighed.

A second operation like the above is carried on by adding 50 cubic centimeters of the standard solution of phosphoric acid, and the strength of the solution thus obtained is marked upon the flask.

If the operation has been properly carried on, three or four duplicates will give exactly the same figures. If there are sensible differences, the whole operation should be done over from the first.

130. Titration of the Solution of Uranium.—In a 150 cubic centimeter flask marked at 75 cubic centimeters, are poured 10 cubic centimeters of the standard solution of phosphoric acid measured with an exact pipette; five cubic centimeters of the acid sodium acetate are added, and distilled water enough to make about 30 cubic centimeters, and the whole carried to the boiling-point. The titration is then carried on by allowing the solution of uranium to fall into the flask from a graduated burette, thoroughly shaking after each addition of the uranium, and trying a drop of the liquor with an equal quantity of a 10 per cent.

solution of potassium ferrocyanid upon a greased white plate. Since the quantity of the uranium solution present will be very nearly 10 cubic centimeters at first, nine cubic centimeters can be run in without testing. Afterwards, the operation is continued by adding two or three drops at a time until the test upon the white plate with the potassium ferrocyanid shows the end of the reaction. When there is observed in the final test a slight change of tint, the flask is filled up to the mark with boiling distilled water and the process tried anew. If in the first part of the operation the point of saturation has not been passed, usually the addition of a drop or two of the uranium solution is required in order to produce the characteristic reddish coloration, and this increase is rendered necessary by the increase in the volume of the liquid. Proceeding in this manner two or three times assures the attainment of extreme precision, inasmuch as the analyst knows just when to look for the point of saturation.

Correction.—The result of the preceding operation is not absolutely exact. It is evident, indeed, that in addition to the quantity of uranium required for the exact precipitation of the phosphoric acid, it has been necessary to add an excess sufficient to produce the reaction upon the potassium ferrocyanid.

This excess is rendered constant by the precaution of operating always upon the same volume, namely, 75 cubic centimeters. It can be determined then, once for all, by making a blank determination under the same conditions but without using the phosphoric acid.

The result of this determination is that it renders possible the correction, which it is necessary to make, by subtracting the quantity used in the blank titration from the preceding result in order to obtain the exact strength of the uranium solution.

The operation is carried on as follows: In a flat-bottomed flask of about 150 cubic centimeters capacity and marked at 75 cubic centimeters, by means of a pipette, are placed five cubic centimeters of the solution of sodium acetate; some hot distilled water is added until the flask is filled to the mark, and it is then placed upon a sand-bath and heated to the boiling-point. It is taken from the fire, the volume made up to 75

cubic centimeters with a little hot distilled water, and one or two drops of the solution of uranium are allowed to flow into the flask from a graduated burette previously filled exactly to zero. After each drop of the solution of uranium, the flask is shaken and the liquid tried upon a drop of potassium ferrocyanid, as has been previously indicated. For a skilled eye, four to six drops are generally necessary to obtain the characteristic coloration, that is, from two-tenths to three-tenths of a cubic centimeter. Beginners often use from five-tenths to six-tenths, and sometimes even more.

The sole important point is to arrest the operation as soon as the reddish tint is surely seen, for afterwards the intensity of the coloration does not increase proportionally to the quantity of liquor employed.

It is well to note that at the end of some time the coloration becomes more intense than at the moment when the solutions are mixed, so that care must be taken not to pass the saturation-point. This slowness of the reaction is the more marked as there is more sodium or ammonium acetate in the standard solutions. This is the reason that it is important to introduce always the same quantity, namely, five cubic centimeters. This is also the reason why the uranium acetate should not be employed in preparing the standard solution of uranium which ought to contain the least possible amount of acetate in order that the necessary quantity which is carried into each test should be as small as possible and remain without appreciable influence. If it were otherwise, the sensibility of the reaction would be diminished in proportion as a larger quantity of uranium solution was employed, giving rise to errors which would be as much more important as the quantities of phosphoric acid to be determined were greater. The correction for the uranium solution having been determined, it is written upon the label of the bottle containing it.

Causes of Error.—In the work which has just been described, some causes of error may occur to which the attention of analysts should be called.

The first is the error which may arise from the consumption of the small quantity of uranium phosphate which is taken with

a stirring rod when the liquid is tested with potassium ferrocyanid. It is very easy to be assured that the end of the reaction has really been reached. For this purpose it is only necessary to note the quantity of the solution already employed and to add to it afterwards four drops; shake, and make a new test with a drop of the potassium ferrocyanid placed near the spot which the last one occupied. If a decidedly reddish tint does not appear at the moment of removing the glass rod, it is to be concluded that the first appearance was an illusion, and the addition of uranium is to be continued. If, on the contrary, the coloration appear of a decided tint, the preceding number may be taken for exact. It is then always beneficial to close the titration by this test of four supplementary drops which will exaggerate the coloration and confirm the figure found.

The second cause of error, and one, moreover, which is the most frequently met with, consists in passing the end of the reaction by adding the uranium too rapidly. In place of giving then a coloration scarcely perceptible, the test with the drop of potassium ferrocyanid gives a very marked coloration. In this case the analysis can still be saved. For this purpose the analyst has at his disposal, a tenth-normal solution prepared with 100 cubic centimeters of the standard solution of phosphoric acid diluted to one liter with distilled water. Ten cubic centimeters of this tenth-normal solution are added, and the titration continued. At the end, the amount of additional phosphoric acid used is subtracted from the total.

A third cause of error is found in the foam which is often found in the liquid, due to shaking. This foam may retain a portion of the last drops of the solution of uranium which fall upon its surface and prevent its mixture with the rest of the liquid. If the glass stirring rod in being removed from the vessel, pass through this froth charged with uranium, the characteristic coloration is obtained before real saturation is reached. Consequently it is necessary to avoid, as much as possible, the formation of the foam, and especially to take care never to take the drop for test after agitation except in the middle of the liquid, where the foam does not exist.

Suppose the titration has been made upon 10 cubic centimeters of the normal solution of phosphoric acid in the conditions which we have just indicated, and the figure for the uranium obtained is 10.2 cubic centimeters; if now the correction, which may be supposed to amount to two-tenths cubic centimeter, be subtracted there will remain 10 cubic centimeters of the uranium solution which would have precipitated exactly 50 milligrams of phosphoric acid.

The quantity of phosphoric acid which precipitates one cubic centimeter of the solution will be consequently expressed by the proportion $50 \div 10 = 5$ milligrams, which is exactly the strength required. In the example which has just been given, the inscription upon the flask holding the standard solution would be as follows: Solution of uranium, one cubic centimeter equals five milligrams of phosphorus pentoxid; correction, two-tenths cubic centimeter.

131. Titration of the Sample.—The strength of the solution of uranium having been exactly determined, by means of this solution the strength of the sample in which the phosphoric acid has been previously prepared as ammonium magnesium phosphate is ascertained. In this case the quantity of phosphoric acid being unknown, it is necessary to proceed slowly and to duplicate the tests in order not to pass beyond the point of saturation. From this there necessarily results a certain error in consequence of the removal of quite a number of drops of the solution of the sample before the saturation is complete. It is, therefore, necessary to make a second determination in which there is at once added almost the quantity of the solution of uranium determined by the first analysis. Afterwards the analysis is finished by additions of very small quantities of uranium until saturation is reached. Suppose, for instance, that the sample was that of a mineral phosphate, five grams of which were dissolved in 100 cubic centimeters, and of which 10 cubic centimeters of the solution prepared as above, required 15.3 cubic centimeters of the standard solution of uranium. We then would have the following data:

Mineral phosphate, five grams of the material dissolved in 20 cubic centimeters of hydrochloric acid.

Water, sufficient quantity to make 100 cubic centimeters.

Quantity used, 10 cubic centimeters=0.50 gram of the sample under examination.

Solution of uranium required 15.3 cubic centimeters.

Correction 0.2 cubic centimeters.

Actual quantity of uranium solution 15.1 cubic centimeters.

Strength of the solution of uranium, one cubic centimeter=five milligrams P_2O_5 .

Then P_2O_5 in 0.50 gram of the material = $5 \times 15.1 = 75.5$ milligrams.

$$\text{Then the per cent. of } P_2O_5 = \frac{75.5 \times 100}{50} = 15.10.$$

The sample under examination ought always to be prepared in duplicate, either by making a single precipitation and re-solution of the ammonium magnesium phosphate which is made up to a certain volume and an aliquot portion of which is taken for the analysis, or by making two precipitations under the conditions previously described. When the content of phosphoric acid in the material under examination is very nearly known, the double operation may be avoided, especially if it be required to have rapid and only approximate analyses, such as those which are made for general control and for the conduct of manufacturing operations. But when analyses are to be used to serve as the basis of a law action or for the control of a market, they should always be made in duplicate, and the results ought not to be accepted when the numbers obtained are widely different, since the agreement of the two numbers will tend to show that the work has been well executed.

This method of analysis, much longer to describe than to execute, gives results perfectly exact and always concordant when it is well carried out, provided that the standard solutions upon which it rests for its accuracy are correctly prepared and frequently verified in the manner indicated.

The strength of the solution of uranium ought to be verified

every three or four days. The strength of the standard solution of phosphoric acid should be verified each time that the temperature of the laboratory undergoes any important change. A solution prepared, for example, in winter when the temperature of the laboratory is from 15° to 18° , would no longer be exact in summer when the temperature reaches 28° or 30° .

132. Volumetric Determination of Phosphoric Acid in Superphosphates.—Superphosphates are the products of the decomposition of phosphates by sulfuric or hydrochloric acid. They contain phosphoric acid combined with water, with lime, with magnesia, and with iron and alumina in various proportions.

These combinations may be classed in three categories: First, those compounds of phosphoric acid soluble in water; second, those insoluble in water, but very soluble in ammoniacal salts of the organic acids such as the citrate and oxalate; and third, phosphates not soluble in any of the above named reagents.

In the products soluble in water are met free phosphoric acid, monocalcium phosphate, acid magnesium phosphate, and the iron and aluminum phosphates dissolved in the excess of phosphoric acid. In the products insoluble in water but soluble in the ammonium citrate are found dicalcium phosphate and iron and aluminum phosphates, which together constitute the phosphates called reverted.

These compounds reduced to a very fine state of division in the process of manufacture are considered to contain phosphoric acid of the same economic value as that soluble in water.

133. Determination of the Total Phosphoric Acid in Superphosphates and Fertilizers.—The process is carried on exactly as for an ordinary phosphate, and with all the care indicated in connection with the sampling, the incineration, the solution by means of hydrochloric acid, and the separation of the phosphoric acid in the state of ammonium magnesium phosphate, and finally in the titration with uranium nitrate.

134. Determination of Soluble and Reverted Phosphoric Acid.—To make this determination a method applicable to all cases consists in extracting, at first, the constituents soluble in distilled water, and following this operation by digesting the residue in

ammonium citrate. The products soluble in water can be determined either separately or at the same time as the products soluble in the ammonium citrate, without the necessity of modifying very greatly the method of operation.

The determination of the total soluble or available phosphoric acid comprises, first, the solution of the soluble constituents in distilled water; second, the solution of the reverted phosphates in ammonium citrate; third, the determination of the phosphoric acid dissolved in the two preceding operations or the determination of the part soluble in ammonium nitrate by difference.

135. Preparation of the Sample for Analysis.—The sample sent to the chemical expert is prepared as has been indicated; that is to say, it is poured on a sieve of which the meshes have a diameter of one millimeter, and sifted upon a sheet of white paper. The parts which do not pass the sieve are broken up either by the hand or in a mortar and added, through the sieve, to the first portions. The product is well mixed and, in this state, the mass presents all the homogeneity desirable for analysis.

Some fertilizers are received in a pasty state, which does not permit of their being sifted. It is necessary in such a case to mix them with their own weight either of precipitated calcium sulfate dried at 160° or with fine sand washed with hydrochloric acid and dried, which divides the particles perfectly and permits of their being passed through the meshes of the sieve.

136. Extraction of the Products Soluble in Distilled Water.—The substance having been prepared as has just been indicated, one and a half grams are placed in a glass mortar. Twenty cubic centimeters of distilled water are added, and the substance gently suspended therein. After standing for one minute, the supernatant part is decanted into a small funnel provided with a filter-paper and placed in a flask marked at 150 cubic centimeters. This operation is repeated five times and is terminated by an intimate breaking up of the matter with distilled water. When the volume of 100 cubic centimeters of the filtrate has been obtained, the residue in the mortar is placed on the filter and the washing is continued until the total volume reaches 150 cubic centimeters. The filtrate is shaken in order to render the liquor homogeneous,

and is transferred to a precipitating glass of about 300 cubic centimeters capacity.

137. Solution of the Reverted Phosphates by Ammonium Citrate.

—The filter from the above process is detached from the funnel and is introduced into a flask marked at 150 cubic centimeters together with 60 cubic centimeters of alkaline ammonium citrate prepared in the following manner:

Pure citric acid, 400 grams.

Ammonia of 22°, 500 cubic centimeters.

The ammonia is poured upon the crystals of citric acid in a large dish. The mass becomes heated, and the solution takes place rapidly. When it is complete and the solution is cold, it is poured into a flask of one liter capacity, and the flask is filled up to the mark with strong ammonia. It is preserved for use in a well stoppered bottle. The solution must be strongly alkaline.

The flask in which the filter paper is introduced, together with the ammonium citrate, is stoppered and shaken violently in order to disintegrate the filter paper and get the reverted phosphates in suspension. There are added then about 60 cubic centimeters of distilled water, and the flask is shaken and left for 12 hours at least, or at most for 24 hours. The volume is made up to 150 cubic centimeters with distilled water, and after mixture the solution is filtered.

There are thus obtained two solutions, one with water and one with the alkaline ammonium citrate, which can be precipitated together or separately, according to circumstances. The usual process is to combine equal volumes of 25, 50, or 100 cubic centimeters, representing one-quarter, one-half or one gram of the material according to its presumed richness, in a precipitating flask to which are added from 10 to 20 cubic centimeters of the solution of magnesia made up as follows:

Magnesium carbonate, 50 grams.

Ammonium chlorid, 100 grams.

Water, 500 cubic centimeters.

Hydrochloric acid, 120 cubic centimeters.

After complete solution of the solid matters in the above, add

100 cubic centimeters of ammonia of 22° strength, and distilled water enough to make one liter.

The solutions are thoroughly mixed in a precipitating glass, an excess of ammonia added, and allowed to stand for 12 hours under a bell jar. The phosphoric acid contained in the liquor is separated as ammonium magnesium phosphate. It is collected upon a small filter, washed with a little ammoniacal water, redissolved, and titrated with the uranium solution in the manner already indicated.

Example.—The following is an example of this kind of a determination:

(1) One and one-half grams of the superphosphate and distilled water enough to make 150 cubic centimeters.

(2) Filter paper with reverted phosphates, 60 cubic centimeters of ammonium citrate, and a sufficient quantity of distilled water to make 150 cubic centimeters.

Aqueous solution (1)	25 cc.	}	= 0.25 gram of the sample.
Citrate solution (2)	25 cc.		

Add magnesium solution 20 cubic centimeters and ammonia in excess, and allow from 12 to 24 hours of digestion, then filter and wash, dissolve and titrate.

Required of solution of uranium 8.55 cubic centimeters (1 cubic centimeter=5 milligrams P_2O_5).

Correction, 0.20 to be deducted=8.35 cubic centimeters.

$8.35 \times 0.005 = 0.04175$ gram P_2O_5 for 0.25 gram of the sample. Then $0.04175 \div 0.25 = 16.7$ per cent.

From the above data there would be 16.7 per cent. of phosphoric acid soluble in water and in ammonium citrate.

If it be desirable to have separately the phosphoric acid soluble in water, a separate precipitation is made of the aqueous solution alone by means of the magnesium citrate solution. The precipitate washed with ammoniacal water is redissolved and titrated in the manner indicated.

In subtracting from the figures obtained with the two solutions together the number obtained for the phosphoric acid soluble in water, the number representing the phosphoric acid soluble in ammonium citrate alone, is obtained.

It is to be noted that the determinations with uranium require always two successive titrations. It would therefore be an advantage in all operations to precipitate a weight of ammonium magnesium phosphate sufficient for allowing this precipitate to be dissolved and made up to 100 cubic centimeters, on which amount it would be possible to execute two, three or four determinations, and thus to obtain a result of great accuracy.

138. Conclusions.—It has been seen from the above data that the French chemists have worked out the uranium volumetric method with great patience and attention to detail. Where many determinations are to be made it is undoubtedly possible for an analyst to reach a high degree of accuracy as well as to attain a desirable rapidity by using this method. For a few determinations, however, the labor of preparing and setting the standard solutions required would be far greater than the actual determinations either by the molybdate or citrate gravimetric methods. For control work in factories and for routine work connected with fertilizer inspection, the method has sufficient merit to justify a comparison with the processes already in use by the official chemists of this country.

The use of an alkaline ammoniacal citrate solution, however, for the determination of reverted acid renders any comparison of the French method with our own impossible. On the other hand, the French method for water-soluble acid is based on the same principle as our own; viz., washing at first with successive small portions of water, and thus avoiding the decomposition of the soluble phosphates, which is likely to occur when too great a volume of water is added at once.

In the matter of the temperature and time as affecting the solubility of reverted acid, the French method is also distinctly inferior to our own. The digestion is allowed to continue from 12 to 24 hours, at the pleasure of the analyst, and meanwhile it is subjected to room temperature. It is not difficult to see that this treatment in the same sample would easily yield disagreeing results between 12 hours at a winter temperature and 24 hours at summer heat.

139. The Ammonio-Manganous Method.—The principle of this

process is based on the separation of the phosphoric acid as the ammonio-manganous salt and the subsequent oxidation of the manganese to peroxid acid.¹² The quantity of the peroxid is determined by the titration with hyposulfite of soda of the iodine liberated from potassium iodide. After a study of the methods of preparing the ammonio-manganous salt according to the procedures of Otto, Heintz and Gibbs, the following process was adopted as the most suitable: To 50 cubic centimeters of a solution of sodium phosphate, containing about 100 milligrams of phosphoric acid, are added 10 cubic centimeters of a 20 per cent. solution of ammonium chloride, 10 cubic centimeters of ammonia, 25 cubic centimeters of a solution of ammonium citrate (150 grams citric acid, 500 cubic centimeters ammonia and 1000 cubic centimeters water), an excess of a manganous salt, and 25 cubic centimeters of a 2.5 per cent. solution of magnesium sulfate.

This mixture shows an immediate yellow coloration, increasing little by little to a greenish brown, but preserves its complete limpidity. After 24 hours the sides of the vessel are found coated with colorless brilliant crystals of ammonio-manganous phosphate, but even after several days the separation of the phosphoric acid is not complete.

If the reagents employed be hot, a different series of phenomena are presented. The yellowish color at first more pronounced, soon disappears and while the liquid is boiling, if it be stirred without striking the walls of the vessel, there are immediately separated brilliant crystals of the salt of a pale rose color. At the end of a few minutes the total phosphoric acid is precipitated. The analysis is conducted as follows: After covering the liquid, in which the phosphoric acid has been separated as above described, the contents of the vessel are thrown on a filter and the precipitate washed with 100 cubic centimeters of a dilute solution of ammonium chloride (0.5 per cent.). The filtration and washing should be made rapidly to avoid danger of solution of the crystals, and the whole operation should last only a few minutes.

Insoluble phosphates are first dissolved in an acid and the phosphoric acid thrown out by ammonium molybdate, the yellow

¹² Lindeman and Motteu, Bulletin de la Société chimique de Paris, 1895, [3], 13 : 523.

precipitate is dissolved in ammonia, and the solution treated as above.

The crystals of ammonio-manganous phosphate are dissolved in dilute hydrochloric acid, the solution, diluted to 300 cubic centimeters, treated with from one to three cubic centimeters of hydrogen peroxid, 20 cubic centimeters of a 10 per cent. solution of potassium hydroxid added and boiled for some time to expel an excess of the peroxid.

After cooling, 20 cubic centimeters of 20 per cent. hydrochloric acid are added and the solution allowed to stand for some time in order to destroy any traces of an alkaline peroxid. After the addition of 20 cubic centimeters of a 10 per cent. solution of potassium iodid, the liberated iodine is titrated by a set solution of sodium hyposulfite. The reactions which take place in these operations are illustrated by the following equations: The hydrogen peroxid converts the manganous salt into the compound $\text{Mn}_6\text{O}_{11} = 5\text{MnO}_2\text{MnO}$. The ammonio-manganous phosphate has the composition $6\text{NH}_4\text{MnPO}_4$. When oxidized by hydrogen peroxid, it yields three molecules of phosphoric anhydrid, $3\text{P}_2\text{O}_5$, and one molecule of the compound $5\text{MnO}_2\text{MnO}$. When the manganic peroxid is treated with potassium iodid the reaction is: $5\text{MnO}_2 + 2\text{OHCl} + 10\text{KI} = 5\text{MnCl}_2 + 10\text{KCl} + 10\text{I}$, and $10\text{I} + 10\text{Na}_2\text{S}_2\text{O}_3 = 5\text{Na}_2\text{S}_4\text{O}_6 + 10\text{NaI}$. Then $10\text{Na}_2\text{S}_2\text{O}_3 = 10\text{I} = 3\text{P}_2\text{O}_5$. From these data the percentage of P_2O_5 is readily calculated.

The method is of interest from the principle involved, but is of little practical value because of the necessity of separating the phosphoric acid from all insoluble phosphates by the molybdate method. The authors have endeavored to avoid this separation and express the hope that a direct way may be found.

THE DETERMINATION OF PHOSPHORIC ACID BY TITRATION OF THE YELLOW PRECIPITATE

140. Pemberton's Volumetric Method.—In order to shorten the work of determining the phosphoric acid, numerous attempts have been made to execute the final determination directly on the yellow precipitate obtained by treating a solution of a phosphate with ammonium molybdate in nitric acid. The composition of this precipitate appears to be somewhat variable, and this fact

has cast doubt on the methods of determination based on its weight. Its most probable composition is expressed by the following formula, $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12}$. For convenience in writing reactions this formula should usually be doubled. Pemberton has described a volumetric determination of phosphoric acid in the yellow precipitate which is easily conducted and is very rapid.¹³

The method as originally proposed by Pemberton has not always given satisfactory results when compared with the molybdate gravimetric process, but as perfected by experience has constantly grown in favor until now it is regarded as entirely trustworthy on account of its original merit and of the extended use in later forms. It has, however, attracted so much attention from analysts as to the principles of the original process, that they are given in some detail.

141. The Process.—The principle of the process is based on the separation of the phosphoric acid as ammonium-phosphomolybdate, freeing the yellow precipitate from any free nitric acid by washing, dissolving the yellow precipitate in an excess of standard alkali and titrating the residual alkali by a standard acid. The process as originally described by Pemberton is carried out as follows: One gram of phosphate rock, or from two to three grams of phosphatic fertilizer, are dissolved in nitric acid and, without evaporation, diluted to 250 cubic centimeters. Without filtering, 25 cubic centimeters are placed in a four-ounce beaker and ammonia added until a slight precipitate begins to form. Five cubic centimeters of nitric acid of one and four-tenths specific gravity are added, and 10 cubic centimeters of saturated solution of ammonium nitrate and enough water to make the volume about 65 cubic centimeters. The contents of the beaker are boiled, and while still hot five cubic centimeters of the aqueous solution of ammonium molybdate added. Additional quantities of the molybdate are used, if necessary, until the whole of the phosphorus pentoxid is thrown out.

After allowing to settle for a moment the contents of the beaker are poured upon a filter seven centimeters in diameter. The pre-

¹³ Journal of the American Chemical Society, 1893, 15 : 382.

precipitate is thoroughly washed with water, both by decantation and on the filter. The filter with its precipitate is transferred to a beaker and dissolved with an excess of standard alkali in the presence of phenolphthalein. The residual alkali is determined by titration with standard acid. Each cubic centimeter of alkali employed should correspond to one milligram of phosphorus pentoxide (P_2O_5).

The reagents have the composition indicated below:

Ammonium Molybdate.—Ninety grams of the crystals of ammonium molybdate are placed in a large beaker and dissolved in a little less than one liter of water. The beaker is allowed to stand over night and the clear liquor decanted. Any undissolved acid is brought into solution in a little ammonia water and added to the clear liquor. If a trace of phosphoric acid be present a little magnesium sulfate is added and enough ammonia to produce a slight alkaline reaction. The volume of the solution is then made up to one liter. It is to be observed that nitric acid is not used in the preparation of this reagent, which is known as the *aqueous* solution. Each cubic centimeter of this solution is capable of precipitating three milligrams of phosphorus pentoxide.

Standard Potassium Hydroxid.—This solution is made of such strength that one cubic centimeter is equivalent to one milligram of phosphorus pentoxide. Treated with acid of normal strength, 100 cubic centimeters are required to neutralize 32.65 cubic centimeters thereof. The strength of the solution can not be safely assumed from the weight and purity of the material, but is to be ascertained by comparison with a solution of a phosphate of known composition.

Standard Acid.—This should have the same strength, volume for volume, as the standard alkali solution. It is made by diluting 326.5 cubic centimeters of normal nitric acid to one liter.

Ammonium Nitrate.—A saturated aqueous solution of the salt is used.

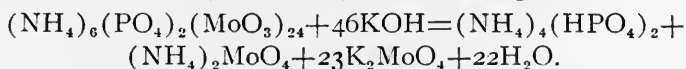
Indicator.—The indicator to be used is an alcoholic solution of phenolphthalein, one gram in 100 cubic centimeters of 60 per cent. alcohol, and half a cubic centimeter of this should be used for each titration.

Thomson has shown that of the three hydrogen atoms in phosphoric acid, two must be saturated with alkali before the reaction with phenolphthalein is neutral.¹⁴ Therefore, when the yellow precipitate is broken up by an alkali, according to the reaction to follow, only four of the six molecules of ammonium are required to form a neutral ammonium phosphate as determined by the indicator employed. The remaining two molecules of ammonium unite with the molybdenum, forming also a salt neutral to the indicator.

Phenolphthalein is preferred because, as has been shown by Long, its results are reliable in the presence of ammonium salts unless they be present in large quantity, and if the solution be cold and the indicator be used in sufficient quantity.¹⁵ To prepare the indicator for this work, one gram of phenolphthalein is dissolved in 100 cubic centimeters of 60 per cent. alcohol. At least one-half of a cubic centimeter of the solution is used for each titration.

The advantages claimed for the method are its speed and accuracy. Much time is saved by avoiding the necessity for the removal of the silica by evaporation. The results of analyses with and without the removal of the silica are practically identical. When the silica is not removed it is noticed that the filtrate from the yellow precipitate has a yellow tint.

The reaction is represented by the following formula:



From this reaction it is seen that the total available acidity of one molecule of the yellow precipitate titrated against phenolphthalein is equivalent to 23 molecules of potassium hydroxid.

Calculation of Results.—The standard alkali is of such strength that one cubic centimeter is equal to one per cent. of phosphoric acid when one gram of material is employed and one-tenth of it taken for each determination. If in a given case one gram of a sample and one-tenth of the solution are used, and 50 cubic centimeters of alkali added to the yellow precipitate, it requires

¹⁴ Chemical News, 1883, 47 : 127, 186.

¹⁵ American Chemical Journal, 1889, 11 : 84.

32 cubic centimeters of standard alkali to neutralize the excess of acid.

The alkali consumed by the yellow precipitate represents 50—32 = 18 cubic centimeters. The sample, therefore, contains 18 per cent. of phosphoric acid.

Comparison with Official Method.—A comparison of the Pemberton volumetric with the official method of the Association of Official Agricultural Chemists has been made by Day and Bryant.¹⁶ The comparisons were made on samples containing from 1.45 to 37.28 per cent. of phosphoric acid and resulted as follows:

Substance.	Per cent. P ₂ O ₅ , Official.	Per cent. P ₂ O ₅ , Pemberton.
No. 1. Florida rock.....	1.45	1.32
" 2. " "	4.40	4.53
" 3. Sodium phosphate.....	19.78	19.99
" 4. " "	19.72	19.73
" 5. Florida rock	37.28	37.22

This near agreement shows the reliability of the method. The comparison of the Pemberton volumetric method with the official gravimetric method was investigated by Kilgore, reporter of the Association of Official Agricultural Chemists, in 1894.¹⁷ The individual variations were found to be greater than in the regular method, but the average results were nearly identical therewith. The method works far better with small percentages of phosphoric acid than with large. Where the average of the results by the official methods gave 12.25 per cent., the volumetric process gave 11.90 per cent., whereas in the determination of a smaller percentage the results were 2.72 and 2.73 per cent., respectively. Kilgore proposes a variation of the method which differs from the original in two principal points.¹⁸ First, the temperature of precipitation in the Pemberton process is 100°; but in the modified form from 55° to 60°. At the higher temperature there is danger of depositing molybdic acid.

The second difference is in the composition of the molybdate solution employed. The official molybdate solution contains about

¹⁶ Journal of the American Chemical Society, 1894, 16 : 282.

¹⁷ Division of Chemistry, Bulletin 43, 1894 : 68.

¹⁸ Division of Chemistry, Bulletin 43, 1894 : 91.

60 grams of molybdenum trioxid in a liter, while the Pemberton solution contains 66 grams. There is, therefore, not much difference in strength. The absence of nitric acid, however, from the Pemberton solution favors the deposition of the molybdic acid when heat is applied.

Kilgore, therefore, conducts the analysis as follows: The solution of the sample is made according to the official nitric and hydrochloric acid method for total phosphoric acid. For the determination, 20 to 40 cubic centimeters are used corresponding to two-tenths or four-tenths gram of the sample. Ammonia is added until a slight precipitate is produced and the volume is then made up, with water, to 75 cubic centimeters. Add some ammonium nitrate solution, from 10 to 15 cubic centimeters, but this addition is not necessary unless much of the nitric acid has been driven off during solution. Heat in the water bath to 60° and precipitate with some freshly filtered official molybdate solution. Allow to stand for five minutes, filter as quickly as possible, wash four times by decantation, using from 50 to 75 cubic centimeters of water each time, and then wash on a filter until all acid is removed. The solution and titration of the yellow precipitate are accomplished as in the Pemberton method. The agreement of the results obtained by this modified method was much closer with the official gravimetric method than those obtained by the Pemberton process.

142. Investigations of the Volumetric Method by the Association of Official Agricultural Chemists.—The great value of the volumetric method by reason of the saving of time in analytical work, especially where great numbers of analyses are to be made, led to a painstaking investigation of its reliability and agreement with the gravimetric process on the part of the official chemists. The results of these investigations are published in detail in the proceedings of the association.¹⁹

¹⁹ Division of Chemistry, Bulletin 47, 1896 : 70.
Division of Chemistry, Bulletin 49, 1897 : 60.
Division of Chemistry, Bulletin 51, 1898 : 47.
Division of Chemistry, Bulletin 56, 1899 : 36.
Division of Chemistry, Bulletin 57, 1899 : 69.
Division of Chemistry, Bulletin 62, 1901 : 35.
Bureau of Chemistry, Bulletin 67, 1902 : 22.
Bureau of Chemistry, Bulletin 81, 1904 : 164.

These investigations have led to the adoption of the volumetric method in the present form, and established its position as a process which can be relied upon to give concordant and reliable results. For all ordinary analytical, routine and control work it may be confidently used. In cases of controversy, and especially before the courts, it is advisable to check the data obtained by the volumetric method against the results of the official gravimetric determination. The principal credit for perfecting this method is due to Kilgore, as is clearly shown by a study of the references given.

143. Optional Volumetric Method.—The principles on which this rapid and accurate process is based have been described in detail in the discussion of the Pemberton process. The method of conducting the determination and the reagents employed as prescribed by the official chemists are as follows:

Reagents Used: Molybdic Acid.—To 100 cubic centimeters of the molybdic acid solution used in the official gravimetric method already described, add five cubic centimeters of nitric acid of 1.42 specific gravity. If cloudy this solution should be filtered before using.

Potassium or Ammonium Nitrate Solution.—Dissolve three grams of the salt in 100 cubic centimeters of water.

Nitric Acid.—Dilute 100 cubic centimeters of nitric acid of 1.42 specific gravity to 1000 cubic centimeters with water.

Potassium Hydroxid.—This solution contains 18.171 grams of KOH in one liter. It is prepared by diluting 323.81 cubic centimeters of a normal solution of pure potassium hydroxid, free of carbonates, to one liter. One milligram of the solution is equivalent to one milligram of phosphorus pentoxid.

Standard Nitric Acid Solution.—The strength of this solution is the same as, or one-half that of, the standard alkali solution, and is determined by titrating against that solution, using phenolphthalein as indicator.

Phenolphthalein Solution.—One gram of phenolphthalein is dissolved in 100 cubic centimeters of alcohol.

Total Phosphoric Acid. Methods of Making Solution.—Dissolve according to the official methods described in paragraph 61,

preferably method 5, when these acids are a suitable solvent, and dilute to 200 cubic centimeters with water.

Determination.—For percentages of phosphoric acid of five or below use an aliquot corresponding to 0.4 gram substance; for percentages between five and 20 use an aliquot corresponding to 0.2 gram substance; and for percentages above 20 use an aliquot corresponding to 0.1 gram substance. Add from five to 10 cubic centimeters of nitric acid, depending on the method of solution (or the equivalent in ammonium nitrate), nearly neutralize with ammonia, dilute to from 75 to 100 cubic centimeters, heat in a water bath to from 60° to 65°, and for percentages below five add from 20 to 25 cubic centimeters of freshly filtered molybdc solution. For percentages between five and 20 add from 30 to 35 cubic centimeters molybdc solution; stir, let stand about 15 minutes, filter *at once*; wash once or twice with water by decantation, using from 25 to 30 cubic centimeters each time, agitating the precipitate thoroughly and allowing it to settle; transfer to filter and wash five or six times, using enough water to make with the decantation washings about 200 cubic centimeters. Transfer precipitate and filter to beaker or precipitating vessel, dissolve in small excess of standard alkali, add a few drops of phenolphthalein solution and titrate excess of alkali with standard acid (nitric).

Water-Soluble Phosphoric Acid.—Dissolve the soluble acid according to directions given under the official method for the gravimetric determination of water-soluble acid, paragraph 67. To an aliquot portion of the solution corresponding to 0.2 or 0.4 gram, add 10 cubic centimeters of concentrated nitric acid and then ammonia until a slight precipitate is formed, dilute to 60 cubic centimeters, and proceed as above described.

Citrate-Insoluble Phosphoric Acid.—(a) *In Acidulated Samples.*—Heat 100 cubic centimeters of strictly neutral ammonium citrate solution of 1.09 specific gravity to 65° in a flask placed in a bath of warm water, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65°, drop into it the filter containing the washed residue from the water-soluble phosphoric acid determination, stopper

tightly with a smooth rubber, and shake violently until the filter paper is reduced to a pulp. Place the flask in the bath and maintain it at such a temperature that the contents of the flask will stand at exactly 65° . Shake the flask every five minutes. At the expiration of exactly 30 minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter the contents as rapidly as possible. Wash thoroughly with water at 65° . Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 cubic centimeters of strong hydrochloric acid, and digest until all phosphate is dissolved; or return the filter with contents to the digestion flask, add from 30 to 35 cubic centimeters strong nitric acid, from five to 10 cubic centimeters strong hydrochloric acid, and boil until all phosphate is dissolved. Dilute the solution to 200 cubic centimeters. If desired, the filter and its contents may be treated according to the methods in paragraph 61 under methods of solution. Mix well; filter through a dry filter; take a definite portion of the filtrate and proceed as under total phosphoric acid.

(b) *In Non-Acidulated Samples.*—In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated samples it is to be made by treating two grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.) the residue insoluble in ammonium citrate is to be treated by one of the processes described under methods of solution, paragraph 61.

Citrate-Soluble Phosphoric Acid.—The sum of the water-soluble and citrate-insoluble subtracted from the total gives the citrate-soluble phosphoric acid.

144. Alkalimetric Estimation of Phosphoric Acid in Connection with the Incineration by Acid Mixture.—Neumann recommends the following process, which is a variation of the ordinary volumetric method in common use in this country for the estimation of phosphoric acid in organic matters which have been incinerated by the wet acid method described by him.²⁰ For carrying

²⁰ Zeitschrift für physiologische Chemie, 1902-3, 37 : 115.

out this method the substance is incinerated by a mixture of sulfuric and nitric acids. From the ash solution obtained by the method described the phosphoric acid is precipitated in the usual manner as phosphomolybdate. The washed precipitate is immediately dissolved in an excess of one-half normal soda-lye and the excess of alkali titrated with one-half normal sulfuric acid, after driving off the ammonia by boiling and allowing the solution to become completely cool.

Since each molecule of the phosphoric pentoxid (P_2O_5) of the yellow precipitate obtained by this method of treatment requires for its complete neutralization, with the use of phenolphthalein as an indicator, 56 molecules of NaOH, so each cubic centimeter of one-half normal soda-lye used corresponds to 1.268 milligrams of P_2O_5 .

The solutions used by Neumann are as follows:

- (1) 50 per cent. ammonium nitrate solution.
- (2) 10 per cent. of ammonium molybdate solution (dissolved, cooled, and filtered).
- (3) One-half normal potash lye and one-half normal sulfuric acid.
- (4) One per cent. alcoholic phenolphthalein solution.

The substance is incinerated according to the method described and the dilution with water, which is recommended at the close of the method, as well as the boiling of the ash solution, are properly modified for the special estimation of the phosphoric acid.

Under the assumption that for the incineration not more than 40 cubic centimeters of the acid mixture have been used, about 140 cubic centimeters of water are added to the ash solution, so that in all the analyst has in amount from 150 to 160 cubic centimeters. It should be remembered in this case that about one-half of the acid mixture has been volatilized during the incineration. After the addition of 50 cubic centimeters of ammonium nitrate, the mixture is heated to from 70° to 80° until bubbles begin to ascend through the liquid. Thereupon, 40 cubic centimeters of ammonium molybdate are added. This quantity is sufficient for at least 60 milligrams of P_2O_5 . It is recommended that the quan-

tity of substance used be so chosen that it contains not more than 50 milligrams of phosphoric acid. If more than 40 cubic centimeters of the acid mixture have been used in the incineration, then the quantity of water added in the dilution and the quantity of ammonium nitrate therein should be proportionately increased.

The flask containing the precipitate is vigorously shaken for a half minute, by which process the precipitate becomes more granular, and it is then allowed to stand at rest for 15 minutes. The filtering and washing are carried on by decantation. Thin, ash-free filter paper is used, which on the subsequent solution of the precipitate in dilute soda-lye is easily torn and the particles of which are evenly divided throughout the liquid. The filter paper, which has a diameter of from five to six centimeters, may be used either as a folded filter or as a smooth filter in a fluted funnel. Before filtration the filter is filled with ice-cold water, in order to draw the filter pores together and to prevent the first portions of the solution, which is still warm, from running through cloudy. In order to conveniently decant the supernatant liquid, the flask is laid upon the ring of the stand somewhat higher than the filter and the neck is drawn down in such a way that the clear liquid runs without intermission upon the filter. In this way only a very small quantity of the precipitate is collected upon the filter, which is always kept about two-thirds full. The washing of the precipitate is conducted with about 150 cubic centimeters of ice-cold water, which is thoroughly incorporated with the precipitate, and after standing is poured through the filter in the way described. The decantation is continued with repeated washing with water until the wash-water no longer gives an acid reaction with litmus paper. The washed filter and its contents are then put back in the flask containing the principal part of the precipitate, 150 cubic centimeters of water added, the filter broken up by vigorous shaking, and the precipitate dissolved by adding a measured portion of one-half normal potash lye with constant shaking and without warming. It is then advisable to add an excess of from five to six cubic centimeters of one-half normal soda-lye and to boil the solution until no longer any ammonia is evolved, which usually requires about

15 minutes and which should be determined by testing with moist litmus paper. After complete cooling, from six to eight drops of the phenolphthalein solution are added and the excess of alkali titrated with one-half normal sulfuric acid.

Calculation.—The number of added cubic centimeters of one-half normal soda-lye, after the subtraction of the number of cubic centimeters of one-half normal acid used, multiplied by 1.268, gives the quantity of P_2O_5 in milligrams.

145. Comparison of the Methods of Weighing and Titrating the Yellow Precipitate.—Baxter gives the result of his experiments upon the estimation of phosphoric acid by weighing the yellow precipitate after heating to 300° and also by titration with standard alkali.²¹

In securing the yellow precipitate in a form sufficiently pure for analytical purposes he states that it can not be washed with water owing to decomposition. Ten per cent. ammonium nitrate solution is therefore used as a wash, but no data are given to prove that washing was carried to the complete removal of the molybdate. Indeed, all the results show that the precipitate still contains considerable quantities of ammonium molybdate or molybdenum oxid. It is stated that the formula of the precipitate washed with the ammonium nitrate solution and dried at 300° is $(NH_4)_3PO_4 \cdot 12MoO_3$, but owing to the occlusion of molybdic acid the theoretical percentage of P_2O_5 (3.783) is never obtained. The precipitate only contains 3.742 per cent. of phosphoric acid.

In the second article evidence is given to show that the washed unheated yellow precipitate has the formula $(NH_4)_2HPO_4 \cdot 12MoO_3$, and that the quantity of hydroxid required in titration corresponds much more nearly to 48 molecules than to 46 molecules for each molecule of phosphorus pentoxid. Owing to the occlusion of some molybdic acid the author gives the following exact formula as that of the unheated washed yellow precipitate actually obtained in analytical work— $(NH_4)_2HPO_4 \cdot 12.143MoO_3$.

Attention is also called to the fact that the composition of the precipitate is more constant and the results more reliable when

²¹ American Chemical Journal, 1902, 28 : 298; 1905, 34 : 204.

the phosphate solution is added to the molybdic solution than the reverse.

There is a number of other minor well known discoveries in this article which need not be mentioned here. The author seems to be entirely unaware of the work of the Association of Official Agricultural Chemists on this subject.

The conclusions seem to be applicable to the conditions under which the author worked, but criticism might be made that the precipitate was not sufficiently washed in any of the experiments, and further, that the quantity of precipitate is very much larger than it is customary to use when working this method, weighing as it does almost three grams. The value of all the work depends on the washing of the yellow precipitate, which, as has been said, was incomplete, and no evidence is given to show that impurities could not have been entirely removed.

146. Estimation of Phosphoric Acid as a Lead Compound.

—In the volumetric lead method, as described by Wavelet, the phosphoric acid is precipitated by the magnesium citrate solution as in the uranium method of Joulie, as practiced by the French chemists, and the washing of the precipitate and its solution of nitric acid are also conducted as in that method.²² After solution in nitric acid, ammonia is added to neutrality and the solution is then made acid with acetic. The phosphoric acid is precipitated in the acid solution by a standard solution of lead nitrate, the precipitate having the formula $P_2O_5 \cdot 3PbO$.

The end reaction is determined by placing a drop of the titrated mixture on a white greased dish in contact with a drop of a five per cent. solution of potassium iodid. When all the phosphoric acid is precipitated, the least excess of the lead salt is revealed by the characteristic yellow precipitate of lead iodid.

The author of the process claims that the lead phosphate is insoluble in the excess of acetic acid, and that the phosphate itself does not give any yellow coloration with potassium iodid. The process is quite as exact as the uranium method and the end reaction is far sharper; the standard reagents are easily made and preserved.²³ The method described merits, at least, a com-

²² *Répertoire de Pharmacie*, 1893 [3], 5 : 153.

²³ *Revue de Chimie analytique appliquée*, 1893, 1 : 113.

parative trial with the uranium process, but can not be recommended as exact until further approved by experience.

The reagents employed have the following composition:

- | | | | | |
|--|--------|-------|-----|-------|
| (1) Disodium phosphate solution containing | 10.085 | grams | per | liter |
| (2) Sodium acetate | 50.000 | " | " | " |
| (3) Lead nitrate | 40.000 | " | " | " |
| (4) Potassium iodid | 50.000 | " | " | " |

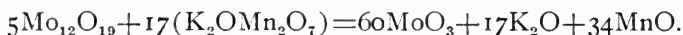
The titrations should be conducted in the cold.

147. Water-Soluble Phosphoric Acid.—Glaser has modified the volumetric method of Kalmann and Meissels for the volumetric estimation of water-soluble phosphoric acid in superphosphates so as to avoid the double titration required by the original method.²⁴ If methyl orange be used as an indicator in the original method, the determination does not at once lead to the tricalcium salt, but the liquid still contains, after neutralization, some monocalcium phosphate, which is determined by a further titration with phenolphthalein as indicator. In the modified method the total phosphoric acid is estimated in one operation as a tricalcium salt. This is secured by adding, at the proper time, an excess of calcium chlorid. Two grams of the superphosphate are shaken with water several times according to the American official method, and finally, after settling, filtered, and the insoluble residue washed on the filter until the total volume of the filtrate is a quarter of a liter. Of this, 50 cubic centimeters are titrated with tenth-normal soda-lye, with addition of two drops of methyl orange, until the acid reaction has entirely disappeared. There is then added neutral calcium chlorid solution in excess. If iron and alumina be present, a slight development of an acid reaction is produced of which no account need be made. Five drops of the phenolphthalein solution are added and the titration continued until the alkaline reaction is noted throughout the whole mass. The alkaline reaction soon disappears and to retain it several tenths cubic centimeters of alkali are necessary, and thus an excess is easily used. To get very sharp results it is advisable to place the solutions in a high beaker, which is kept in vigorous rotation until the alkaline reac-

²⁴ Chemiker-Zeitung, 1894, 18 : 1533.

tion is first established. The burette is quickly read and a few tenths more alkali added to be certain that the unit point has not been missed. On cloudy days the light may be concentrated by a lens, for which a flask filled with clear water conveniently serves. Each cubic centimeter of the soda-lye corresponds, in the first titration, to 7.1 and in the second to 3.55 milligrams of phosphoric acid.

148. Estimation of Phosphoric Acid in the Presence of a Large Excess of Iron.—The volumetric method given below, due to Emmerton, depends upon the precipitation of a phosphomolybdate, of constant composition, in the presence of a large excess of iron, as in the analysis of iron and steel and iron ores.²⁵ The molybdenum trioxid obtained is reduced by zinc to $\text{Mo}_{12}\text{O}_{19}$. The action of permanganate on this compound is shown in the following equation:



Seventeen molecules of permanganate are equal to 60 molecules of molybdenum trioxid. The iron or steel is dissolved in nitric acid, evaporated to dryness, heated, and redissolved in hydrochloric acid, then treated again with nitric acid and evaporated until a clear and concentrated solution is obtained free from hydrochloric acid.

The solution obtained is diluted to 40 cubic centimeters with water and washed into a 400 cubic centimeter flask, making the total volume about 75 cubic centimeters. Add strong ammonia, shaking after each addition, until the mass sets to a thick jelly from the ferric hydroxid. Add a few more cubic centimeters of ammonia and shake thoroughly, being sure the ammonia is present in excess. Add next nitric acid gradually, with shaking, until the precipitate has all dissolved; add enough more nitric acid to make the solution a clear amber color. The volume should now be about 250 cubic centimeters. Bring the solution to 85° and add at once 40 cubic centimeters of molybdate solution of the following strength: Dissolve 100 grams of molybdic acid in 300 cubic centimeters of strong ammonia and 100 cubic centimeters of water, and pour the solution into 1250

²⁵ Blair, *Chemical Analysis of Iron*, Second Edition, 1891 : 95.

cubic centimeters of nitric acid (of 1.20 specific gravity); close the flask with a rubber stopper, wrap it in a thick cloth, and shake violently for five minutes. Collect the precipitate on a filter, using a pump, and wash with dilute nitric acid ($1\text{HNO}_3:50\text{H}_2\text{O}$). If a thin film of the precipitate should adhere to the flask it can be removed by the ammonia in the next operation. Wash the molybdate precipitate into a 500 cubic centimeter flask with dilute ammonia ($1\text{H}_3\text{N}:4\text{H}_2\text{O}$), using about 30 cubic centimeters. Add 80 cubic centimeters of hot dilute sulfuric acid ($1\text{H}_2\text{SO}_4:4\text{H}_2\text{O}$) and cover the flask with a small funnel. Add 10 grams of granulated zinc and heat until rapid action begins, and then heat gently for five minutes. The reduction is then complete. During the reduction the colors, pink, plum, pale green and dark green, are seen in the molybdate solution, the latter color marking the end of the reaction.

To remove the zinc, pour through a large folded filter, wash with cold water, and fill up the filter once with cold water. But little oxidation takes place in this way. A port wine color is seen on the filter, but this does not indicate a sufficient oxidation to make an error.

In titrating, the color becomes fainter and finally the solution is perfectly colorless and shows a single drop in excess of the permanganate. The permanganate solution, for convenience, is made so that one cubic centimeter is equal to 0.0001 gram of phosphorus. With iron its value is one cubic centimeter equals 0.006141 gram of iron; and one cubic centimeter equals 0.005574 gram of molybdenum trioxid.

In the case of iron ores 10 grams are dissolved in hydrochloric acid, evaporated to dryness, taken up with hydrochloric acid, evaporated to a small bulk and the residual hydrochloric acid expelled by heating with nitric acid. The insoluble residue is removed by filtration and the rest of the process conducted as above described. This method of determination is advisable in the solution of ores rich in phosphorus, intended for the manufacture of iron or steel where basic phosphoric slag is to be utilized as a by-product.

149. Variation of Dudley and Noyes.—The method of Em-

merton for the determination of small quantities of phosphoric acid or of phosphorus in the presence of a large excess of iron, has been modified by Dudley and Pease,²⁶ and by Noyes and Royse.²⁷ As modified, the method is not intended for fertilizer analysis, but the principle on which it rests may some time, with proper modifications, find application in fertilizer work. The reduction is accomplished in a Jones tube, much simplified, so as to render it suitable for common use.²⁸ The molybdic acid is reduced to a form, or series of forms, corresponding to molybdenum sesquioxide, as in the Emmerton method, and subsequently, as in that method, titrated by a set solution of potassium permanganate.

The iron or steel filings, containing phosphorus, are brought into solution by means of nitric acid. For this purpose two grams of them are placed in a half liter flask together with 50 cubic centimeters of nitric acid of 1.18 specific gravity. The mixture is boiled for one minute, and 10 cubic centimeters of permanganate solution of one and a quarter per cent. added. Boil again until the pink color disappears. Ferrous sulfate solution is next to be carefully added, shaking meanwhile, until the solution clears. Cool to 50° and add eight cubic centimeters of ammonia of 0.90 specific gravity, stopper the flask, and shake until any precipitate which may form is redissolved. Cool or warm, as the case may be, until the solution is as many degrees above or below 60° as the molybdic solution is above or below 27°. Add 60 cubic centimeters of molybdic solution, stopper, and shake on a machine or by hand for five minutes. After remaining at rest for five minutes pour into a nine centimeter filter of fine texture, and wash with the acid ammonium sulfate solution in quantities of from five to 10 cubic centimeters each time. The filtrate and washings must be perfectly bright. Continue the washings until the filtrate gives no color with hydrogen sulfid.

Dissolve the yellow precipitate with 12 cubic centimeters of 0.96 ammonia diluted with an equal volume of water, and

²⁶ *Journal of Analytical and Applied Chemistry*, 1893, **7** : 108.

Journal of the American Chemical Society, 1894, **16** : 224.

²⁷ *Journal of the American Chemical Society*, 1895, **17** : 129.

²⁸ Blair, *Analysis of Iron*, Second Edition, 1891 : 99.

wash the filter with 100 cubic centimeters of water. Finally add to the filtrate and wash-water 80 cubic centimeters of water and 10 of strong sulfuric acid. Pass the mixture through the jones reducing tube and follow it with 200 cubic centimeters of water, taking care that no air enter the tube during the operations. The solution collected in the flask should be at once titrated with potassium permanganate.

In cases where the content of phosphorus is very high the solution of the yellow precipitate is made to a definite volume and the reduction and titration performed on an aliquot thereof.

Solutions Used: (1) *Nitric Acid*.—One part of nitric acid of 1.42 specific gravity and two parts of water by volume. The specific gravity of the mixture is about 1.18.

(2) *Permanganate Solution for Oxidizing*.—Dissolve 12.5 grams of potassium permanganate in one liter of water.

(3) *Ferrous Sulfate*.—Fresh crystals not effervesced and free from phosphorus.

(4) *Ammonia*.—The strong ammonia used should have a specific gravity of about 0.90 and the dilute of 0.96 at 15.5°.

(5) *Molybdic Solution*.—Dissolve 100 grams of molybdic anhydrid in 400 cubic centimeters of ammonia of 0.96 specific gravity and pour the solution slowly, with constant stirring, into one liter of nitric acid of about 1.20 specific gravity. Heat the mixture to 45° and add one cubic centimeter of a 10 per cent. solution of sodium phosphate, stir vigorously, and allow to stand in a warm place for 18 hours. The object of adding the sodium phosphate is to remove any substance which may contaminate the yellow precipitate. Filter before using.

(6) *Acid Ammonium Sulfate*.—To half a liter of water add 27.5 cubic centimeters of 0.96 ammonia and 24 cubic centimeters of strong sulfuric acid, and make the volume one liter with water.

(7) *Potassium Permanganate for Titration*.—Dissolve four grams of potassium permanganate in two liters of water, heat nearly to boiling for an hour, allow to stand for 18 hours, and filter on asbestos felt. The solution must not come in contact with rubber or other organic matter. The solution may be standardized with pure iron (piano wire), with thoroughly air-

dried ammonium oxalate in solution, with a little dilute sulfuric acid and with ammonium ferrous sulfate partly crystallized in small crystals from a slightly acid solution. The crystals should be well washed and quickly air-dried in a thin layer. The factors $\frac{112}{142}$ and $\frac{1}{7}$ should be used, respectively, to calculate the iron equivalent. The phosphorus equivalent is obtained by multiplying the iron equivalent by $\frac{31}{36 \times 56} = 0.01538$.

Reduction Apparatus.—The reduction of the molybdic acid to molybdenum trioxid is accomplished in a tube first proposed by Jones. The apparatus is shown in Figure 8. A piece of moder-

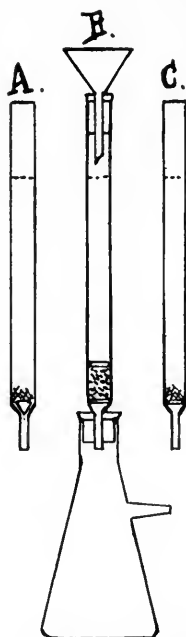


Fig. 8. Jones' Reduction Tube.

ately heavy glass tubing 35 centimeters long, with an internal diameter of two centimeters, is drawn out at the lower end so as to pass into the stopper of a flask. A circular piece of perforated platinum or porcelain rests on the constricted portion of the tube and this is covered with an asbestos felt. The tube is then nearly filled with powdered zinc, which is washed, before using, with

dilute sulfuric acid (1 : 20). A, B, and C represent different methods of filtering the molybdic solution. In A a platinum cone is placed in the constricted portion of the tube and the asbestos felt placed thereon and the tube then filled with the granulated zinc. In B there is first inserted a perforated disk, then some very fine sand, and this is covered with another disk. In C there is a perforated disk which is covered with asbestos felt. The filtering arrangement should be such as to prevent any zinc particles from reaching the flask and yet permitting the filtration to go on without much difficulty. A blank determination is first made by adding to 180 cubic centimeters of water 12 of 0.96 ammonia and 10 of strong sulfuric acid. This is poured through the reducing tube and followed with 200 cubic centimeters of water, taking care that no air enter the apparatus. Hydrogen peroxid is formed if air enters. Even after standing for a few moments the tube should be washed with dilute sulfuric acid before again using it. The filtrate should be titrated with the permanganate solution and the amount required deducted from the following amounts obtained with the molybdic salt.

Calculations.—The calculations of the amount of phosphorus in a given sample of iron or steel are made according to the following data:²⁹ In a given case let it be supposed that the permanganate solution is set with a solution of piano wire containing 99.27 per cent. of pure iron, and it is found that one cubic centimeter of permanganate liquor is equal to 0.003466 gram of metallic iron. It is found that 90.76 parts of molybdic acid will produce the same effect on permanganate as 100 parts of iron. Hence one cubic centimeter of permanganate solution is equivalent to $0.003466 \times 0.9076 = 0.003145$ gram of molybdic acid. In the yellow precipitate formed, in the conditions named for the analysis it is found that the phosphorus is one and nine-tenths per cent. of the molybdic acid present. Therefore, one cubic centimeter of permanganate liquor is equal to $0.003145 \times 0.019 = 0.0000597$ gram of phosphorus. If then, for example, in a sample of iron or steel eight and six-tenths cubic centimeters of permanganate

²⁹ Dudley and Pease, *Journal of Analytical and Applied Chemistry*, 1893, 7 : 112.

solution, after correction, be found necessary to oxidize the molybdic solution after passing through the jones reducing tube, the amount of phosphorus found is $0.0000597 \times 8.6 = 0.051$ per cent.

150. Methods of the International Steel Standards Committee.³⁰

—This method was adopted by the committee appointed to consider all the rapid methods for the determination of phosphorus in iron and steel, and was recorded as giving the best methods of procedure which are known at present and securing data which are of great accuracy if the details of the process are carefully observed. The process is conducted as follows:

From one to two grams of the drillings of iron or steel, according to the phosphorus which they contain, are placed in a 250 cubic centimeter erlenmeyer flask and covered with 100 cubic centimeters of nitric acid of 1.135 specific gravity. The flask is covered with a watch-glass and the mixture is heated until the solution is complete and the nitric acid is boiled off. Ten cubic centimeters of strong potassium permanganate solution are added and boiling continued until the pink color has disappeared and the manganese dioxid has separated. Afterwards a few drops of the solution of sulfurous acid are added and a small crystal of ferrous sulfate, or a solution of 0.5 gram of sodium hyposulfite in 10 cubic centimeters of water. The addition of these reagents is continued at short intervals until the precipitated manganese dioxid is dissolved. After boiling for two minutes the flask is placed in cool water or allowed to stand until it is cool, and then 40 cubic centimeters of dilute ammonia of 0.96 specific gravity are added. The precipitated ferric hydrate will redissolve when the liquid is thoroughly mixed. After cooling to about room temperature the flask is stoppered and shaken for five minutes, either by hand or in a shaking machine. After standing for a few minutes, the contents of the flask are poured on a filter and washed with acid ammonium sulfate, prepared by adding 15 cubic centimeters of strong ammonia to one liter of water and 25 cubic centimeters of strong sulfuric acid, until two or three cubic centimeters of the wash-water give no reaction for molybdenum with a drop of ammonium sulfid. Any

³⁰ Blair, *The Chemical Analysis of Iron*, 6th Edition, 1906 : 92.

adhering ammonium phosphomolybdate is dissolved with ammonia and added to the precipitate in the filter, and the filtrate is collected in a 250 cubic centimeter griffin beaker. The flask is washed with water which is poured upon the filter and the filter is thoroughly washed until the solution measures about 60 cubic centimeters. To this are added 10 cubic centimeters of strong sulfuric acid and the solution is passed through the reductor, similar in construction to the jones reductor already described. Care should be exercised to keep the end of the small tube of the reductor just below the surface of the liquid in the flask. The heat which is caused by mixing the strong sulfuric acid with the ammoniacal solution immediately before passing it through the reductor is sufficient to insure a complete reduction. The other precautions which have already been described to prevent the access of air should be observed, and the operations should be so continued that the whole reduction occupies about three or four minutes. The liquid as it passes through the reductor should be bright green in color. Permanganate solution is added and the green color disappears. The solution becomes first, brown, then pinkish yellow, and ultimately colorless. The addition of permanganate is continued drop by drop until the solution assumes a faint pink coloration, which remains at least one minute. From the reading of the burette the amount of permanganate consumed in the blank determination, obtained as described under the method for standardizing permanganate solution, is subtracted and the number of cubic centimeters thus obtained is multiplied by the value of one cubic centimeter in terms of phosphorus. This product is multiplied by 100 and divided by the weight of the sample used and the resulting quotient is the percentage of phosphorus in the steel.

151. Standardization of the Solution of Potassium Permanganate.—This solution is prepared by dissolving two grams of crystallized potassium permanganate in one liter of distilled water and filtering through asbestos. For determining its value from 0.15 to 0.25 gram of clean soft steel wire, in which the content of iron has been carefully determined, is put in an erlenmeyer flask of 125 cubic centimeters capacity and covered with 30 cubic

centimeters of distilled water and 10 of strong sulfuric acid. The flask is covered with a watch-glass and heated until the solution of the wire is complete. A sufficient amount of the strong solution of potassium permanganate is added to oxidize the iron and destroy the carbonaceous matter, avoiding however any ex-

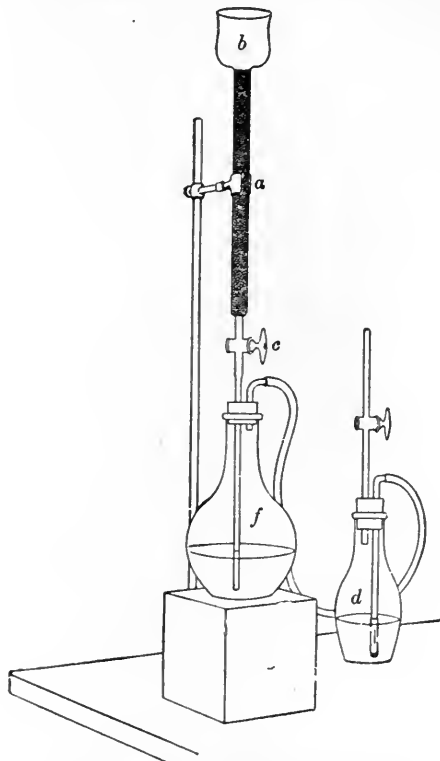


Fig. 9. Reductor and Filter Attachment.

(Courtesy of A. H. Blair and J. B. Lippincott Co.)

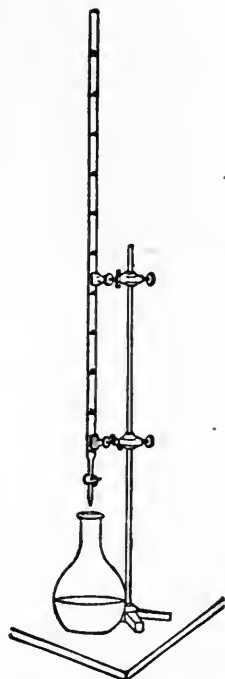


Fig. 10. Permanganate Burette.

cess which would cause a precipitate of manganese dioxide. If any precipitate is formed it is redissolved by adding a very few drops of sulfurous acid and boiling until every trace is removed. After cooling 10 cubic centimeters of dilute ammonia are added and the solution passed through a Jones reductor.

152. Operation of the Reductor.—Everything in connection with the reductor should be clean and proved to be in good order by previous treatment with dilute sulfuric acid and washing with

distilled water. To this end the flask should be attached to the filter pump as shown in the figure. One hundred cubic centimeters of warm dilute sulfuric acid are placed in the funnel *b*, and the stop-cock *c* opened. When the funnel is almost empty, the solution which is to be reduced is transferred thereto. The solution should be hot, but not boiling. The vessel which held the solution should be washed with dilute sulfuric acid, and this added to the funnel again when it is nearly empty in such a way as to wash it thoroughly and this should be followed with about 200 cubic centimeters more of warm dilute sulfuric acid, and 50 cubic centimeters of hot distilled water. In no case is the funnel allowed to become empty, and the stop-cock *c* is closed when there is still a little of the wash-water left in the funnel above the surface of the zinc. In this way air is prevented from passing into the reductor tube. Blank determination is made by passing through the reductor a mixture containing 10 cubic centimeters of strong phosphoric acid, 10 cubic centimeters of dilute ammonia, and 50 cubic centimeters of water. This is preceded and followed by the dilute acid as described above. The amount of potassium permanganate required to give this blank a distinct color is subtracted from the amount required to give the same color to each reduced solution. To estimate the value of the solution the weight of the iron wire used is multiplied by the percentage of the iron in the wire and divided by the number of cubic centimeters of potassium permanganate in terms of metallic iron. The result is multiplied by the factor 0.88163 which is the ratio of molybdic acid to iron, and this product by 0.01794 which is the ratio of phosphorus to molybdic acid, and the result is the value of one cubic centimeter of the permanganate solution in terms of phosphorus. The formula of the reduced molybdic acid is given as $\text{Mo}_{24}\text{O}_{37}$.

153. Calculating Results.—To illustrate the method of calculating results Blair gives the following example: The weight of the wire represented by 0.1745 gram requires 50 cubic centimeters of permanganate to give the required color. A blank determination carried on as described above shows 0.1 cubic centimeter of permanganate, so the quantity required by the

wire is 49.9 cubic centimeters permanganate. The wire contains 99.87 per cent. of iron. We have then the following equation; namely, $0.1745 \times 0.9987 \div 49.9 = 0.0034923$. This shows that one cubic centimeter of permanganate is equivalent to that quantity expressed as 0.0034923 gram metallic iron. Multiplying the value in iron by the ratio of molybdic acid to iron, namely, 0.88163, and the product by the ratio of phosphorus to molybdic acid, namely, 0.01794, the product is found to be 0.000055238. This indicates that one cubic centimeter of permanganate is equivalent to 0.000055238 gram of phosphorus. If the precipitated ammonium phosphomolybdate from two grams of steel require 35.5 corrected cubic centimeters, then the percentage of phosphorus in steel is obtained by the following formula: $35.5 \times 0.000055238 \times 100 \div 2 = 0.098$, which is equivalent to the percentage of the phosphorus of the steel. For further details of the process the work of Blair, already cited, should be consulted.

154. The Silver Method.—The separation of the phosphoric acid by silver according to the method of Perrot has been investigated by Spencer, who found the process unreliable.³¹ By a modification of the process, however, Spencer obtained fairly satisfactory results. The principle of this method depends on the separation of the phosphoric acid by silver carbonate and the subsequent titration thereof with standard uranium solution after the removal of the excess of silver. The operation is conducted as follows: The fertilizer is first ignited until all organic matter and residual carbon are destroyed. Solution is then accomplished by means of nitric acid and the volume completed to a definite quantity. To an aliquot part of the slightly acid (nitric) solution, after filtration, varying with the supposed strength of the solution so as to contain about 100 milligrams of phosphorus pentoxid, freshly prepared silver carbonate is added in excess, that is, sufficient to saturate any free acid present and also to combine with all the phosphoric acid. Wash thoroughly with hot water and then dissolve the mixed phosphate and silver carbonate in nitric acid, and remove the silver from the solution with

³¹ Eighth Annual Report of Purdue University, 1882 : 240.

sodium chlorid. The phosphoric acid is determined in the filtrate by means of a standard solution of uranium nitrate in the manner already described. Spencer found that the separation of the phosphoric acid by the silver method was more exact than by the Joulie magnesium citrate process. With practice on the part of the analyst in determining the end reaction, the process is both rapid and accurate. The method is also inexpensive, as both the silver and uranium are easily recovered from the waste.

155. Volumetric Silver Method.—Holleman has proposed a modification of the silver method for the volumetric determination of phosphoric acid, having for its chief purpose the more accurate and easy determination of the end reaction, which is conducted as described below.³² The reaction which takes place is represented by the equation, $\text{Na}_2\text{HPO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 + 2\text{NaNO}_3 + \text{HNO}_3$. Although silver phosphate is insoluble in water, the nitric acid formed holds some of it in solution. To prevent this, acetate of soda is added in excess, and thus the whole of the phosphoric acid is obtained as a silver salt. The light is to be excluded during the determination by wrapping the flask in a black cloth to avoid a discoloration of the silver compound. Volhard's reaction for silver is based on the fact that when solutions of silver and an alkaline thiocyanate are mixed in the presence of a ferric salt, silver is precipitated as thiocyanate.³³ As soon as the least excess of thiocyanate is added, brown ferric thiocyanate is formed, and this marks the end point of the solution.

In a flask of 200 cubic centimeters capacity are placed 50 cubic centimeters of the liquid to be analyzed, which should not contain more than two-tenths gram of phosphoric acid. The solution is treated with 10 cubic centimeters of a normal solution of sodium acetate and afterwards with a slight excess of decinormal silver solution, four and five-tenths cubic centimeters for each 0.01 gram of phosphoric acid. The solution is neutralized with tenth-normal sodium hydroxid, the amount required having been previously determined by titrating 10 cubic centimeters of the liquid to be analyzed, using phenolphthalein as an indicator. Five times

³² *Recueil des Travaux chimiques des Pays-Bas*, 1893, 12 : 1.

³³ *Liebig's Annalen der Chemie*, 1877, 190 : 1.

the quantity required for the neutralization of the 10 cubic centimeters is added, less one-half cubic centimeter. By this treatment the phosphoric acid in the presence of sodium acetate is completely precipitated as silver phosphate. The excess of silver is determined by diluting the mixture to 200 cubic centimeters, filtering, and titrating 100 cubic centimeters of the filtrate with ammonium thiocyanate, using a ferric salt (ferric-potassium-alum) as indicator. The presence of sulfuric and nitric acids does not interfere with the reaction, but, of course, hydrochloric acid must be absent. Alkalies and alkaline earth metals may be present, but not the heavy metals.

When iron and aluminum are present 100 cubic centimeters of the solution are precipitated with 30 cubic centimeters of normal sodium acetate, the phosphoric acid is determined in 50 cubic centimeters of the filtrate, and the precipitate of iron and aluminum phosphates is ignited and weighed, and its weight multiplied by 2.225 is added to the phosphoric anhydrid found volumetrically. If ammonia be present it must be removed by boiling, as otherwise it affects the titration with phenolphthalein.

For agricultural purposes this method can have but little value, inasmuch as the phosphates to be examined almost always have a certain proportion of iron and aluminum. Moreover, since the amount of these bases has to be determined gravimetrically, there would be no gain in time and no simplification of the processes by the use of the volumetric method as proposed.

TECHNICAL DETERMINATION OF PHOSPHORIC ACID

156. Desirability of Methods.—In the preceding paragraphs, has been given a statement of the principal methods now in use by chemists and others connected with fertilizer control for the scientific and agronomic determinations of phosphoric acid, and its agricultural value.

A résumé of the important methods, in a form suited to use in a factory for preparing phosphatic fertilizers for the market, seems desirable. In these factories the chemists have been accustomed to use their own, or private methods, and there has not been a general disposition among them to publish their methods and experience for the common benefit. For factory processes,

a method should be not only reasonably accurate, but also simple and rapid. It is evident, therefore, that the general principles already indicated must underlie any method which would prove useful in factory work. The final determination by the technical chemist for the purpose of labeling and complying with the laws of the various States, should in all cases be conducted by the official methods. Albert has made a résumé of methods applicable for factory control, and these are given here for convenience, although they are, in many respects, but condensed statements of methods already described.³⁴

157. Reagents. Molybdate Solution.—One hundred and ten grams of pure molybdic acid are dissolved in ammonia of nine-tenths specific gravity and diluted with water to one liter. The solution is poured into one liter of nitric acid, of one and two-tenths specific gravity, and, after standing a few days, filtered.

Concentrated Ammonium Nitrate Solution.—Seven hundred and fifty grams of pure ammonium nitrate are dissolved in water and made up to one liter.

Magnesia Mixture.—Fifty-five grams of magnesium chlorid, 70 grams of ammonium chlorid and 130 cubic centimeters of ammonia of nine-tenths specific gravity are dissolved and diluted with water to one liter.

Two and One-Half Per Cent. Ammonia.—One hundred cubic centimeters of ammonia of nine-tenths specific gravity are diluted with water to one liter.

Joulié's Citrate Solution.—Four hundred grams of citric acid are dissolved in ammonia of nine-tenths specific gravity and diluted to one liter with ammonia of the same strength.

Wagner's Citrate Solution.—One hundred and fifty grams of citric acid are exactly neutralized with ammonia, then 10 grams of citric acid added and diluted to one liter with water.

Sodium Acetate Solution.—One hundred grams of crystallized sodium acetate are dissolved in water, treated with 100 cubic centimeters of acetic acid, and diluted to one liter with water.

Calcium Phosphate Solution.—About 10 grams of dry, pure tribasic calcium phosphate are dissolved in nitric acid and dilu-

³⁴ Zeitschrift für angewandte Chemie, 1891, 4 : 278.

ted with water to one liter. In this solution the phosphoric acid is determined gravimetrically by the molybdate or citrate method, and the value of the solution marked on the flask containing it.

Titrated Uranium Solution.—Two hundred and fifty grams of uranium nitrate are dissolved in water, 25 grams of sodium acetate added, and the whole diluted to seven liters. One cubic centimeter of this solution corresponds to about 0.005 gram of phosphorus pentoxid. In order to determine its exact value proceed as follows. Twenty-five cubic centimeters of the calcium phosphate solution which, for example, has been found to contain 0.10317 gram of phosphorus pentoxid, are neutralized in a porcelain dish with ammonia, acidified with acetic, treated with 10 cubic centimeters of sodium acetate solution and warmed. Through a burette as much uranium solution is allowed to flow as is necessary to show in a drop of the solution taken out of the dish, when treated with a drop of pure potassium ferrocyanid, a slight brown color. In order to be certain, this operation is repeated two or three times with new quantities of 25 cubic centimeters of calcium phosphate solution. Example:

Twenty-five cubic centimeters of the calcium phosphate solution containing 0.10317 gram of phosphorus pentoxid, gave as a mean of three determinations 23.2 cubic centimeters of the uranium solution necessary to produce the brown color with potassium ferrocyanid. Consequently $\frac{0.10317}{23.2} = 0.00445$ gram of

phosphorus pentoxid equivalent to one cubic centimeter of uranium solution. If, for instance, a quantity of fertilizer weighing exactly five grams, requires 10 cubic centimeters of the uranium solution for the complete precipitation of its phosphoric acid, then the quantity of phosphoric acid contained in the fertilizer would be equivalent to 10×0.00445 , equivalent to 0.0445 gram of phosphorus pentoxid. The fertilizer, therefore, contains 0.89 per cent. of phosphorus pentoxid.

Conduct of the Molybdate Method.—This method rests upon the precipitation of the phosphorus pentoxid by a solution of ammonium molybdate in nitric acid, solution of the precipitate in ammonia, and subsequent precipitation with magnesia.

Manipulation.—Twenty-five or 50 cubic centimeters of a solution of the phosphate which has been made up to a standard volume and contains about one-tenth gram of phosphorus pentoxid, are placed in a beaker together with 100 cubic centimeters of the molybdate solution and treated with as much ammonium nitrate solution as will be sufficient to give the liquid a content of 15 per cent. of ammonium nitrate. The contents of the beaker are well mixed and warmed for about 20 minutes at from 60° to 80.° After cooling, they are filtered and the precipitate washed on the filter with cold water until a drop of the filtrate saturated with ammonia does not become opaque on treatment with ammonium oxalate. The filtrate is washed from the filter with 2.5 per cent. ammonia solution and precipitated slowly and with constant stirring by the magnesia mixture. After standing for two hours the ammonium magnesium phosphate is separated by filtration, washed with 2.5 per cent. ammonia until the filtrate contains no more chlorin, and ignited.

Conduct of the Citrate Method.—The principle of this method depends upon the fact that when a sufficient quantity of ammonium citrate is added to phosphate solutions, iron, alumina, and lime are retained in solution when, on the addition of the magnesia mixture in the presence of free ammonia, the phosphoric acid is completely precipitated as ammonium magnesium phosphate.

Manipulation.—From 10 to 50 cubic centimeters of the solution of the phosphate to be determined are treated with 15 cubic centimeters of the Joulie citrate solution avoiding warming. A few pieces of filter paper, the ash content of which is known, are thrown in and, with stirring, 15 cubic centimeters of magnesia mixture slowly added and if necessary also some free ammonia. By the small pieces of filter paper the collection of the precipitate against the sides of the vessel and on the stirring rod is prevented and in this way the production of the precipitate hastened. After standing from one-half an hour to two hours the mixture is filtered, ignited, and weighed. If it be preferred to estimate the phosphoric acid by titration, the precipitate is dissolved in a little nitric acid made slightly alkaline with ammonia,

and then acid with acetic and then afterwards titrated with the standard uranium solution.

Conduct of the Uranium Method.—The principle upon which this method rests depends upon the fact, that uranium nitrate or acetate precipitates uranium phosphate from solutions containing phosphoric acid and which contain no other free acid except acetic. In the presence of ammonium salts the precipitate is uranium ammonium phosphate having the formula $\text{PO}_4\text{NH}_4\text{UO}_2$. The smallest excess of soluble uranium salt is at once detected by the ordinary treatment with potassium ferrocyanid.

Manipulation.—In all cases the solution is first made slightly alkaline with ammonia and then acid by a few drops of acetic so that no free mineral acid may be present.

(1) *With liquids free of iron:*

If, on the addition of ammonium or sodium acetate, no turbidity be produced, the liquid is free of iron and alumina. In this case from 10 to 50 cubic centimeters of the solution containing about one-tenth gram of phosphorus pentoxid are treated with 10 cubic centimeters of sodium acetate, and afterwards with a quantity of uranium solution corresponding, as nearly as possible, to its supposed content of phosphorus pentoxid, and heated to boiling. From the heated liquid, by means of a glass rod, one or two drops are taken and placed upon a porcelain plate and one drop of a freshly prepared solution of potassium ferrocyanid allowed to flow on it. If no brown color be seen at the point of contact of the two drops, additional quantities of the uranium solution are added and, after boiling, again tested with potassium ferrocyanid until a brown color is distinctly visible. The quantity of the uranium solution thus having been determined, duplicate analyses can be made and the whole quantity of the uranium solution added at once with the exception of the last drops which are added as before.

(2) *Solutions containing iron and alumina.*

The solution is treated with the ammonium citrate solution of Joulie, the magnesia mixture added slowly, and the precipitate collected on a filter and washed with 2.5 per cent. ammonia. The precipitate is then dissolved in nitric acid, made alkaline with

ammonia, and then acid with acetic. This solution is treated with 10 cubic centimeters of sodium acetate and titrated with uranium, as described in (1). As an alternative method, 200 cubic centimeters of the superphosphate solution may be treated with 50 cubic centimeters of sodium acetate, allowed to stand for some time, and filtered through a filter of known ash content. In 50 cubic centimeters of the filtrate, which correspond to 40 cubic centimeters of the original solution, phosphoric acid may be determined as described above. The precipitate, consisting of iron and aluminum phosphates, is washed three times on the filter with boiling water, dried, and ignited in a platinum dish. The weight of ignited precipitate, diminished by the weight of the ash contained in the filter and divided by two, gives the quantity of phosphorus pentoxid which it is necessary to add to that obtained by titration.

158. Determination of the Phosphoric Acid in all Phosphates and Basic Slags.

(1) *Total Phosphoric Acid:*

Five grams of the fine phosphate meal, or slag meal, are moistened in a flask of 500 cubic centimeters content with some water and boiled on a sand bath with 40 cubic centimeters of hydrochloric acid of from 16° to 20° Beaumé. The boiling is continued until only a few cubic centimeters of a thick jelly of silicic acid remain. After cooling, some water is added and the phosphate shaken until the thick lumps of silica are finely divided. The flask is then filled to 500 cubic centimeters and its contents filtered. Fifty cubic centimeters of the filtrate are mixed with 15 cubic centimeters of the Joulie solution and treated in the manner described with magnesia mixture, precipitated, ignited and weighed. The precipitate can also be dissolved and treated with uranium solution as described.

The method used by Oliveri for basic slags may also be employed and it is carried out as indicated in the following description.³⁵

A weighed quantity of the slag is reduced to a fine powder. To five grams of the sample is added three times its weight of

³⁵ *Le Stazioni sperimentali agrarie italiane*, 1891, 20 : 159.

potassium chlorate and the whole is intimately mixed. The mixture is then placed in a porcelain dish and hydrochloric acid is added, little by little, until the potash salt is completely decomposed. It is evaporated until the mass is dry. The material is then treated with fuming nitric acid, and the determination of the phosphorus is made by the ordinary gravimetric method.

By carrying on the operation as described above, a reduction of phosphoric acid is avoided, and the presence of an abundant quantity of potash prevents the formation of basic iron phosphate which is insoluble in nitric acid.

(2) *Citrate-Soluble Phosphoric Acid*.—One gram of the basic slag or phosphate is placed in a 100 cubic centimeter flask and covered with Wagner's acid citrate solution making the total volume up to 100 cubic centimeters. With frequent shaking the flask is kept at 40° for an hour, or it may be allowed to stand for 12 hours at room temperature with frequent shaking. In 50 cubic centimeters of the filtrate from this flask the phosphoric acid is determined by the magnesia mixture as described. Since, in the present case, the precipitate of ammonium magnesium phosphate contains some silicic acid it can not be directly ignited but must be treated in the following manner: The precipitate and the filter are thrown into a porcelain dish, the filter paper torn up into shreds with a glass rod, the precipitate dissolved in nitric acid, neutralized with ammonia, acidified with acetic, and treated with uranium solution. The phosphoric acid may also be estimated by the gravimetric method by dissolving the precipitate again in hydrochloric or nitric acid, evaporating to dryness, and drying for one hour at from 110° to 120°, dissolving again in hydrochloric acid, filtering, and washing the precipitate well. The filtrate, which is now free from silica, can be treated with Joulie's solution, precipitated with magnesia mixture, the precipitate washed, ignited, and weighed as described. The molybdate method is preferred in the estimation of citrate-soluble phosphoric acid, especially in slags. For this purpose 50 cubic centimeters of the filtrate from the solution of one gram of slag in 100 cubic centimeters of Wagner's citrate liquid are treated with 100 cubic centimeters of molybdenum solution and 30 cubic

centimeters of ammonium nitrate solution, warmed for 20 minutes at 80° , filtered after cooling, and the yellow precipitate washed with cold water. The water will gradually dissolve all the silicic acid from the yellow precipitate and carry it into the filtrate. The yellow precipitate is then dissolved in 2.5 per cent. liquid ammonia and precipitated with magnesia mixture and the precipitate washed, ignited and weighed in the way described.

159. Determination of Phosphoric Acid in Superphosphates.

—(1) *Citrate-Soluble Phosphoric Acid.*—Five grams of the superphosphate are rubbed with 100 cubic centimeters of Wagner's acid citrate solution in a mortar and washed into a flask of 500 cubic centimeters content and diluted to 500 cubic centimeters with water. With frequent shaking, the flask is allowed to stand for 12 hours, after which its contents are filtered. Fifty cubic centimeters of the filtrate are treated with 10 cubic centimeters of the Joulie solution and 15 cubic centimeters of the magnesia mixture and, if necessary, made distinctly alkaline with ammonia, vigorously stirred, and, after two hours, filtered. The precipitate is washed, ignited, and weighed as described, or titrated, after solution in nitric acid and the addition of sodium acetate, with uranium solution. Example: The weighed precipitate has 0.1272 gram $Mg_2P_2O_7$, then the phosphate contains $12.72 \times 2 \times 0.64 = 16.28$ per cent. of citrate-soluble P_2O_5 .

(2) *Water-Soluble Phosphoric Acid.*—Twenty grams of superphosphate are rubbed in a mortar and washed into a flask of one liter content and made up to the mark with water. After two hours digestion with frequent shaking, the contents of the flask are filtered through a folded filter. Twenty-five cubic centimeters of the filtrate equivalent to 0.5 gram of the substance are precipitated with magnesia mixture, the precipitate filtered, washed, ignited, and weighed, or the moist filtrate may be dissolved upon the filter with a little nitric acid, treated with sodium acetate and titrated, as described, with uranium solution.

Example: 14.5 cubic centimeters of the uranium solution are required for the precipitate from 25 cubic centimeters of the original solution = 0.5 gram superphosphate; it contains then $14.5 \times$

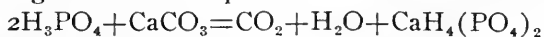
0.00445=0.0645 gram P_2O_5 . Consequently the superphosphate contains 12.90 per cent. of water-soluble P_2O_5 .

Total Phosphoric Acid.—Twenty grams of the superphosphate are boiled with 50 cubic centimeters of hydrochloric acid of from 16° to 18° Beaumé for about 10 minutes and, after cooling, made up to one liter with water and filtered. Twenty-five cubic centimeters of the filtrate are treated with 10 cubic centimeters of Joulie's citrate solution, a few pieces of filter paper thrown in, 15 cubic centimeters of magnesia mixture added, and the whole thoroughly stirred. After standing two hours the contents of the flask are filtered, the precipitate is washed with dilute ammonia, and the filter and the precipitate are placed in a platinum crucible. The crucible is heated slowly until the moisture is driven off and the filter burned. Then the temperature is gradually raised to a white heat. The residue is cooled and weighed.

Example: The precipitate weighs, after the subtraction of the filter ash, 0.1390 gram; then the superphosphate contains $13.90 \times 2 \times 0.64 = 17.79$ per cent. phosphoric acid.

160. Determination of Free Acid in Phosphates for Technical Purposes.—A speedy and approximately accurate method of determining free phosphoric acid in superphosphates is useful in technical work, and for this purpose Gerhardt has proposed the following process.³⁶ There are valid objections to both the methods in common use. When the free acid is extracted with water and the acidity of the extract determined by titration with an alkali, the end reaction is obscured by the separation of acid calcium phosphate, $CaHPO_4$. On the other hand, when absolute alcohol is used to dissolve the acid, the separation is not exact because of the water content of the sample, and drying the sample would cause a decomposition and the formation of new compounds of the free phosphoric acid. The principle of the following process is based on the addition of an excess of calcium carbonate to the sample and the subsequent determination of the undecomposed portion.

When pure phosphoric acid is shaken with calcium carbonate the following reaction takes place:



³⁶ Chemiker-Zeitung, 1905, 29 : 178.

The sulfates of iron and aluminum disturb the accuracy of the reaction, since they also react with carbonates. Inasmuch as the mineral phosphates entering the factory have been examined for iron and alumina, the magnitude of this disturbance can be ascertained and due allowance made therefor, or the iron may be thrown out previous to the determination by potassium ferrocyanid. The process is conducted as follows:

Twenty grams of the sample are shaken for half an hour in a liter flask with water, and one gram of ferrocyanid of potash dissolved in water added thereto, the flask filled to the mark, shaken, and the contents poured on a filter. To 100 cubic centimeters of the filtrate a known weight of calcium carbonate is added, stirred for half an hour, the undecomposed carbonate separated by filtration, washed with a small quantity of water, dried, ignited gently and weighed. The quantity of calcium carbonate thus determined deducted from the whole amount used, represents the quantity decomposed by the free acids and the iron and aluminum compounds above noted. The constant error, due to the last named source, is applied as a correction and the quantity of free acid thus approximately determined.

The carbon dioxide contained in the residue above mentioned is determined more rapidly and with greater precision by decomposing it with an acid and weighing or measuring the evolved gas.

The carbonate remaining in the residue may also be determined by titration as follows: The residue is placed in a flask of 200 cubic centimeters capacity and decomposed with 25 cubic centimeters of normal hydrochloric acid, filled to the mark, shaken and the contents poured through a dry filter. One hundred cubic centimeters of the filtrate are titrated with half-normal soda-lye, using methyl orange as indicator. The correction for iron and aluminum must again be made, since any iron and aluminum phosphate which is found with the residue of calcium carbonate decomposes corresponding quantities of the hydrochloric acid. Since the fresh superphosphate always contains some free sulfuric acid, it is advisable to report the result as degree of acidity, comprising therein the free phosphoric acid, the free sulfuric acid and all other com-

pounds of an acid character which react with calcium carbonate to form carbon dioxide.

When an aqueous solution of $\text{CaH}_4(\text{PO}_4)_2$ and free phosphoric acid is titrated with an alkali in the presence of methyl orange, no precipitate is produced; and, therefore, the precipitate in the above method, ascribed to the formation of CaHPO_4 , is rather to be accredited to the production of a phosphate of iron or alumina.³⁷ The alcohol method of extraction is not, therefore, as Gerhardt has supposed, inapplicable because superphosphate may go into solution, since this does not interfere with the reaction when methyl orange is used as indicator, but it is to be rejected for other reasons. The errors, however, due to iron and alumina may amount to as much as one or two per cent. and are not constant.

Gerhardt maintains in a later publication that Zöckler is mistaken respecting the non-formation of CaHPO_4 and regards his method as above described as satisfactory, especially when the calcium carbonate is titrated instead of ignited.³⁸

161. Ostersetzer's Method.—The "free" acid in superphosphates may consist of several kinds, free phosphoric acid, free sulfuric acid and acid phosphates which react as free acid. An indicator that may be used in a purely technical way to indicate the proportion of such free acid to the total acid present is alizarin sulfonic acid.³⁹ The determination of total free acidity is made as follows:

Dissolve 10 grams of superphosphate in 400 cubic centimeters of water in a 500 cubic centimeter flask. Shake for the usual time and add four cubic centimeters of a solution containing two and a half grams of alizarin sodium sulfonate in 500 cubic centimeters of water. Complete the volume to the mark, filter, titrate 50 cubic centimeters of the filtrate, representing one gram of the sample, with half-normal sodium hydroxid solution to transition between yellow and brown, comparing with an equal volume of the original solution to better distinguish the changed color. The free acidity is calculated from the data obtained and compared with the total acidity determined in the usual way.

³⁷ Zöckler, *Chemiker-Zeitung*, 1905, **29** : 226, 338.

³⁸ *Chemiker-Zeitung*, 1905, **29** : 276.

³⁹ *Chemical News*, 1905, **91** : 215.

BASIC PHOSPHATIC SLAGS

162. **Uses of Basic Slag.**—The importance of basic Bessemer slag, the residue of the process of manufacturing steel by the basic process from ores rich in phosphorus, is everywhere acknowledged. The use of this material in the United States has not been very extensive, chiefly for the reason that practically none of it is produced in this country, steel not being made from phosphatic ores. It is, however, made in very large quantities in Europe, and it is stated that over 2,000,000 tons of it are used annually in Germany alone for manurial purposes.

Leavens has given the following reasons for believing that basic slag is a superior quality of phosphatic fertilizer:⁴⁰

I. The phosphoric acid in basic slag is in a form which can not revert or go back to more insoluble forms when mixed with the soil as is the tendency with all superphosphates.

II. The phosphoric acid in basic slag is not washed from the soil by the heavy rains and leached away in the drainage waters as is the case with many other phosphates.

III. Since the phosphoric acid in basic slag never wastes after application to the soil, it follows that basic slag may be applied at any time, either fall, spring, summer, or even in winter without danger of loss.

IV. In addition to its high content of phosphoric acid, the large amount of lime in basic slag greatly adds to its value. Instead of having a souring effect upon the land, as do superphosphates, basic slag on account of its strong alkaline reaction sweetens acid soils and restores them to a productive condition.

The lime also possesses the valuable property of making available the potash already in the soil and has a similar effect on crude forms of organic nitrogen. In addition to the chemical effects already mentioned, lime greatly improves the physical quality of the land, loosening up compact clay soils, thus making them more permeable, and compacting light sandy soils rendering them more retentive of moisture and plant food.

V. Basic slag also contains a considerable amount of magnesia which is extremely valuable in changing crude forms of plant

⁴⁰ Basic Slag and its Uses, 1906 : 5.

foods in the soil into forms which the plant may take up readily. So powerful is its action in this direction that it is often spoken of as "a chemical plow."

VI. The large amount of iron in the basic slag should not be overlooked. "Iron," says Prof. Sorauer, in his excellent treatise on the physiology of plants, "is necessary in the building of chlorophyll," the substance that gives the green color to all foliage "As it is the function of chlorophyll to form new plastic material under the influence of the sunlight, it is natural that the absence of iron, which is shown by the paleness of the leaves, should cause a cessation of assimilation."

This accounts for the deep green color and splendid healthy condition of the foliage of the plants and trees fertilized with basic slag.

VII. In addition to all of the above, basic slag commends itself strongly on account of the high degree of availability to plants possessed by its phosphoric acid. While little or none of its phosphoric acid is soluble in pure distilled water, it is soluble in the secretions of the plant roots which feed upon it readily.

Experiments indicate that the total phosphoric acid of basic slag is practically as effective as the available phosphoric acid of acid phosphate.⁴¹

It should be borne in mind that this high degree of availability is not due to any treatment of the basic slag with sulfuric acid. There is a marked reaction all over the country against using acidulated fertilizers, as their continued use under improper conditions has rendered many thousands of acres of valuable land infertile.

The average total results show that insoluble phosphoric acid, that is phosphates which have not been treated or dissolved in sulfuric acid (oil of vitriol), have more pounds of crop, both straw and marketable grain, than the phosphoric acid in the soluble and reverted forms; that is, in phosphates which have been dissolved in sulfuric acid.⁴²

VIII. The comparative low cost of basic slag with resulting

⁴¹ Ohio State Agricultural Experiment Station, Bulletin 100, 1899 : 137.

⁴² Maryland Agricultural Experiment Station, Bulletin 68, 1900 : 28.

economy in crop production, is a matter that should appeal to every practical farmer.

Slag phosphate plots produced a greater yield and at a less cost than the average of the soluble phosphoric acid plots and the bone meal plots. All yields were produced at less cost with slag phosphates than with bone meal.⁴³

IX. While basic slag generally should not be mixed with materials containing nitrogen in organic forms such as dried blood, ground bone, dried fish or tankage, many highly desirable and splendid combinations of it with nitrate of soda and potash salts may be made.

By varying the amount of nitrate of soda and potash salts mixed with the slag, fertilizers adapted for use on all of our leading crops may be prepared.

Wheeler states that basic slag is an effective source of phosphoric acid for use upon all kinds of soils, and on account of its lime it is of special promise in the reclamation of exhausted acid soils, particularly such as are rich in organic matter, like many marsh or muck soils.⁴⁴

Basic slag has been found useful for peaches, apples, grapes, oranges, and fruits in general, and for all the cereals. It has also proved very beneficial to clover, alfalfa, and the grasses; in fact, all kinds of crops which are benefitted by phosphatic fertilizers respond more readily to the fertilizer when in the shape of basic slag. Since it is quite likely that it may come into much more general use in this country, a detailed study of the methods of determining its value is advisable.

163. History and Manufacture.—The basic process for the manufacture of Bessemer steel is known in Europe as the Thomas or Thomas and Gilchrist process, and the slags rich in phosphate, one of the waste products of the process, are known by the same name. In this country all the phosphatic slags which have been made in the manufacture of steel have been obtained working chiefly under the patents of Reese, and, when prepared for the market, are known as odorless phosphate. The only places where

⁴³ Maryland Agricultural Experiment Station, Bulletin 68, 1900 : 28, 29.

⁴⁴ U. S. Department of Agriculture, Farmers' Bulletin 77, 1905 : 18.

these slags have been made in this country are Pottstown, Pennsylvania and Troy, New York. Comparatively small quantities have been manufactured and the industry has not assumed any commercial importance. In Europe they are extensively manufactured in England, France and Germany, and their use for agricultural purposes has increased until it is quite equal to that of superphosphates.

The quantity of basic slag manufactured in Germany in 1893 was 750,000 tons; in England 160,000; in France 115,000, making the total production of central Europe about 1,000,000, a quantity sufficient to fertilize nearly 5,000,000 acres. During the year 1907 it is estimated that German agriculture made use of from 1,500,000 to 1,600,000 tons of basic phosphate slags. The total output of basic slag is undoubtedly not far from 2,000,000 tons. The total production of basic slag is therefore approximately one-half of that of crude phosphates.

The following table in metric terms shows the estimated production of crude phosphates for the whole world for 1906 and 1907:⁴⁵

	1907	1906
United States.....	1,917,000	2,052,000
Tunis.....	1,040,000	758,000
Algeria.....	325,000	302,000
South Sea Islands.....	300,000	250,000
France.....	375,000	425,000
Belgium.....	180,000	155,000
All other places.....	100,000	100,000
	4,237,000	4,042,000

164. Process of Manufacture.—The principle of the process depends upon the arrangement of the furnaces, by means of which the phosphoric acid in the iron ore or pig iron is caused to combine with the lime, which is used as a flux in the converters. A general outline of the process is as follows:

The pigs, which contain from two to four per cent. of phosphorus, are melted and introduced into a Bessemer converter lined with dolomite powder cemented with coal-tar, into which has previously been placed a certain quantity of freshly burned lime.

⁴⁵ Der Saaten-, Dünger-und Futtermarkt, 1908, No. 7 : 205.

For an average content of three per cent. of phosphorus in the pig iron, from 15 to 20 pounds of lime are used for each 100 pounds of pig iron. As soon as the melted pig iron has been introduced into the converter, the air-blast is started, the converter placed in an upright position, and the purification of the mass begins. The manganese in the iron is converted into oxid, the silicon into silica, the carbon into carbon dioxid and oxid, and the phosphorus into phosphoric acid.

By reason of the oxidation processes, the whole mass suffers a rise of temperature amounting in all to about 700° above the temperature of the melted iron. At this temperature the lime which has been added, melts and, in this melted state, combines with the phosphoric acid, and the liquid mass floats upon the top of the metallic portion, which has by this process been converted into steel.

As soon as the process, which occupies only about 15 minutes, is completed, the fused slag is poured off into molds, allowed to cool, broken up, and ground to a fine powder. For each five tons of steel which are made in this way, about one ton of basic slag is produced.

In another process, in order to make a slag richer in phosphoric acid, a lime is employed which contains a considerable percentage of phosphate. Although the slag thus produced is richer in phosphoric acid, it is doubtful whether it is any more available for plant growth than that made in the usual way with lime free from phosphoric acid. In other words, when a basic slag is made with a lime free from phosphoric acid, nearly the whole of the phosphoric acid is combined as tetrabasic calcium phosphate. On the other hand, when the lime employed contains some of the ordinary mineral phosphate, the basic slag produced becomes a mixture of this mineral phosphate with the tetracalcium salt. The mineral phosphate is probably not rendered any more available than it was before.

It is easily seen from the above outline of the process of manufacture that basic slags may have a very widely divergent composition. When made from pig iron poor in phosphorus, the slag will have a large excess of uncombined lime and consequently the

content of phosphoric acid will be low. When made from pigs rich in phosphorus there may be a comparative deficiency of iron in the slag, and in this case the content of tetrabasic calcium phosphate would be unusually high.

It is found also that the content of iron in the slag varies widely. In general, the greater the content of iron the harder the slag and the more difficult to grind. If the pig iron contain sulfur, as is often the case, this sulfur is found also in the slag in combination with the lime, either as a sulfid or sulfate.

No certain formula can therefore be assigned to basic slags and the availability of each one must be judged by its chemical composition.

165. Composition of Slag Phosphate.—The slags produced by the method above outlined may be amorphous or crystalline. When large masses are slowly cooled the interior often discloses a crystalline composition. In some samples analyzed in the laboratory of the Division of Chemistry the crystals were found to be of two forms, viz., acicular and tabular.⁴⁶ They had the following composition:

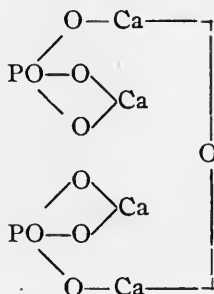
	CALCULATED PER CENTS. AS						
	CaO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	MgO.	V ₂ O ₅ .	P ₂ O ₅ .	SiO ₂ .
Acicular crystals.....	42.69	20.98	3.71	0.49	0.18	27.06	4.96
Tabular crystals.....	53.61	9.64	0.91	0.08	...	33.92	1.75

These data show that the two sets of crystals belong to two distinct mineral forms. The presence of vanadium in one of the samples is worthy of remark, and leads to the suggestion that in the slags made of phosphoriferous pigs may be found any of the rare metals which may exist in the ores from which the pigs were made. The amorphous portions may have a widely varying composition and consequent variable content of phosphoric acid. In all good slags, however, whether in crystalline form or as amorphous powder, the lime and phosphoric acid will be found combined as tetracalcium phosphate ($\text{Ca}_4\text{P}_2\text{O}_9$).

166. Molecular Structure of Tetracalcium Phosphate.—Several theories have been advanced in respect of the atomic arrangement of the elements contained in a molecule of tetracalcium phosphate. It must be confessed that so little is known concern-

⁴⁶ Journal of Analytical and Applied Chemistry, 1891, 5 : 685.

ing the reactions of this body as to make theories of its constitution largely visionary. But the existence in definite crystalline form of this salt shows that it is not merely an intimate mechanical mixture, but a true molecular form. As a type of the supposed arrangement of its particles, the graphic formula proposed by Kormann may be consulted; viz.,



The crystals of this salt, as may be seen by inspection of the analytical data, contain other bodies than calcium, oxygen and phosphorus. It would be of interest to push the investigation of their constitution further and see if crystals of pure tetracalcium phosphate could be obtained, and under what conditions they would be contaminated by other metallic oxides. Usually, by the color of the crystals, it will be easy to determine something of the nature, if not the extent, of the contamination.

167. Solubility of Phosphatic Slags.—The high agricultural value of basic slags led to an early study of their solubility in ammonium citrate, citric acid, and other organic solutions. Even finely ground mineral phosphates and bones are soluble to some extent in ammonium citrate, as was pointed out as long ago as 1882.⁴⁷ The most common solvents for basic slags are ammonium citrate and citric acid. The ammonium citrate should be the same as that used for the determination of reverted phosphoric acid and the citric acid solution commonly used contains five grams in a hundred cubic centimeters. The slags of different origin and even of different age vary greatly in respect of the quantity of soluble matter they contain. It is believed, however, that a very fair idea of the agricultural value of a slag

⁴⁷ Wiley, *Journal of Analytical and Applied Chemistry*, 1889, 3 : 413.

may be obtained by determining its degree of solubility in one of the menstrua named.

168. Separation by Sifting.—The relative availability of a slag, as in the case of a mineral phosphate, is determined very largely by the percentage of fine material it contains. Sieves of varying apertures are used to determine this percentage. A one-half millimeter or a one-quarter millimeter circular aperture is best, and the percentage of the total material passing through is determined. A method used in Germany consists in sifting the slag in a sieve 20 centimeters in diameter, the meshes of which are from 0.14 to 0.17 millimeter square and which measure diagonally from 0.22 to 0.24 millimeter.

169. Solution of Phosphatic Slags.—Sulfuric acid has been found to be an excellent solvent for basic slags preparatory to the determination of total phosphoric acid. There is, however, no unanimity of opinion concerning the best method or means of solution. Aqua regia and nitric acid are objected to because they may convert any phosphorus in combination with the iron into phosphoric acid and thus increase the quantity present.⁴⁸ But iron phosphid is seldom found in slags, and therefore this objection is not always tenable. Sulfuric acid has also been deemed objectionable because the gypsum separated is likely to carry with it some of the other substances to be determined.

Hydrochloric acid is also excluded by some from the list of solvents because it dissolves so many of the foreign elements in the slag and thus tends to complicate the subsequent determinations, especially of magnesia. Besides, a hydrochloric acid solution is not suited to the use of the citrate method formerly much employed in the determination of total phosphoric acid. When hydrochloric acid is used, moreover, the dissolved silica must be removed and thus the time required for making a phosphoric acid determination is much increased.

If the sample be sufficiently fine the occlusion of undissolved phosphate particles by the gypsum formed when sulfuric acid is used is not to be feared, and the disturbance of volume by the gypsum is nearly constant and can be allowed for. When

⁴⁸ von Reis, *Zeitschrift für angewandte Chemie*, 1888, 1 : 354.

five grams of slag are used the mean volume of gypsum in the solution is about two cubic centimeters.

170. Estimation of Total Acid.—In the determination of total phosphoric acid in a slag, 25 cubic centimeters of the strongest sulfuric acid are placed in an erlenmeyer having a wide neck, and with careful shaking five grams of the fine slag meal gradually added. The flask is heated over a naked flame until solution is complete. When the mass is cold it is washed into a quarter liter flask; again allowed to cool, filled with water to the mark, and two cubic centimeters of water, corresponding to the volume of gypsum undissolved, are added, well mixed, and filtered. In 50 cubic centimeters of the filtrate, the phosphoric acid is determined by either the molybdate or citrate methods already described.

171. Alternate Method.—The following method may also be used: Ten grams of the substance are heated with 50 cubic centimeters of concentrated sulfuric acid until white vapors have been evolved for some time. The operation lasts for about 15 minutes and can be carried on in a half-liter flask or in a porcelain dish. Without regarding the undissolved material, the volume of the liquid is now made up to half a liter and filtered. The filtered liquid becomes turbid after some time through the separation of calcium sulfate, but this turbidity should not be regarded. To 50 cubic centimeters of the solution, corresponding to one gram of substance, 20 cubic centimeters of citric acid (500 grams citric acid to the liter) are added, and it is afterwards nearly neutralized by the addition of 10 per cent. ammonia and the liquid, which is warmed by this operation, cooled. There are added 25 cubic centimeters of the ordinary magnesium chlorid mixture and the solution stirred until turbidity is produced, one-third of its volume of 10 per cent. ammonia added, and again stirred for about a minute to promote precipitation.

Instead of the addition of the citric acid and ammonia, ammonium citrate prepared as follows may be added: Fifteen hundred grams of citric acid are dissolved with water, made up to three liters, five liters of 24 per cent. ammonia and seven liters

of water added. The rest of the operation is carried on in the usual manner.

172. Halle Method for Basic Slag.—The total phosphoric acid is estimated at the Halle Station by the following process:⁴⁹

Ten grams of the substance are moistened in a porcelain dish with a few drops of water and about five cubic centimeters of a one to one solution of sulfuric acid added, and after the mass has hardened, which takes place very soon, 50 cubic centimeters of concentrated sulfuric acid are added and stirred with a glass rod until evenly distributed throughout the whole mass. In stirring this mixture the greatest care must be taken, otherwise some of the substance will remain attached to the sides of the dish, which during later heating would cause loss through spurting. The complete solution takes place after a few hours heating on a sand-bath. During the cooling, the jelly-like mass must be stirred with a glass rod, and after it is cool, by means of a washing bottle, gently along the sides of the dish, water is added, and when the mixture becomes hot it is again cooled and washed into a half-liter flask, which is made up to the mark at a temperature of $17^{\circ}.5$ and filtered. When the acid filtrate stands for some time there is often a separation of gypsum that, however, does not in any way influence the subsequent analysis, which is made in the usual manner.

Fifty cubic centimeters of the filtrate, representing one gram of the original substance, are placed in an erlenmeyer. In the case of double superphosphates, which often contain large quantities of pyrophosphates, 25 cubic centimeters of the filtrate just obtained, equivalent to 0.5 gram of the substance, are diluted with 75 cubic centimeters of water, 10 cubic centimeters of nitric acid of 1.42 specific gravity added, and heated on a sand-bath to convert the pyro- into orthophosphates. The heating should be continued until the liquid is reduced to its original volume of 25 cubic centimeters. The strongly acid liquid is saturated with ammonia and with the addition of a drop of rosolic acid as an indicator, again acidified with nitric acid, and treated as with superphosphates.

⁴⁹ Bieler und Schneidewind, Die agrikultur-chemische Versuchsstation Halle, a/S. ihre Einrichtung und Thätigkeit, 1892 : 61.

173. Dutch Method for Basic Slag.—Heat 10 grams of the sample with 50 cubic centimeters of sulfuric acid (1.84 specific gravity) till white vapors are evolved, shaking or stirring constantly. After cooling, make the fluid up to 500 cubic centimeters with water, taking no account of the undissolved substance. Filter, and to 50 cubic centimeters of the filtrate add 100 cubic centimeters of the ammoniacal citrate solution, and after cooling, 25 cubic centimeters of magnesia mixture. Stir or shake for a sufficient time. After the lapse of two hours the precipitate is to be separated by filtration and treated in the usual manner.

174. Estimation of Citrate-Soluble Phosphoric Acid in Basic Slag.—Experience has shown that the manurial value of basic slags does not depend alone on their content of phosphoric acid. Slags may contain tri- as well as tetracalcium phosphate, and even this latter salt may exist in states of differing availability. In determining the availability of basic slag for manurial purposes, its solubility in ammonium citrate is considered the best standard. But this solubility will evidently be influenced by the basicity of the sample or, in other words, by the quantity of lime present. A slag rich in calcium oxid would deport itself differently with a given ammonium citrate solution from one in which the lime had been chiefly converted into carbonate. If possible, therefore, all samples should be reduced to the same state of basicity before the action of any given solvent is determined.

Wagner proposes to neutralize the basicity of a slag in the following manner:⁵⁰ Five grams of the slag are placed in a half-liter flask, which is then filled up to the mark with a one per cent. solution of citric acid and placed for half an hour in a rotating shaker. After filtering, 50 cubic centimeters are titrated with a standard soda solution, using phenolphthalein as indicator. This gives the quantity of citric acid necessary to neutralize the slag. To a second portion of five grams of the sample in a half-liter flask are added 200 cubic centimeters of water and enough five per cent. citric acid solution to neutralize the lime, and then 200 cubic centimeters of acid ammonium citrate made as indicated

⁵⁰ *Chemiker-Zeitung*, 1894, 18 : 1153.

below. After filling to the mark with water it is shaken for half an hour and filtered. To 50 cubic centimeters of the filtrate are added 100 cubic centimeters of molybdic solution and the whole heated to 80°. After cooling, the precipitate is filtered and the phosphoric acid estimated in the usual way.

The acid ammonium citrate solution used is made as follows: Dissolve 160 grams of citric acid with enough ammonia to represent about 28 grams of nitrogen and make up with water to one liter.

The molybdic solution is made by dissolving 125 grams of molybdic acid in a slight excess of 2.5 per cent. of ammonia, adding 400 grams of ammonium nitrate, diluting to one liter and pouring the solution into one liter of nitric acid having a specific gravity of 1.19. After allowing to stand at room temperature for one day the mixture is filtered and is then ready for use.

175. Wagner's Method for Phosphoric Acid.—The directions given by Wagner for determining the phosphoric acid in slags and raw phosphates soluble in citrate solutions are the following:⁵¹ Five grams of the material as it is sent into commerce, without grinding or sifting, are placed in a half-liter flask, covered with nearly a quarter liter of water, and then 200 cubic centimeters of citrate solution added, prepared as described below. The flask is filled to the mark with water. The flasks, which are of the shape shown in the figure, are closed with rubber stoppers, and without delay placed for half an hour in a rotating apparatus, (Fig. 11), which is turned on its axis from 30 to 40 times a minute. If a shaking apparatus be used instead of the one mentioned, 200 cubic centimeters of the citrate solution should be placed in a half-liter flask, filled to the mark with water, and the contents poured into a liter flask containing the phosphate. This flask should be placed in a nearly horizontal position in the apparatus and the agitation be continued for half an hour. On removal from the apparatus the mixture is filtered and 50 cubic centimeters thereof treated with double that quantity of molybdic solution at 80° and the precipitate separated after cooling. The precipitate is carefully washed with one per cent. nitric acid mix-

⁵¹ *Chemiker-Zeitung*, 1894, 18 : 1933.

ture, after which the filter is broken and the precipitate washed into a beaker with two per cent. ammonia and the filter washed therewith until about 100 cubic centimeters have been used. If the solution is turbid from the presence of silicic acid it should be precipitated a second time by addition of molybdic solution. The

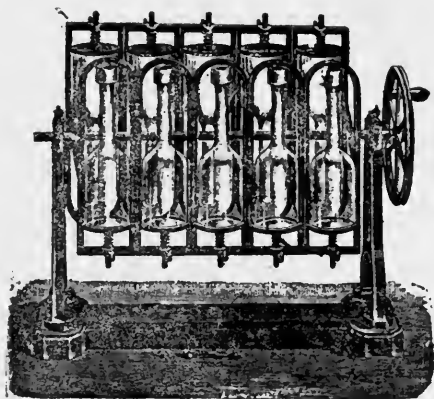


Fig. 11. Wagner's Digestion Apparatus for Slags.

ammoniacal solution of the yellow precipitate is treated, drop by drop, with constant stirring, with 15 cubic centimeters of magnesia mixture, and set aside for two hours. The precipitate is collected, washed, ignited and weighed in the usual manner. The direct precipitation of the phosphoric acid by the magnesia solution in presence of citrate is not advisable because of the almost general presence of silicic acid, which would cause the results to be too high.

The chief objection to this method of Wagner lies in the failure to control the temperature at which the digestion with citrate solution is made. Huston has shown, as will be described further on, that the temperature exercises a great influence in digestion with citrate. Since the laboratory temperature, especially in this country, may vary between 10° and 40° , it is evident that on the same sample the Wagner method would give very discordant results at different seasons of the year unless the digestions were made at one temperature. In order to control the temperatures

of digestion, the apparatus devised by the author may be used.⁵²

176. Solutions Employed in the Wagner Method.—1. *Ammonium Citrate.*—In one liter there should be exactly 150 grams of citric acid and 27.93 grams of ammonia, equivalent to 23 grams of nitrogen. The following example illustrates the preparation of 10 liters of the solution: In two liters of water and 3.5 liters of eight per cent. ammonia, 1500 grams of citric acid are dissolved and the cooled solution made up exactly to eight liters.* Dilute 25 cubic centimeters of this solution to 250 cubic centimeters and treat 25 cubic centimeters of this with three grams of calcined magnesia and distill into 40 cubic centimeters of half-normal sulfuric acid. Suppose the ammonia nitrogen found corresponds to 20 cubic centimeters of fourth-normal soda-

lye. Then in the eight liters are contained $\frac{20.0 \times 0.0035 \times 8000}{2.5}$

=224 grams of ammonia nitrogen. In order to secure in the 10 liters the proper quantity of ammonia there must be added two liters of water containing 230—224=six grams of nitrogen or 7.3 grams ammonia; viz., 94 cubic centimeters of 0.967 specific gravity.

2. *Molybdate Solution.*—Dissolve 125 grams of molybdic acid in dilute 2.5 per cent. ammonia, avoiding a large excess of the solvent. Add 400 grams of ammonium nitrate, dilute with water to one liter and pour the solution into one liter of nitric acid of 1.19 specific gravity. Allow the preparation to stand for 24 hours at 35° and filter.

3. *Magnesia Mixture.*—Dissolve 110 grams of pure crystallized magnesium chlorid and 140 grams of ammonium chlorid in 700 cubic centimeters of eight per cent. ammonia and 130 cubic centimeters of water. Allow to stand several days and filter.

177. Analysis of Basic Slags by the Method of the German Agricultural Experiment Stations.—The methods of determining the fertilizing value of basic slags (Thomas Meal) have been studied by a committee of the German experiment stations.⁵³

⁵² Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1: 394.

⁵³ Wagner, Bestimmung der zitronensäurelöslichen Phosphorsäure in Thomasmehlen, 1903.

A full statement of the problem is given in the first part of the report. In the second part the sources of error are discussed, together with the precautions to be observed in order that these errors may be avoided. In the third part are given the methods of procedure which in the opinion of the committee give the most acceptable results.

These conclusions show:

1. That the use of molybdc acid in separating the dissolved phosphate is generally unnecessary.
2. The phosphate soluble in the citric acid employed should be precipitated immediately after its preparation.
3. The precipitation should be accomplished by the iron-citrate-magnesia mixture to be described.
4. The iron-citrate-magnesia mixture should be added with constant stirring.
5. The shaker should have a speed of from 250 to 300 revolutions or vibrations a minute.
6. The temperature of the mixture should not go above 18°.

If the above rules are followed results are obtained which correspond with those secured by other exact methods. Even slags which have an exceptional content of silicic acid can be examined by this method with certainty in the results. It may be considered, therefore, that all the difficulties have been removed, and that a simple method of precipitation which, upon the whole, is much more reliable than those formerly employed, can be applied to the examination of basic phosphatic slags. The solutions employed are as follows:

First.—Concentrated Citric Acid Solution, 10 Per Cent. Exactly one kilogram of chemically pure crystallized uneffloresced citric acid is dissolved in water, diluted to 10 liters, and for the purpose of preventing the growth of mould and other decomposition products, five grams of salicylic acid are dissolved in the mixture.

Second.—Dilute Citric Acid Solution, Two Per Cent. Exactly one volume of the concentrated citric acid solution, above mentioned, is diluted with four volumes of water.

Third.—Molybdc Solution. One hundred and fifty grams of

chemically pure ammonium molybdate are dissolved in about 500 cubic centimeters of water. This solution is poured into one liter of nitric acid, 1.19 specific gravity, 400 grams of ammonium nitrate added thereto, and the mixture diluted with water to two liters. The solution is allowed to stand 24 hours at about 35° temperature and filtered.

Fourth.—Magnesia Mixture. One hundred and ten grams of crystallized magnesium chlorid and 140 of ammonium chlorid are dissolved in 1300 cubic centimeters of water and 700 cubic centimeters of ammonia water containing eight per cent. of NH_3 added thereto. After standing several days the solution is filtered.

Fifth.—Citrate-Magnesia Mixture. Two hundred grams of citric acid are dissolved in 20 per cent. of ammonia and the volume made up to one liter with 20 per cent. ammonia. This solution is mixed with one liter of the magnesia mixture described under "fourth."

Sixth.—Iron-Citrate-Magnesia Mixture. One liter of the citrate-magnesia mixture described under "fifth" is mixed with 10 cubic centimeters of a 20 per cent. ferrous chlorid solution.

Preparation of the Basic Slag for Analysis.—The basic slag which is intended for analysis is passed through a two millimeter mesh sieve in order to remove any large pieces which may be present. All loss of dust during this operation is to be carefully avoided and to this end the sieve is to be closed with a well fitting cover and nicely adjusted to the vessel receiving the sifted material. Any residue remaining upon the sieve is weighed and is excluded from analysis, but is included in the results on the total sample in order to determine the percentage thereof. Thus prepared the material will yield a typical sample for analysis.

178. Preparation of the Citric Acid Extract.—Five grams of the basic slag, prepared as above, are placed in a half-liter flask into which previously five cubic centimeters of alcohol has been poured and the flask filled with the dilute two per cent. citric acid solution at a temperature of 17.5° the flask closed with a rubber stopper and without delay placed in a revolving shaking apparatus rotating at from 30 to 40 times a minute for 30 minutes. The contents of the flask are then immediately filtered.

179. Treatment of the Citric Acid Extract.—The filtrate obtained as above is as soon as possible subjected to the following treatment: Fifty cubic centimeters of the filtrate in a beaker are placed in a stutzer shaking apparatus, which is set in rapid motion from about 250 to 300 vibrations per minute; 50 cubic centimeters of the iron-citrate-magnesia mixture, above noted, are then added, and with the temperature at from 14° to 18° the shaking is continued for half an hour. The precipitate is put in a gooch crucible or upon an ash-free filter, washed with two per cent. ammonia, ignited and weighed in the usual way. If the citric acid solution obtained above is exceptionally light colored or entirely colorless the duplicate estimation is not made according to the described method, but by the molybdate method or by the Naumann method.⁵⁴

The molybdate method is carried out as follows: Fifty cubic centimeters in a beaker or flask are treated with from 50 to 80 cubic centimeters of the molybdic solution, above mentioned, and warmed in a water bath to about 65° . The beaker is then withdrawn from the water bath, cooled and its contents filtered, and the molybdic precipitate carefully washed with a one per cent. nitric acid solution and dissolved in about 100 cubic centimeters of two per cent. ammonia. The ammoniacal solution, with constant stirring, is treated with 15 cubic centimeters of the magnesia mixture, the beaker covered with a glass plate and set aside for two hours. The precipitated ammonium magnesia phosphate is collected upon an ash-free filter or gooch, ashed with two per cent. ammonia, dried, the filter paper, if used, ashed over a bunsen burner and finally ignited in a blast for two minutes, cooled and weighed.

180. Preparation of the Citric Acid Extract of Basic Slag.—The details of the preparation and treatment of the extract are important. It is self-evident that the citric acid solution with which the slag is treated must be prepared exactly as described, and thus must contain 20 grams of chemically pure crystallized uneffloresced citric acid to the liter. For the purpose of diminishing the amount of work it is advisable to keep on hand a quantity

⁵⁴ *Chemiker-Zeitung*, 1903, 27: 12, 27, 120, 155.

of 10 per cent. citric acid solution, which is preserved by the addition of half a gram of salicylic acid per liter. From this store the other solution of citric acid can be prepared. It is important that the citric acid solution which is used, should be as nearly as possible at a mean temperature of 17.5° . Any departure from this temperature is apt to produce errors. For this reason, the shaking machine should be in a room approximately of the same temperature. It is advisable to have the apparatus protected with felt.

In pouring 500 cubic centimeters of citric acid solution on five grams of the sample it is sometimes noticed that small lumps of the slag are produced, which resist for a long while the entrance of the solvent. For this reason it is advisable to use, previously to the introduction of the citric acid solution, five cubic centimeters of alcohol into which the sample of basic slag is poured.

It is inadvisable to use a shaking apparatus in place of the rotating apparatus described. Wagner uses a rotating apparatus made in Darmstadt, which is constructed of metal and driven by a gas motor. The flasks which are to be used in the rotating apparatus are made especially for this purpose according to the specifications of Wagner, and have a neck diameter of at least 20 millimeters and the mark is at least eight centimeters below the mouth. Some care must be exercised in this matter, for if the diameter of the neck is too narrow or the mark too high, the movement of the fluid during rotation is restricted, and thereby the results may be influenced. The rotating apparatus should have a velocity of from 30 to 40 rotations per minute, but any variation of the rate of rotation between these two figures is without any marked influence upon the results.

The filtration ought to take place immediately after the end of the 30 minutes rotation, and it is advisable to use a folded filter of sufficient size so that the whole contents of the flask may be brought at once upon the filter. Small and badly working filters by reason of delay in the filtrations, can easily produce errors in the result. If the filtrate should be at first turbid, it is thrown back upon the filter.

181. Remarks on the Conduct of the Direct Precipitation Method.—The citric acid extract of the basic slag changes by long standing, so far as the external appearance is concerned, very little. It remains for days either completely clear or only slightly turbid, without the production of any precipitate. In spite of this, however, important changes go on in relation to the application of the direct precipitation method, which consist in the fact that any silicic acid in the extract passes over into a precipitable condition upon the addition of ammonia or ammoniacal citrate solution. The precipitability of the silicic acid increases from hour to hour, and it is therefore necessary to precipitate the filtrate extract immediately, or at longest, within an hour.

The precipitability of silicic acid is greatly increased by heat. The shaking apparatus is, therefore, to be supplied with a water bath by which the mixtures during the summer time may be cooled.

The precipitability of silicic acid is very little immediately after the citric acid solution of the phosphoric acid is made. The more, therefore, the precipitation of the phosphoric acid with the magnesia mixture is hastened, the more certainly is avoided any contamination of the precipitate with silicic acid. The precipitation of the phosphoric acid is also hastened as follows:

a. If the ammoniacal citrate solution is not added first, and then the magnesia mixture, but the mixture of both is added to the citric acid extract;

b. The iron-citrate-magnesia mixture is poured into the citric acid extract in the shaking apparatus, which is already in active movement;

c. The shaking apparatus is to be placed in the shortest possible time at its maximum vibration of from 250 to 300 vibrations per minute.

The precipitability of the silicic acid is heightened through a lack of iron in solutions which are rich in silicic acid and poor in iron, therefore a pure precipitate is obtained only when the iron-citrate-magnesia mixture is employed.

182. The Conduct of the Molybdate Method.—a. Great care must

be exercised that the reagents employed in the preparation of the molybdc solutions be absolutely pure.

b. Molybdc solutions before using should be tested for purity by means of a solution of disodium phosphate.

c. The mixture of the citric acid extract and the molybdc solution is to be taken from the water bath when the prescribed temperature has been reached. If the time of digestion be markedly extended a contamination of the precipitate with silicic acid arises, especially when the citric acid extract is not in a fresh condition, but only after from six to 12 hours standing is treated with the molybdc solution.

d. A contamination of the molybdc precipitate with the silicic acid is recognized by the following: Slow solution of the precipitate in ammonia and the production of a solution not completely clear or becoming only slowly so. Under these conditions the process already advised, namely, a reprecipitation of the magnesia precipitate, is to be applied.

183. The Official German Method for Slags Rich in Silicic Acid.

—When the slags are very rich in soluble silicic acid the process of analysis is conducted as follows:⁵⁵

The sample is to be tested for silicic acid by the method of Kellner, which consists in boiling for one minute 50 cubic centimeters of the citric acid extract with 50 cubic centimeters of ammoniacal citrate solution and allowing to stand for a few minutes.⁵⁶ If there is sufficient silicic acid present to interfere with the direct (Böttcher) precipitation of the phosphoric acid, a precipitate is separated which is not entirely soluble in hydrochloric acid. The ammoniacal citrate solution, employed above, contains in 10 liters, 1100 grams of nitric acid, 4000 grams of 24 per cent. ammonia, and water to the mark.

The presence of a disturbing amount of silicic acid having been thus determined, it is separated in the following manner: To 100 cubic centimeters of the citric acid extract of the slag are added 7.5 cubic centimeters of hydrochloric acid of 1.12 specific gravity or five cubic centimeters of fuming hydrochloric

⁵⁵ Die landwirtschaftlichen Versuchs-Stationen, 1904, 60 : 374; 1905, 61 : 351.

⁵⁶ Chemiker-Zeitung, 1902, 26 : 1151.

acid and the mixture evaporated to a thick sirup, smelling of hydrochloric acid. To the hot residue, from 1.5 to two cubic centimeters of hydrochloric acid, 1.12 specific gravity, are added, and the mixture thoroughly stirred and dissolved in enough water to make the volume 100 cubic centimeters. The phosphoric acid is determined in 50 cubic centimeters of the filtrate by the direct method.

The process consists in adding 50 cubic centimeters of the citrate-magnesia mixture to the same volume of the filtered citric acid extract of the slag. The magnesia mixture contains 550 grams of magnesium chlorid and 700 grams of ammonium chlorid dissolved in 3.5 liters of eight per cent. ammonia, and 6.5 liters of water. The ammoniacal citrate solution for mixing with the magnesia mixture, mentioned above, contains 2000 grams of citric acid dissolved in 20 per cent. ammonia, and the volume made up to 10 liters with the same reagent. Before use, equal parts of the magnesia mixture and the ammoniacal citrate solution are mixed together.

184. Böttcher Method.—The Böttcher modification of the direct citrate method of determining the phosphoric acid dissolved from basic slags by citric acid is as follows:⁵⁷

In 50 cubic centimeters of the solution of a slag in citric acid according to Wagner's method, the phosphoric acid is thrown down in the prescribed manner by magnesium citrate solution, the precipitate collected on a filter, washed several times with five per cent. ammonia, and the moist filter ashed. The ash is dissolved in warm hydrochloric acid, the dilute solution passed through a small filter, washed with hot water, and the phosphoric acid again precipitated with the citrate magnesia.

The important point is that after the addition of the citrate of magnesia, the mixture be immediately vigorously shaken and then, without a moment's delay, filtered. Even standing for from half an hour to an hour may cause serious annoyance and introduce serious errors into the results.

The direct precipitation of the phosphoric acid by ammoniacal citrate of magnesia was adopted as the official method in the

⁵⁷ Chemiker-Zeitung, 1897, 21: 168.

general meeting of the delegates of the German agricultural experiment stations, at Cassel, in 1903, both for slags and tricalcium phosphates, and for the general separation of phosphoric acid.⁵⁸

Böttcher, in a later communication, expresses the opinion that if the direct precipitation of the phosphoric acid be carried on with all the promptitude which he has recommended, the previous separation of the silicic acid, when an excess has been indicated by the Kellner test, is rarely necessary.⁵⁹

The great point to be observed is that all the manipulations be conducted without delay. The preliminary test by the Kellner method is chiefly valuable in showing with what samples special precautions are necessary.

185. Separation of Silicic Acid in the Estimation of Phosphoric Acid in Basic Slag, Bone Meal, Etc.⁶⁰—Attention is called by Böttcher to the fact that after the Association of Agricultural Experiment Stations of the German Empire had determined to estimate the citric-acid-soluble phosphoric acid in basic slag by the direct precipitation method in all cases where the preliminary test by boiling with 50 cubic centimeters of ammoniacal citrate solution did not show a high content of silicic acid, the opinion has again come into consideration that the separation of the silicic acid by evaporation with hydrochloric acid is necessary with all basic slags because the direct precipitation sometimes gives results which are too high, even if the preliminary test shows no especially high content of silicic acid, and the solutions very often filter too slowly. Böttcher, however, affirms anew that the conduct of the direct precipitation citrate method never leads to any difficulties of filtration nor to any differences in the results. As he pointed out in a former place, and as he has shown by subsequent analyses, which are given, he has obtained absolutely correct results with all normal basic slags, which with two per cent. citric acid solution gave bright green solutions, even when the preliminary treatment has shown a high content of silica.⁶¹ In

⁵⁸ Die landwirtschaftlichen Versuchs-Stationen, 1904, **60** : 221.

⁵⁹ Chemiker-Zeitung, 1903, **27** : 247.

Zeitschrift für angewandte Chemie, 1904, **17** : 988.

⁶⁰ Chemiker-Zeitung, 1905, **29** : 1293.

⁶¹ Chemiker-Zeitung, 1903, **27** : 247.

all cases, however, the method which he has proposed must be carefully followed out, that is, all the manipulations must follow each other directly without delay, a condition which is easily secured. If, on the contrary, the citric acid extract, or the precipitations with citrate solution and magnesia mixture, or the citrate-holding magnesia mixture, are allowed to stand for several hours, which, in spite of the precise directions given, still sometimes happens, it can readily occur that large quantities of silicic acid come down with the phosphoric acid precipitate and the results are, in consequence, too high. In such cases it is easy to explain why the precipitated phosphoric acids filter badly. In carrying out of the method in cases of bad filtration, it has been observed by Böttcher, in the conduct of over 800 determinations, that if a solution filters badly it is a proof that in some way or other silicic acid has been precipitated, and naturally in such a case, the silicic acid must be removed by evaporation with hydrochloric acid in order that correct results be obtained.

Many comparisons are given by the author of the data obtained by direct precipitation and by precipitation after the separation of the silicic acid. The differences are in all cases negligible between the two methods.

Following are the data from two samples in which the magnesia pyrophosphate was obtained by four different methods, namely:

- (1) Direct precipitation.
- (2) Direct precipitation after separation of silicic acid.
- (3) Direct precipitation by molybdate method.
- (4) Direct precipitation by molybdate method after separation with silicic acid.

The data obtained are as follows:

Method	Weight of Sample I.	Weight of Sample II.
	Grams.	Grams.
(1)	0.1472	0.1435
(2)	0.1466	0.1410
(3)	0.1475	0.1420
(4)	0.1476	0.1436

These analytical data show that basic slags which are not capable of being correctly analyzed by the direct citrate precipitation method are of very seldom occurrence. Nevertheless a pre-

liminary treatment by the citric acid test for silicic acid should not be omitted, since it is a safe means of discovering those samples which must be treated with particular care.

186. Comparison of the Direct and the Molybdate Method for the Estimation of the Total Phosphoric Acid in Basic Slag, Bone Meal, Etc.⁶²—V. Schenke has stated that the direct precipitation of total phosphoric acid in bone meal and basic slags, according to the method of the Association of Agricultural Experiment Stations of Germany, that is, direct precipitation of magnesia mixture, gives from 0.3 to 0.4 per cent. less phosphoric acid than the molybdate method.⁶³ He, therefore, considers it necessary that the strongly acid phosphate solution before precipitation with magnesia mixture should be almost neutralized and only half the quantity, namely, 50 cubic centimeters instead of 100 cubic centimeters, should be treated with the ammonium citrate solution. It has, however, already been shown by the earlier data of Maercker and Halenke, as well as by the latest researches of Mach⁶⁴ that this view of Schenke is not correct, and also the analyses of Böttcher indicate the same fact, and that neutralization of the solution before the precipitation with the citrate solution and the magnesia mixture either by aqua regia or by sulfuric acid is not necessary.⁶⁵ Böttcher says it is claimed by many analysts that by solution of bone meal, etc., with aqua regia and subsequent direct precipitation with citrate solution and magnesia mixture, incorrect and, indeed, higher results are obtained than when sulfuric acid is used for the solution. As a reason for this it is said that the compensation for the errors which take place in the aqua regia solutions is irregular, according to the kind and quantity of the bases which are present in the solution. It is also supposed that in bone meals and other organic substances by reason of the incomplete oxidation with aqua regia, organic acids are formed whose lime salts are equally soluble in the ammonium citrate solution and are, therefore, carried down by the precipitate. In the solutions by sulfuric acid the proportions re-

⁶² *Chemiker-Zeitung*, 1905, **29** : 1294.

⁶³ *Die landwirtschaftlichen Versuchs-Stationen*, 1905, **62** : 3.

⁶⁴ *Die landwirtschaftlichen Versuchs-Stationen*, 1905-6, **63** : 81.

⁶⁵ *Chemiker-Zeitung*, 1905, **29** : 1294.

main essentially more favorable, since not all, but always an equally proportionate part, of the bases go into solution.

In order to prove whether these objections against the solution with aqua regia were correct, Böttcher in different bone meals carried out the estimation of the total phosphoric acid, both by solution with aqua regia and with sulfuric acid. In samples of 50 cubic centimeters of the acid phosphate solution the phosphoric acid was precipitated, according to the methods of the German association, by direct precipitation with citrate solution and magnesia mixture, and in other samples of 50 cubic centimeters according to the modification of Schenke, that is, the approximate neutralization of the solutions with ammonia before the addition of the citrate solution and magnesia mixture.

The data which were obtained show that the objections urged by Schenke are not well founded and that in the case of bone meals, etc., as good results were obtained by solution with aqua regia as with sulfuric acid. If sometimes lower results are obtained after solution in sulfuric acid, the reason lies perhaps in the fact that after the treatment of strong sulfuric acid phosphate solutions with ammoniacal citrate solution a marked heating of the mixture takes place and it is not sufficiently cooled before the addition of the magnesia mixture. This subsequent cooling before precipitation is necessary since otherwise the results fall too low.

187. Estimation of Phosphoric Acid in Slags.—The further discussion of determining the phosphoric acid in slags by the citrate method by Schenke and Mach has introduced certain modifications of an unimportant character, in the process.⁶⁶

In the estimation of the citrate-soluble phosphoric acid in slags by the molybdate method, Schenke follows in general the Wagner method, heating the precipitate only 15 to 30 minutes in a water bath at 80° or 90° and allowing to cool for two or three hours. By this method the precipitation of molybdic acid is most certainly avoided and a bright and clear solution of the precipitate is easily secured in cold dilute ammonia. Impurities due to silicic acid are also avoided.

⁶⁶ Die landwirtschaftlichen Versuchs-Stationen, 1905, 62 : 3 ; 1906, 64 : 87.

In all cases the complete precipitation of phosphoric acid is rendered certain by an addition of molybdate solution to the filtrate.

Schenke calls attention to the important point that if the method of the German stations is strictly followed with the citrate method of determination no precipitate at all of phosphoric acid is obtained where only very small quantities are present. This is the case both with certain soils which contain only a trace of phosphoric acid and certain cattle foods. In such cases the above stated molybdate method gave agreeing results even in these small quantities. The reason for this is said to be the increased solubility of the precipitate of magnesium ammonium phosphate in the double quantity of ammonium citrate solution which is used.

188. Estimation of Total Phosphoric Acid in Basic Slags Soluble in Citric Acid Solutions.—Since the value of basic slag is no longer determined solely by the total content of phosphoric acid therein, the agricultural analysts have never been able to agree upon a satisfactory plan for the valuation of phosphoric acid available for plant growth. The use of citric acid solutions for dissolving the supposed available phosphoric acid is the one which is most commonly employed. It is easily seen, however, that the activity of a solution of this kind depends upon the amount of free lime in the sample, its state of subdivision, the temperature at which the solution takes place and the agitation to which the mixture is subjected. The disturbing influence of silicic acid is also to be taken into consideration and this has been fully discussed. Mach has found in a large number of determinations that the Wagner method in most cases gives satisfactory results while the direct precipitation by the Böttcher method sometimes fails, and in its present form is not to be regarded as reliable as the German experiment station method with previous separation of silica.⁶⁷ It is concluded, therefore, that as a result of the study of all the various methods, the one which is based upon the previous separation of the silicic out of the citric acid extract is the most reliable.

In a study of the different forms of precipitation of total phos-

⁶⁷ Die landwirtschaftlichen Versuchs-Stationen, 1905-6, 63 : 81.

phoric acid in basic slags, Mach also found that while some forms of the citric method of direct precipitation gave very good results, the molybdate method, especially in the case of sulfuric acid solutions of slags, must be regarded, without doubt, as the most reliable.

189. Association and Other American Methods for Basic Slag.—The question of adopting a method for determining the availability of phosphoric acid in slag, has been before the Association of Official Agricultural Chemists for the past three years, and quite a number of reagents and processes have been proposed for this purpose. The practical absence of this form of fertilizer from the American market has prevented the manifestation of much interest in the discussion. Solubility has been determined in 1.09 ammonium citrate, in one per cent. citric acid, in two per cent. citric acid, and in all these after preliminary treatment with water or with five per cent. sugar solution followed by five per cent. ammonium chlorid solution as suggested by Macfarlane.⁶⁸ The referee for 1902 shows that the Wagner method indicates about 80 per cent. of the phosphoric acid in slag as available and the ammonium citrate method, 30 per cent. The former is regarded as too high, and the latter, too low. He suggests that a percentage be established that may be regarded as representing the amount of availability, and a method could then be devised to give this amount.⁶⁹ While no action was taken, the sentiment of the association appeared to be in favor of a valuation based on the determination of phosphoric acid and of fineness as is now the usage in the case of raw bone.

Hilgard has called attention to the increasing use of phosphatic slags in California and attributes their good effects to the large quantity of lime in the arid soils. This condition secures the reversion of the water-soluble acid in superphosphates within the first three or four inches of the surface of the soil. Deep plowing is, therefore, necessary to bring the phosphoric acid into contact with the lower roots of the crop. Such plowing would also mix basic phosphates with the deeper layers of the soil, and

⁶⁸ Division of Chemistry, Bulletin 62, 1901 : 46.

⁶⁹ Bureau of Chemistry, Bulletin 73, 1903 : 16.

since the slags are cheaper than the superphosphates in California, he recommends their use. He is also in accord with the sentiment of the association to value these basic slags, at least provisionally, by their total content in phosphoric acid and their degree of fineness.⁷⁰

Huston and Jones show that the strength of citric acid, time and temperature of digestion, all exert a marked effect on the amount of phosphoric acid dissolved from slags, as does also the relation of quantity of material to volume of solvent.⁷¹ It was found that even when basicity of the slag was corrected the reaction with citric acid was far from complete in 30 minutes at a temperature of 65°. The same conclusion holds with neutral ammonium citrate, though here the differences are not so marked. The work indicates that in a relatively short time all the phosphoric acid will be dissolved, even by dilute citric acid at any temperature, this indicating, further, that the phosphate of basic slag has practically a uniform composition.

190. German Manufacturers' Method.—In the examination of phosphatic slags, the Union of German Fertilizer Manufacturers determine total phosphatic acid after solution, (a) in hydrochloric acid, and (b) in sulfuric acid. In the hydrochloric acid method 10 grams of finely ground phosphatic slag, which has passed through a two millimeter sieve, are placed in a flask of one-half liter capacity, 80 cubic centimeters of concentrated hydrochloric acid added and the mixture evaporated on a sand-bath to a sirupy consistence. The mixture is dissolved in water, treated with a few drops of hydrochloric acid, and after cooling the flask is filled to the mark. In 50 cubic centimeters of the filtrate, after the addition of 100 cubic centimeters of the ammonia-citric acid solution, made up according to the method of Maercker, namely, 1500 grams of citric acid, 5000 cubic centimeters of 24 per cent. ammonia and water to 15 liters, the phosphoric acid is now precipitated by 25 cubic centimeters of the ordinary magnesia mixture, stirred for one-half hour in a shaking apparatus, and after standing two hours, filtered and treated as has already been described for the estimation of phosphoric acid soluble in water.

⁷⁰ Bureau of Chemistry, Bulletin 81, 1904 : 169.

⁷¹ Division of Chemistry, Bulletin 49, 1897 : 68.

In the sulfuric acid method, 10 grams of phosphatic slag, prepared as above described, are covered with a few cubic centimeters of sulfuric acid (one to two) and well shaken. After the addition of 50 cubic centimeters of concentrated sulfuric acid, the mixture is heated at first to boiling and afterwards just to the boiling point, until the mass is evaporated to a thick fluid and violent bumping begins. After cooling, water is gradually added to the mark and the phosphoric acid determined either by the citrate or molybdic acid method.

Estimation of Citric-Acid-Soluble Phosphoric Acid in Basic Slag.—The method of estimating the citric acid soluble phosphoric acid in basic slag is that of Wagner, which has already been described.

191. Estimation of Lime.—When the lime is to be determined in basic slags, some difficulty may be experienced by reason of danger of contamination of the oxalate precipitate with iron and especially manganese, which is often present in slags.

Holleman proposes to estimate the lime in basic slag by modification of the methods of Classen and Jones.⁷² The manipulation is as follows: Fifty cubic centimeters of an acid solution of slag, from which the separated silica has been removed by filtration, equivalent to one gram of substance, are evaporated to a small volume, 20 cubic centimeters of neutral ammonium oxalate solution (one to three) added to the residue and heated on a water bath, with frequent stirring, until the precipitate is pure white and free from lumps. The time required is usually about 10 minutes. The precipitate is collected on a filter and washed with hot water until the filtrate contains no oxalic acid. The precipitated calcium oxalate must be snow-white. The filter is broken and the calcium oxalate washed through, first with water and finally with warm, dilute hydrochloric acid (one to one). The calcium oxalate is dissolved by adding 15 cubic centimeters of concentrated hydrochloric acid, the solution evaporated to a volume of about 25 cubic centimeters, and 10 cubic centimeters of dilute sulfuric acid (one to five), and 150 cubic centimeters of 96 per cent. alcohol added. After standing three hours or

⁷² Chemiker-Zeitung, 1892, 16 : 1471.

more the precipitate is separated by filtration and washed with 96 per cent. alcohol until the washings show no acid reaction with methyl orange. The calcium sulfate precipitated is dried to constant weight. This method gives a pure precipitate of calcium sulfate, containing only traces of manganese.

192. Estimation of Caustic Lime.—The lime mechanically present in basic slags is likely to be found as oxid or hydroxid, especially when the sample is of recent manufacture. In the form of oxid the lime may be determined by solution in sugar. In this process one gram of the fine slag meal is shaken for some time with a solution of sugar, as suggested by Stone and Scheuch.⁷³ The dissolved lime may be titrated directly with standard hydrochloric acid, or the lime is separated as oxalate from the hydrochloric acid solution by treatment of the solution with ammonium oxalate. The calcium oxalate may be determined by ignition in the usual way or volumetrically by solution in sulfuric acid and titration of the free oxalic acid with potassium permanganate solutions. The standard solution of permanganate should be of such a strength as to have one cubic centimeter equivalent to about 0.01 gram of iron. The iron value of the permanganate used multiplied by 0.5 will give the quantity of calcium oxid found.

193. Detection of Adulteration of Phosphatic Slags.—The high agricultural value of phosphatic slags has led to their adulteration and even to the substitution of other bodies. Several patents have also been granted for the manufacture of artificial slags of a value said to be an approximation to that of the by-products of the basic pig iron process.

(1) *Method of Blum.*—One of the earliest methods of examining basic slag for adulterations is the method of Blum.⁷⁴ This method rests upon the principle of the determination of the carbon dioxid in the sample. The basic phosphatic slag is supposed to contain no carbon dioxid. This is true only in case it is freshly prepared. The tetrabasic phosphate, after being kept for some time, gradually absorbs carbon dioxid from the air. As high as 19 per cent. of carbon dioxid have been found in slags

⁷³ Journal of the American Chemical Society, 1894, 16 : 721.

⁷⁴ Zeitschrift für analytische Chemie, 1890, 29 : 408.

which have been kept for a long while. When the slag has absorbed so much of carbon dioxide and water from the air as to be no longer profitable for market, it can be restored to its original condition by ignition. Any great loss on ignition is a ground for suspicion concerning the purity and utility of a slag.

(2) *Method of Richters-Förster*.—One of the common adulterants of tetrabasic phosphate is aluminum (Rodonda) phosphate. The method of detecting this when mixed with the slag is described by Richters-Förster.⁷⁵ The method depends on the fact that soda-lye dissolves the aluminum phosphate, although it does not dissolve any calcium phosphoric acid from the slag. Two grams of the sample to be tested are treated with 10 cubic centimeters of soda-lye of from 7° to 8° B. in a small vessel, with frequent shaking, for a few hours at room temperature. After filtration the filtrate is made acid with hydrochloric and afterwards, slightly alkaline with ammonia. With pure basic slag there is a small trace of precipitate produced, but this is due to a little silica, which can be dissolved in a slight excess of acetic acid. If, however, the basic slag contains aluminum phosphate, a dense jelly-like precipitate of aluminum phosphate is produced.

(3) *Method of Jensch*.—Edmund Jensch determines the tetrabasic phosphate in slags by solution in organic acids, and prefers citric acid for this purpose.⁷⁶ This method was also recommended by Blum.⁷⁷

It is well known that the tetrabasic phosphate in slags is completely soluble in citric acid, while the tribasic phosphate is only slightly, if at all, attacked. The neutral ammonium salts of organic acids do not at first attack the tribasic phosphate at all, and they do not completely dissolve the tetrabasic phosphate. The solution used by Jensch is made as follows: Fifty grams of crystallized citric acid are dissolved in one liter of water. A weaker acid dissolves the tetrabasic phosphate too slowly and a stronger one attacks the tribasic phosphate present.

⁷⁵ *Mitteilungen der deutschen Landwirtschafts-Gesellschaft*, 1890-91, 5 : 131.

Zeitschrift für angewandte Chemie, 1890, 3 : 595.

⁷⁶ *Zeitschrift für angewandte Chemie*, 1889, 2 : 299.

⁷⁷ *Zeitschrift für analytische Chemie*, 1890, 29 : 409.

Schucht recommends the following method of procedure.⁷⁸ One gram of the slag, finely ground, is treated in a beaker glass with about 150 cubic centimeters of Jensch's citric acid solution and warmed for 12 hours in an air-bath at from 50° to 70° with frequent shaking. Afterwards it is diluted with 100 cubic centimeters of water, boiled for one minute and filtered. The filter is washed thoroughly with hot water and the phosphoric acid is estimated in the filtrate in the usual way. With artificial mixtures of basic slags and other phosphates, the quantity of basic slag can be determined by the above method.

(4) *Method of Wrampelmeyer*.—According to Wrampelmeyer, the most convenient method for discovering the adulteration of basic slag is the use of the microscope.⁷⁹ All finely ground natural phosphates are light colored and with a strong magnification, appear as rounded masses. In basic slags the particles are mostly black, but there are often found red-colored fragments having sharp angles, which retract the light in a peculiar way, so that, with a very little experience, they can be recognized as being distinctive marks of pure basic slag.

In artificial mixtures of these two phosphates, which we have made in the laboratory of the Division of Chemistry, we have been able to detect with certainty as little as one per cent. of added mineral phosphate.

One form of adulterating natural mineral phosphates has been mixing them with finely pulverized charcoal or soot to give them the black appearance characteristic of the basic slags. This form of adulteration is at once disclosed by simple ignition or by microscopic examination.

(5) *Loss on Ignition*.—If all doubts cannot be removed by the use of the microscope, the loss on ignition should be estimated. Natural phosphates all give a high loss on ignition, ranging from eight to 24 per cent., while a basic slag gives only a very slight loss on ignition, especially when fresh. A basic slag which has stood for a long while and absorbed carbon dioxide and moisture, may give a loss on ignition approximating, in a maximum case, the minimum loss on ignition from a natural phosphate.

⁷⁸ Zeitschrift für angewandte Chemie, 1890, 3 : 594.

⁷⁹ Die landwirtschaftlichen Versuchs-Stationen, 1894, 43 : 183.

In experiments made in the laboratory of the Division of Chemistry in testing for loss on ignition, we have uniformly found that natural mineral phosphates will lose from nearly one to 2.5 times as much on ignition as a basic slag which has been kept for two years. A basic slag in the laboratory more than two years old gave, as loss on ignition, 4.12 per cent. Several samples of finely ground Florida phosphates gave the following percentages of loss on ignition, as compared with a sample of slag:

Odorless phosphate (slag), 4.12.

Florida phosphates, 8.06, 6.90, 9.58, 6.40, 10.38 and 10.67, respectively.

There are some mineral phosphates, however, which are ignited before being sent to the market. We have had one such sample in the laboratory from Florida which gave, on ignition, a loss of only 1.4 per cent. In this case it is seen that the application of the process of ignition would not discriminate between a basic slag and a mineral phosphate.

It may often be of interest to know what part of the loss, on ignition, is due to loosely held water in form of moisture. In such cases the sample should first be dried to constant weight and then ignited. In the following data are found the results obtained with samples treated as above indicated and also ignited directly. Number one is a basic slag two years old and the others are Florida phosphates.

	Heated to 100° C. then ignited.			Ignited directly.
	Loss at 100° C.	Loss on ignition.	Total loss.	Loss on ignition.
No. 1 (Slag).....	2.57	1.77	4.34	4.12
No. 2 (Rock).....	2.61	5.19	7.80	8.06
No. 3 ".....	1.09	5.77	6.86	6.90
No. 4 ".....	0.42	9.20	9.62	9.58
No. 5 ".....	1.81	4.83	6.64	6.40
No. 6 ".....	4.36	6.52	10.88	10.83
No. 7 ".....	3.31	7.01	10.32	10.67

(6) *Presence of Sulfids.*—Another point noticed in the laboratory of the Division of Chemistry is that the basic slags uniformly contain sulfids which are decomposed upon the addition of an acid with an evolution of hydrogen sulfid.

(7) *Presence of Fluorin.*—In applying the test for fluorin, it has been uniformly found here, that the mineral phosphates respond

to the fluorin test, while the basic slags, on the contrary, respond to the hydrogen sulfid test. This test, however, was applied only to the few samples we have had and may not be a uniform property.

The absence of fluorin might not prove the absence of adulteration, but its presence would, I believe, certainly prove the fact of the adulteration in that particular sample.

The fluorin test is applied by Böttcher in the following manner:⁸⁰ From 10 to 15 grams of the slag are placed in a beaker 10 centimeters high and from five to six centimeters in diameter, with 15 cubic centimeters of concentrated sulfuric acid, stirred with a glass rod, and covered with a watch-glass, on the under side of which a drop of water hangs. If there be formed upon the drop of water a white murky rim, it is proof that a mineral phosphate containing fluorin has been added. After from five to 10 minutes you can notice on the clean watch-glass the etching produced by the hydrofluoric acid. According to Böttcher an adulteration of 10 per cent. of raw phosphate in slag can be detected by this method.

(8) *Solubility in Water.*—Solubility in water is also a good indication, natural phosphates being totally insoluble in water, while a considerable quantity of the basic slag will be dissolved in water on account of the calcium oxid or hydroxid which it contains. If the loss on ignition is low, and the volume-weight and water-solubility high, the analyst may be certain that the sample is a pure slag.

In comparative tests made in the laboratory of the Division of Chemistry with a sample of basic slag and seven samples of Florida phosphate, the percentages of material dissolved by water and by a five per cent. solution of citric acid were found to be as follows:

	Water-soluble. Per cent.	Soluble in 5 per cent. citric acid Per cent.
Basic slag.....	0.97	16.10
Florida phosphate.....	0.01	4.15
“ “.....	0.09	4.66
“ “.....	0.02	3.43
“ “.....	0.08	3.61
“ “.....	0.02	3.79
“ “.....	0.05	4.46
“ “.....	0.02	4.24

⁸⁰ Chemiker-Zeitung, 1894, 18 : 565.

From the above data it is seen that the solvent action of water especially would be of value, inasmuch as it dissolves only a mere trace of the mineral phosphates, approximating one per cent. of the amount dissolved from basic slag. In the case of the citric acid it is found that the amount of materials soluble in this solvent for basic slag is fully four times as great as for the mineral phosphates. Both of these processes, therefore, have considerable value for discriminating between the pure and adulterated article of basic slag.

(9) *Specific Gravity*.—The estimation of the specific gravity is also a good indication for judging of the purity of the slag. This is best done by weighing directly a given volume. Basic slag will have a specific gravity of about 1.9, while natural phosphates will have about 1.6.

(10) *Conclusions*.—From the above résumé of the standard methods which are in use for determining the adulteration of basic slag, it is seen that there are many cases in which grave doubt might exist even after the careful application of all the methods mentioned. If we had only to consider the adulteration of basic slag with certain of the mineral phosphates, that is, tricalcium phosphate, the problem would be an easy one, but when we add to this the fact that iron and aluminum phosphates are employed in the adulteration, and that artificial slags may be so used, the question becomes more involved.

Of the single tests, examination with the microscope appears to be the most fruitful.

In doubtful cases, one after another of the methods should be applied until there is no doubt whatever of the judgment which should be rendered.

DETERMINATION OF OTHER CONSTITUENTS IN NATURAL PHOSPHATES

194. *Water and Organic Matters*.—The sample used for determining water and organic matters, according to the practice of Chatard, should be ground fine enough to leave no residue on an 80 mesh sieve, and should be thoroughly mixed by passing it three times through a 40 mesh sieve.⁸¹

⁸¹ Transactions of the American Institute of Mining Engineers, 1892-93, 21 : 165.

Two grams are placed in a tared platinum crucible, which, with its lid, is placed in an air bath at 105° and heated for at least three hours. The lid is then put on, and the crucible is placed in a desiccator and weighed as soon as cold. The loss in weight is the moisture. The organic matter is determined as below.

Wyatt recommends that two grams of the fine material be heated in ground watch-glasses, the edges of which are separated so as to allow the escape of the moisture.⁸² The heating is continued for three hours at 110° , the watch-glasses then closed and held by the clip, cooled in a desiccator, and weighed. This method is excellent for very hygroscopic bodies, but where quick-acting balances are used, scarcely necessary for a powdered mineral.

The residue from the moisture determination is brought into a platinum crucible and gradually heated to full redness over a bunsen, and then ignited over the blast-lamp. This operation is repeated after weighing until a constant weight is obtained. The loss (after deducting the percentage of carbon dioxide as found in another portion) may be taken as water and organic matter. This method is sufficient for all practical purposes, but when minerals containing fluorin are strongly ignited, a part of the fluorin is expelled; hence, if more accurate determinations are required, the loss of fluorin must be taken into account. It has been proved that a pure calcium fluorid undergoes progressive decomposition at a bright red heat with formation of lime.

195. Carbon Dioxid.—Many forms of compact apparatus have been devised for this estimation, but none of them is more satisfactory than Knorr's apparatus, described in Volume I. Many phosphates must be heated to the boiling point with dilute acid to effect complete decomposition of the carbonates. The distillation method described by Gooch is excellent, and when once the apparatus is set up its work will be found to be rapid and satisfactory.⁸³

Wyatt regards the estimation of carbon dioxide as one of the

⁸² *Phosphates of America*, 4th Edition, 1892 : 144.

⁸³ U. S. Geological Survey, Bulletin 47, 1888 : 16.

most important for factory use. The carbonates present in a sample indicate the loss of an equivalent amount of acid in the process of conversion into superphosphate.⁸⁴

The apparatus employed for estimating carbon dioxide may be any one of those in ordinary use for this purpose. The principle of the process depends on the liberation of the gas with a mineral acid, its proper desiccation, and subsequent absorption by a caustic alkali, best in solution. The methods described for soils in Volume I are generally applicable to this class of materials.

The weight of the sample should be regulated by the content of carbonate. When this is very high, from one to two grams will be found sufficient; when low, a larger quantity must be used. Hydrochloric is preferred as the solvent acid. Those forms of apparatus which are weighed as a whole and the carbon dioxide determined by reweighing after its expulsion, are not as reliable as the absorption apparatus mentioned.

196. Soluble and Insoluble Matter.—To determine the insoluble and by difference the soluble and volatile contents of a mineral phosphate, five grams of the finely ground phosphate are put into a beaker, 25 cubic centimeters of nitric acid (specific gravity 1.20), and 12.5 cubic centimeters of hydrochloric acid (specific gravity 1.12) are added. The beaker, covered with a watch-glass, is placed upon the water bath for 30 minutes. The contents of the beaker are well stirred from time to time, and at the end of the period the beaker is removed from the bath, filled with cold water, well stirred, and allowed to settle. The solution is filtered into a half-liter flask, and the residue is thoroughly washed with cold water, partially dried, and then ignited (finishing with the blast-lamp), and brought to constant weight. The figures thus obtained will, however, be incorrect, because the fluorine liberated during the solution of the phosphates dissolves a portion of the silica. Hence the results are too low. Nevertheless, as the same action would occur in the manufacture of a superphosphate from the same material, the determination may be considered as a fair approximation to commercial practice. The ignited residue must be tested for phosphorus pentoxide.

⁸⁴ Phosphates of America, 4th Edition, 1892 : 145.

197. Treatment of the Solution.—The flask containing the filtrate is filled to the mark with cold water, and the solution is thoroughly mixed by twice pouring into a dry beaker and returning to the flask. Cold water is used for washing the residue, since if hot water be used, the sesquichlorids are apt to become basic and insoluble, and hence to remain in the residue and on the filter paper. Besides, as the flask is to be filled to the mark, the contents must be cold before any volumetric measurements can be made. The solution may then be used for the general determination of the dissolved matters therein.

198. Silica and Insoluble Bodies.—Wyatt describes the following method for determining the total insoluble or siliceous matters in a mineral phosphate.⁸⁵ Five grams of the fine sample are placed in a porcelain dish with about 30 cubic centimeters of aqua regia. The dish is covered with a funnel, placed on a sand bath, and, after solution is complete, evaporated to dryness with care to prevent spluttering. When dry, the residue is moistened with hydrochloric acid and again dried, rubbing meanwhile to a fine powder. The heat of the bath is then increased to 125° and maintained at this temperature for about 10 minutes. When cool, the residue is treated with 50 cubic centimeters of hydrochloric acid for 15 minutes. The acid is then diluted and filtered on a gooch, which is washed with hot water until the filtrate amounts to a quarter of a liter. The residue in the crucible is dried, ignited and weighed. Unless the solution be subsequently boiled with nitric acid, all the phosphoric acid may not be retained in the ortho form.

199. Loss of Silica and Fluorin.—It is difficult to estimate the total silica by the ordinary methods of mineral analysis. This is due to the fact that in an acid solution of a substance containing silicates and fluorids the whole of the silica or the fluorin, as the case may be, may escape as silicofluorid on evaporation. Again, it is not easy to decompose calcium phosphate by fusing with sodium carbonate. If an attempt be made to do this, however, the process should be conducted as follows: A portion of the sample is ground to an impalpable powder in an agate mortar. From one to two grams of the substance are mixed with

⁸⁵ Phosphates of America, 4th Edition, 1892 : 147.

five times its weight of sodium carbonate and fused with the precautions given in standard works on quantitative analysis. The fused mass is digested in water, boiled, and filtered, and the residue washed first with boiling water and afterwards with ammonium carbonate. The filtrate contains all the fluorin as sodium fluorid, and, in addition to this, sodium carbonate, silicate and aluminate. The filtrate is mixed with ammonium carbonate and heated for some time, replacing the ammonium carbonate which evaporates. The silicic acid and aluminum hydroxid which are formed, are separated by filtration and washed with ammonium carbonate. To separate the last portions of silica from the filtrate, add a solution of zinc oxid in ammonia. Evaporate until no more ammonia escapes and separate by filtration the zinc silicate and oxid. Determine the silica in this precipitate by dissolving in nitric acid, evaporating to dryness, taking up with nitric acid and separating the undissolved silica by filtration. In the alkaline filtrate the fluorin may be estimated by the usual method as calcium salt.

200. Estimation of Lime.—The following is the Glaser-Jones method, as practiced by Chatard in the Geological Survey:⁸⁶ One hundred cubic centimeters of the solution (containing one gram of the original substance) are evaporated in a beaker to about 50 cubic centimeters; 10 cubic centimeters of dilute sulfuric acid (one to five) are added; and the evaporation is continued on the water bath until a considerable crop of crystals of gypsum has formed. The solution is allowed to cool, when it generally becomes pasty, owing to the separation of additional gypsum, and 150 cubic centimeters of 95 per cent. alcohol are slowly added, with continual stirring, and the whole is allowed to stand for three hours, being stirred from time to time, filtered, with the aid of a filter-pump, into a distillation flask, and the crystalline precipitate washed with 95 per cent. alcohol. The filter, with the precipitate, is removed from the funnel and inverted into a platinum crucible, so that, by squeezing the point of the filter, the precipitate is made to fall into the crucible, and the paper can be pressed down smoothly upon it. On gentle

⁸⁶ Transactions of the American Institute of Mining Engineers, 1892-93, 21 : 168.

heating of the crucible, the remaining alcohol burns off; and when the paper has been completely destroyed, the heat is raised to the full power of a bunsen for about five minutes. After cooling in a desiccator the crucible containing the calcium sulfate is weighed. The filtration may also be accomplished on asbestos felt.

201. The Ammonium Oxalate Method.—This method has been extensively used in this country in commercial work, and is carried out as described by Wyatt.⁸⁷ The total filtrates from the iron and alumina precipitates, secured as described in paragraph 196, are well mixed and concentrated to a volume of about 100 cubic centimeters. There are added about 20 cubic centimeters of a saturated solution of ammonium oxalate, and, after stirring, the mixture is allowed to cool and remain at rest for six hours. The supernatant liquid is poured through a filter, the residue washed three times by decantation with hot water and brought upon the filter. The beaker and precipitate are washed at least three times. The precipitate is dried and ignited at low redness for 10 minutes. The temperature is then raised by a blast and the ignition continued for five minutes longer, or until the lime is obtained as oxid. The precipitate is likely to contain some magnesia. The magnesia is estimated in the filtrates from the lime determination by first mixing them and concentrating to 100 cubic centimeters, which, after cooling, are made strongly alkaline with ammonia. After allowing to stand for 12 hours, the ammonium magnesium phosphate is collected and reduced to magnesium pyrophosphate by the usual processes. If one gram of the original material has been used, the pyrophosphate obtained, multiplied by 0.36, will give the weight of magnesia contained therein.

202. Lime Method of Immendorff.—The tedious processes required to determine the lime in the presence of iron, alumina, and large quantities of phosphoric acid are well known to analysts. Immendorff has published a method, accompanied by experimental data, based on the comparative insolubility of calcium oxalate in a very dilute solution of hydrochloric acid. He has shown in the data given that the lime is all precipitated in the conditions named and that the precipitate, when properly pre-

⁸⁷ Phosphates of America, 4th Edition, 1892 : 153.

pared, is not contaminated with weighable amounts of the other substances found in the original solution.⁸⁸ The ease with which oxalic acid can be determined volumetrically with potassium permanganate solution aids greatly in the time-saving advantages of the process.

In a hydrochloric acid solution of a mineral phosphate an aliquot part of the filtrate representing about 250 milligrams of calcium oxid, usually about 100 cubic centimeters, is used for the analysis. Ammonia is added in slight excess and then the acid reaction restored with hydrochloric until shown plainly by litmus. The solution is then heated and the lime thrown down by adding a solution of ammonium oxalate in excess. In order to secure a greater dilution of the hydrochloric acid after the precipitation has been made, water is added until the volume is half a liter. Before filtering, the whole is cooled to room temperature. The precipitate is washed first with cold and afterwards with warm water. The well washed precipitate is dissolved in hot dilute sulfuric acid and the solution, while hot, titrated with a standard solution of potassium permanganate set by a solution of ammonio-ferrous sulfate.

If one cubic centimeter of the permanganate represent 0.007 gram of iron it will correspond almost exactly to 0.0035 gram of calcium oxid. The presence of iron in the original solution does not seem to affect the results.

Example.—Sample of mineral phosphate, five grams in half a liter. Strength of potassium permanganate, one cubic centimeter, equivalent to 0.00697 gram of iron and to 0.003484 gram of calcium oxid.

Twenty-five cubic centimeters of the solution, representing one quarter of a gram, in which the lime was precipitated as above described, required 38.4 cubic centimeters of the potassium permanganate to saturate the oxalic acid. Then $38.4 \times 0.003484 = 0.133786$ gram, or 53.51 per cent. of calcium oxid. The method is also applicable to basic slags.

203. Estimation of Iron and Alumina in Mineral Phosphates.

—When mineral phosphates are to be used for the manufacture

⁸⁸ Die landwirtschaftlichen Versuchs-Stationen, 1887, 34 : 379.

of superphosphates by treatment with sulfuric acid their content of iron and alumina becomes a matter of importance. By reason of the poor drying qualities of the sulfates of these bases their presence in any considerable excess of a few per cent. becomes exceedingly objectionable. The quantity of sulfuric acid required for the formation of the sulfates is also a matter of economic importance. The accurate estimation of these ingredients is not only then a matter of scientific interest, but one of great commercial significance to the manufacturer.

The conventional methods so long in use depending on the precipitation of the iron and alumina as phosphates in the presence of acetic acid have been proved to be somewhat unreliable. Not only does the acetic acid fail to prevent the precipitation of some of the lime, but it also dissolves more or less of the iron and aluminum phosphates. The solution of the precipitate and its reprecipitation by the addition of ammonia, may free the second precipitate from lime, but it increases the error due to the solubility of the aluminum salt. The methods recently introduced for the estimation of iron and alumina in presence of excess of lime and phosphoric acid are not entirely satisfactory, but are the best which can now be offered.

204. The Acetate Method.—The principal of this process is based on the fact that in a solution containing iron, alumina, lime and phosphoric acid, the iron and aluminum phosphates can be thrown down in a slightly acid solution by ammonium acetate while the calcium phosphate remains in solution. The acidity in the older methods is due to acetic and can be secured by making the solution slightly alkaline with ammonia and adding acetic to slight acidity. One of the methods of conducting the operation is that of C. Glaser.⁸⁹ This modification of the older processes is based on the assumption that at 70° the iron and aluminum phosphate is quantitatively precipitated by ammonium acetate in a dilute solution containing no free chlorine and that the mixed precipitate of iron and aluminum phosphates obtained at this temperature is free of lime. The operation is conducted in the following manner:

The hydrochloric acid solution of the phosphate must contain

⁸⁹ *Zeitschrift für analytische Chemie*, 1892, **31** : 383.

no free chlorin and is treated with a few drops of methyl orange solution. Ammonia is added until nearly neutral, but the acid reaction is retained, as shown by the indicator. A few cubic centimeters of ammonium acetate are added, which produce a yellow coloration of the liquid and also a complete precipitation of the iron and aluminum phosphates when warmed to 70° . At this temperature the precipitation of any calcium phosphate is avoided. A small quantity of the lime may be carried down mechanically and therefore the precipitate should be dissolved in hydrochloric acid and the precipitation again made as above after the addition of some sodium phosphate. If the original solution contains any free chlorin, as may be the case when aqua regia is employed as solvent, before beginning the separation, ammonia should be added in slight excess and the acidity restored by hydrochloric acid after adding the indicator. In washing the precipitates, water of not over 70° must be used. As has been shown by Hess in the work cited in the next paragraph, the statement that the precipitates obtained as above are free of lime has not been proved to be strictly correct. The process, however, is a distinct improvement over the older methods and forms the basis of the amended process given below, which appears to be sufficiently accurate to entitle the acetate method to favorable consideration.

205. Method of Hess.—Hess has made an investigation of the standard methods of determining iron and aluminum oxids in the presence of phosphoric acid and has shown that the assumption, that the composition of the precipitate is represented by the formula $\text{Al}_2(\text{PO}_4)_2 + \text{Fe}_2(\text{PO}_4)_2$, is erroneous.⁹⁰

In the washing of the precipitated iron and aluminum phosphates, there is a progressive decomposition of the compound with the production of the basic salt. The composition of the precipitate at the end is dependent chiefly upon the way in which the washing takes place. It is quite difficult to always secure a washing in exactly the same way, and the final composition of the precipitate varies with almost every determination. It is not, therefore, an accurate proceeding to take half the weight of the precipitate as phosphoric acid or as iron oxid and

⁹⁰ Zeitschrift für angewandte Chemie, 1894, 7 : 679, 701.

alumina. In every case it is necessary to dissolve the precipitate and determine the phosphoric acid in the regular way. Hess proposes the following method for carrying out the acetate process of separation:

The mineral phosphate should be dissolved in hydrochloric acid and the solution made up to such a volume as shall contain in each 50 cubic centimeters one gram of the original substance. This quantity of the solution is diluted with two or three times its volume of water to which a drop of methyl orange solution (1:100) is added, and ammonia added with constant stirring until the solution is just colored and still reacts slightly acid. Without taking any account of the precipitate which is produced by this approximate neutralization of the solution, there are added 50 cubic centimeters of acid ammonium acetate which, in one liter, contains 250 grams of commercial ammonium acetate. The acidity of the solution is due to an excess of acetic in the commercial salt. The temperature is carried to 70° and the precipitate produced immediately separated by filtration, washed four times with water below 70°, and again dissolved in dilute hydrochloric acid. The solution is mixed with 10 cubic centimeters of a 10 per cent. ammonium phosphate solution and again almost neutralized as described above, and 25 cubic centimeters of the ammonium acetate solution added and warmed to 70°.

The precipitate obtained is once more dissolved and precipitated as above described, and is then collected upon a filter, washed ignited and weighed. The residue after ignition is dissolved in the crucible by heating with a little concentrated hydrochloric acid, and washed into a beaker. Any silicic acid present is separated by filtration, ignited, weighed, and subtracted from the total weight of the precipitate. To the filtrate is added ammonia to diminish the acidity, but not sufficient to produce a precipitate, and the clear solution is mixed with 30 cubic centimeters of the ordinary ammoniacal citrate solution and 15 cubic centimeters of magnesium mixture, and the precipitation of the ammonium magnesium phosphate hastened by stirring with a glass rod.

It is advisable to make the filtrate from the third precipitation slightly ammoniacal and to boil it for a long time. If the opera-

tion has been carried on correctly, there occurs only a slight precipitate of $\text{Ca}_3\text{P}_2\text{O}_8$ amounting only to a few milligrams. In some cases it may be necessary to dissolve the precipitate and reprecipitate the iron and aluminum phosphates a fourth time.

The whole time required for the triple precipitation, according to Hess, if all the operations be properly conducted, is from three to four hours. It is therefore possible by this variation of the acetate method to secure a determination of the iron and alumina as phosphates in the same time which is occupied by the Glaser-Jones method, when the separation of lime is taken into account.

If the solution of the mineral phosphate employed contains any notable quantity of organic material, it must be destroyed by boiling with bromin or some other oxidizing agent, before the precipitation by the acetate method is commenced.

The presence of silicic acid need not be taken into special consideration since this can be detected and determined in the phosphate precipitates after they have been ignited and weighed. The determinations of the phosphoric acid were made by direct precipitation with ammonium in the presence of citrate; they agreed perfectly with the previous precipitations with molybdic solution.

206. Method of Eugen Glaser.—The principle on which this method rests, depends on the preliminary removal of the lime by conversion into calcium sulfate and its precipitation in the presence of strong alcohol.⁹¹ This process does not require the use of acetic acid which in the old method dissolved more or less of the aluminum phosphate, thus introducing errors of considerable magnitude in those cases where the mineral phosphates contained notable quantities of alumina. It is conducted as follows:

Five grams of the phosphate are dissolved in a mixture of 25 cubic centimeters of nitric acid of 1.2 specific gravity and about 12.5 cubic centimeters of hydrochloric acid of 1.12 specific gravity, made up to a volume of half a liter, and filtered. One hundred cubic centimeters of the filtrate, equivalent to one gram of the substance, are placed in a quarter-liter flask and 25 cubic

⁹¹ Zeitschrift für angewandte Chemie, 1889, 2 : 636.

centimeters of sulfuric acid of 1.84 specific gravity added. The flask is allowed to stand for about five minutes and meanwhile shaken a few times. About 100 cubic centimeters of 95 per cent. alcohol are added and then the flask is filled with alcohol to the mark and well shaken. A certain degree of concentration takes place, and this is compensated for by lifting the stopper and filling again with alcohol to the mark and shaking a second time. After allowing to stand for half an hour the contents of the flask are filtered, and 100 cubic centimeters of the filtrate, equal to four-tenths gram of the substance, evaporated in a platinum dish until the alcohol is driven off. The alcohol-free residue is heated to boiling in a beaker with about 50 cubic centimeters of water. Ammonia is added to alkaline reaction, but in order to avoid strong effervescence it is not added during the boiling. The excess of ammonia is evaporated, the flask allowed to cool, the contents filtered, precipitate and filter washed with warm water, dried, ignited and the phosphates of iron and alumina weighed. Half of the weight of the precipitate represents the weight of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$. The estimation, as before indicated, should be carried on without delay, the whole time required not exceeding from one and a half to two hours.

207. Difficulties of the Glaser-Alcohol Method.—The objections on the part of English chemists to the method of freeing dissolved phosphate from lime by means of alcohol preparatory to the separation of iron and alumina are as follows:⁹²

1. To working upon a solution representing as little as 0.4 gram of phosphate.

2. To employing nitro-hydrochloric acid as the solvent for the raw phosphate and consequently to including in the oxids of iron and alumina any iron previously present as pyrite.

3. To the plan of dividing the phosphates of iron and alumina found by two to obtain the oxids of iron and alumina, instead of determining the phosphoric acid in the precipitates and deducting its weight from the total.

4. Should the phosphate under examination contain magnesia, the phosphates of iron and alumina obtained in the foregoing

⁹² Shepherd, *Chemical News*, 1891, 63 : 251.

process must be freed from this impurity by removing the precipitate from the filter, boiling with water and a little nitrate of ammonia and repeating this treatment, if after the first application of it, the filtrate still shows the presence of magnesia.

208. Jones' Variation.—The method of E. Glaser described above, has been found by Jones to be inaccurate on account of the alcohol not being added in sufficient quantity in the precipitation of calcium sulfate and for the additional reason that the amount of sulfuric acid added is more than is actually necessary.⁹³ A further objection to the method is found in the small quantity of the original material, viz., 0.4 gram, which gives only a small precipitate of iron and alumina, especially in those cases where the samples contain only small quantities of these substances. Jones modifies the method as follows: Ten grams of the material are dissolved in nitro-hydrochloric acid and the solution made up to 500 cubic centimeters and filtered. Fifty cubic centimeters of this solution, representing one gram, are evaporated to 25 cubic centimeters and, while still hot, 10 cubic centimeters of dilute sulfuric acid (one to five) added. The mixture is well stirred and 150 cubic centimeters of 95 per cent. alcohol added and, after stirring, the solution is allowed to stand three hours. The calcium sulfate is collected on a filter, washed with alcohol, and the filtrate and washings collected in an erlenmeyer. The washing is completed when the last 10 drops, after dilution with an equal volume of water, are not reddened with a drop of methyl orange. The filtration is conveniently hastened by a moderate vacuum.

The moist calcium sulfate is transferred to a platinum crucible, the filter placed on it, the alcohol burned off, the filter incinerated, and the calcium sulfate ignited and weighed. The precipitate is not sufficiently hygroscopic to offer any difficulties to conducting the operations in an open dish. The contents of the flask are heated to expel the alcohol, which is contaminated with hydrochloric or nitric acid and can not be used again until distilled over an alkali. The residue is washed into a beaker, made slightly alkaline with ammonia, and again heated till all the ammonia is

⁹³ *Zeitschrift für angewandte Chemie*, 1891, 4 : 3.

driven off. This treatment is necessary to prevent the iron phosphate precipitate from being contaminated with magnesia. The precipitate is collected on a filter, washed four times with hot water, or water containing neutral ammonium nitrate, dried, ignited, and weighed. One-half of the weight of the precipitate represents the weight of the ferric and aluminic oxids. The magnesia is thrown out of the filtrate by saturation with ammonia and allowing to stand 12 hours. The phosphoric acid, alkalies and sulfuric acid are determined in the original sample by the usual methods. Jones' variation of the E. Glaser method has been generally approved by experience and is to be recommended in general in place of the original process.⁹⁴

209. Estimation of Iron and Alumina in Phosphates by Crispo's Method.—The phosphate of ferric iron is subject to a slight decomposition in presence of both hot and cold water with a tendency to the production of basic compounds. It is soluble to a slight extent in hot and cold acetic acid, almost insoluble in ammonium acetate, and quite insoluble in ammonium chlorid and nitrate. Aluminum phosphate is likewise soluble, to a slight degree, in acetic acid and ammonium acetate, and insoluble in ammonium chlorid and nitrate. The method of Crispo, as practiced in the laboratory at Antwerp, for the separation of iron and alumina in phosphates is based on the above properties.⁹⁵ Five grams of the mineral phosphate are dissolved in 500 cubic centimeters of aqua regia, containing 40 cubic centimeters of hydrochloric acid of 1.10, and 10 of nitric acid of 1.20 specific gravity. To 50 cubic centimeters of the filtered solution are added two of ammonia (0.96) and 50 of a half-saturated solution of ammonium chlorid, and the whole boiled. The liquid should remain clear, but if it becomes cloudy add a little dilute nitric acid, drop by drop, until the turbidity is removed, and then 10 cubic centimeters of a saturated solution of ammonium acetate, boil for three minutes, cool, and filter. The precipitate is washed twice with a 10 per cent. solution of ammonium chlorid and redissolved with two cubic centimeters of nitric acid, and the filter

⁹⁴ von Grüber, *Zeitschrift für analytische Chemie*, 1891, **30** : 206.

⁹⁵ First International Congress of Applied Chemistry, Brussels, 1894, *Proceedings* : 20.

washed with hot water. The phosphoric acid is separated by 40 cubic centimeters of molybdate solution, and the precipitate washed three or four times with a one per cent. nitric acid solution.

To the filtrate are added 50 cubic centimeters of a half-saturated ammonium chlorid solution, ammonia is added in slight excess to produce precipitation and the mixture boiled for a few minutes. After filtering, the precipitate is washed with hot water three or four times, dissolved in two cubic centimeters of nitric acid, and the filter washed with hot water. Again, 50 cubic centimeters of half-saturated ammonium chlorid solution are added and the precipitate thrown down once more by ammonia in slight excess. The precipitate is washed with hot water and finally ignited and weighed as iron and aluminum oxids.

According to Crispo, the original Glaser method, with its various modifications, is not to be considered reliable, and the choice lies between the molybdate method as usually practiced, and his own for the accurate estimation of iron and alumina. Manganese disturbs the accuracy of the results unless the directions given are carefully followed. Manganese phosphate is soluble at all temperatures below 50. If then the mixture of the phosphates be allowed to cool before filtering, the iron and aluminum salts are not contaminated with manganese. This method of Crispo is somewhat tedious, but it is claimed that these variations render it exact in respect of the determination of iron and alumina.

210. Variation of the Alcohol Method.—Chatard conducts the Glaser-Jones process as follows:⁹⁶ The distillation flask containing the alcoholic filtrate is connected with its condenser and heated on a water bath until no more alcohol comes over. This distillate, if mixed with a little sodium carbonate and redistilled over quicklime, can be used over and over again, so that the expense for alcohol is really very slight, while in the use of the Glaser method, with its large amount of sulfuric acid, all the alcohol is lost.

When the distillation is ended the residue in the flask is

⁹⁶ Transactions of the American Institute of Mining Engineers, 1892-93, 21 : 169.

washed into a platinum dish and evaporated to a small bulk on the water bath. The dark brown color produced is due to the presence of organic matter and this must be destroyed, as it prevents the complete precipitation of the phosphate in the subsequent operation.

The organic matter is best destroyed by removing the dish from the bath, adding a small quantity of pure sodium nitrate, and heating very carefully over the naked flame, keeping the dish well covered with a watch-glass to avoid spattering. The mass fuses to a colorless, viscous liquid, becoming glassy when cooled and is readily soluble in a hot, very dilute solution of nitric acid. The solution transferred to a beaker is made distinctly alkaline with ammonia and carefully neutralized with acetic acid, diluted with hot water, boiled, and the precipitate of iron and alumina phosphates allowed to settle, after which it is separated by filtration.

After the precipitate has been completely transferred to the filter, the washing is completed with a dilute solution of ammonium nitrate. The precipitate is dried, ignited, cooled, and weighed.

The determinations should be made in pairs, and one of the precipitates used for the estimation of phosphoric acid, by fusing with a little sodium carbonate, and the other, after fusion with sodium carbonate, is dissolved with sulfuric acid and the iron reduced and titrated with potassium permanganate solution. The filtrate from the iron and alumina determination is evaporated to a small bulk, made strongly ammoniacal and allowed to stand for some time, when the magnesia present separates as ammonium magnesium phosphate, which is determined in the usual way.

If, during the evaporation of the filtrate, any flocculent matter separates, it should be removed by filtration and examined before precipitating the magnesia.

211. Variation of Marioni and Tasselli.—The old and classic method of separating iron and alumina in the presence of ammonium acetate has been shown to be subject to errors by Marioni and Tasselli in the following respects:⁹⁷

⁹⁷ *Le Stazioni sperimentali agrarie italiane*, 1892, **23** : 31.

1. The precipitation of a small quantity of calcium phosphate with the ferric and aluminum phosphates.

2. The possible precipitation of basic phosphates if all the iron and alumina are not combined with phosphoric acid in the mineral.

3. The partial solubility of ferric and aluminum phosphates in dilute acetic acid.

4. The decomposition of ferric orthophosphate into soluble acid phosphate and insoluble basic salt by washing with boiling water.

To avoid these errors the following procedure is proposed: From one to five grams of the sample according to its richness in phosphoric acid is boiled in a flask for 10 minutes with 15 cubic centimeters of strong hydrochloric acid, and afterwards diluted with a double volume of water. A few crystals of potassium chlorate are added, or several drops of nitric acid, and the liquid boiled to expel chlorine. The solution is filtered and the filter washed until the volume of the filtered liquid amounts to 150 cubic centimeters. After cooling, a half-gram of neutral ammonium phosphate in solution is added, and two cubic centimeters of glacial acetic acid, followed by ammonia, drop by drop, until a slight precipitate persists on stirring. The mixture is made decidedly alkaline by adding ammonia gradually until the alkaline reaction is established. Again the same quantity of acetic acid is added as above, well shaken, and left for two hours. The precipitate is collected on a filter and washed with a 10 per cent. ammonium phosphate solution. The precipitate is dissolved by a minimum quantity of hydrochloric acid and the solution collected in the same vessel in which the precipitation took place. A second precipitation is conducted just as described above. The precipitate is washed as above described and ignited at a dull red heat. Half the weight obtained represents the ferric oxide and alumina.

Following these variations, in which the principal novelty is the solvent action on the mixed precipitates produced by ammonia, by which all are dissolved save the iron and aluminum phosphates, the authors claim to get accurate results.

212. Suggestion of Ogilvie.—When a phosphate is dissolved in a mineral acid preparatory to the separation of the various substances which pass into solution, most authorities advise that the solutions be brought to dryness before proceeding to separate the calcium. Some analysts, however, neglect this part of the process, and, as Ogilvie has shown, with a chance of error.⁹⁸ It appears from this fact that in the analyses of the majority of the phosphatic products in use for manurial purposes, special care must be exercised to procure a pure and perfectly granular precipitate of magnesium ammonio-phosphate, either by evaporating the first solution to dryness, or by separating the precipitate which forms on the addition of ammonia to the solution containing citric acid.

213. Method of Krug and McElroy.—Krug and McElroy show that when sufficient alcohol is added to precipitate all of the calcium sulfate in the Glaser method, it will also cause a precipitation of a considerable quantity of iron, by means of which the calcium sulfate will be colored.⁹⁹ The presence of potassium and ammonium salts also affects very notably the precipitation of calcium. The procedure suggested, in order to avoid these sources of error, is based on the separation of the phosphoric acid by the molybdate method and is as follows:

One hundred cubic centimeters, equivalent to one gram of the substance, in a nitric acid solution, are placed in a half-liter flask and a solution of ammonium molybdate added until all the phosphoric acid has been precipitated. The addition of ammonium nitrate will hasten the separation of the ammonium phosphomolybdate. The liquid should be allowed to stand for 12 hours. The flask is filled to the mark, the contents well shaken, filtered through a dry filter, and duplicate samples of 200 cubic centimeters each of the filtrate subjected to examination.

A small quantity of ammonium nitrate is dissolved in the liquid, and ammonia cautiously added, keeping the solution as cool as possible. The iron and alumina are precipitated as

⁹⁸ Crookes, *Select Methods in Chemical Analysis*, 4th Edition, 1905 : 499.

⁹⁹ *Journal of Analytical and Applied Chemistry*, 1891, 5 : 671.

Zeitschrift für angewandte Chemie, 1891, 4 : 170, 243, 357.

Zeitschrift für analytische Chemie, 1891, 30 : 206.

Chemical News, 1891, 63 : 251.

hydroxids. The mixed hydroxids are collected on a filter, washed with water, the filtrate and washings being collected in a beaker.

The precipitate is dissolved with a small quantity of a solution of ammonium nitrate and nitric acid, again precipitated with ammonia, filtered, washed, ignited, and weighed. This treatment is for the purpose of excluding all possibility of error from the presence of molybdic anhydrid. After weighing, the mixed oxids are fused with sodium bisulfate, the magma dissolved in water, and the iron determined volumetrically with potassium permanganate after reduction to the ferrous state.

McElroy has shown later that even the molybdate method of separating the iron and alumina from phosphoric acid with the improvements as first suggested by Krug and himself, may not always give reliable results.¹ In a solution containing ferrous iron equivalent to 56.4 milligrams of ferric oxid, was placed enough of a solution of sodium phosphate to correspond to 100 milligrams of phosphorus pentoxid. The precipitate was dissolved by adding nitric acid, oxidized with bromin water, and the phosphoric acid thrown out with ammonium molybdate. The precipitate was washed with weak nitric acid and the combined filtrate and washings neutralized with ammonia. The resultant precipitate was dissolved in a solution of ammonium nitrate and nitric acid, filtered, and again precipitated with ammonia. In two instances the quantities of material recovered after ignition were 56.9 and 57.3 milligrams, respectively, instead of the theoretical amount, viz., 56.4 milligrams.

When the work was repeated after the addition of 400 milligrams of calcium oxid the weight of the precipitate recovered was 62.3 and 63.1 milligrams in duplicate determinations. Similar determinations were made with a known weight, viz., 35.6 milligrams of alumina. The treatment of the mixture was precisely as indicated above for iron. The quantity of alumina finally obtained was 28.9 and 29.3 milligrams, respectively, in duplicate determinations. When the lime was added, however, the weights of alumina recovered fell to 19.8 and 20.6 milligrams respectively. These results show that the molybdate method for

¹ Journal of the American Chemical Society, 1895, 17 : 260.

the separation of iron and alumina in the presence of a large excess of lime and phosphoric acid is subject to widely varying results, but that the error due to the excess of iron in the weighed product is partly corrected by the one due to the deficiency of alumina.

214. Method of Wyatt.—A method, formerly very extensively used in this country, both in private laboratories and by fertilizer factories, for determining iron and alumina is described by Wyatt.² It is claimed for this method, which is a modification of the acetate process, that, while it may not be strictly accurate, yet it is rapid and easy, and in the hands of trained analysts yields concordant results. Fifty cubic centimeters of the first solution of the sample in aqua regia, or an amount thereof equivalent to one gram of the phosphate, are rendered alkaline by ammonia. The resulting precipitate is first redissolved by hydrochloric acid, and then a slight alkalinity is again produced with ammonia. Fifty cubic centimeters of strong acetic acid are added, the mixture stirred, placed in a cool place and left until cold. The precipitate is separated by filtration and washed twice with boiling water. The vessel holding the filtrate is replaced by the beaker in which the precipitation was made. The precipitate is dissolved in a little 50 per cent. hot hydrochloric acid and the filter washed with hot water. After rendering slightly alkaline, as in the first instance, the treatment with acetic acid is repeated as described. The precipitate is washed this time, twice with cold water containing a little acetic acid and three times with hot water. The precipitate is dried, ignited, and weighed as iron and aluminum phosphate. Half of this weight may be taken to represent the quantity of iron and aluminum oxids, for all the general purposes of the factory or the control of the daily work at the mines.

To separate the iron and alumina the ignited precipitate just described is dissolved in hot hydrochloric acid, filtered into a 100 cubic centimeter flask, and made up to the mark by hot wash-water.

The phosphoric acid is determined in one-half of the filtrate and in the remaining half the iron is reduced with zinc and

² Phosphates of America, 4th Edition, 1892 : 150.

determined with potassium permanganate in the usual way. The phosphoric acid and iron having been thus determined, the alumina is estimated by difference. The chief objection to this process is in the excessive quantity of acetic acid used and the danger of solution of the precipitated phosphates caused thereby.

215. Estimation of the Lime and Magnesia.—The filtrate and washings from the first precipitation, (paragraph 213) of iron and alumina in the method of Krug and McElroy, above described, are collected and sufficient ammonium oxalate is added to precipitate the calcium. The precipitated calcium is very fine and should be collected on a gooch, without pressure. The filtrate and washings from the calcium precipitate are again collected, and a solution of sodium phosphate added to precipitate the magnesia. The solution must be kept cool and slightly alkaline with ammonia during the above operations in order to prevent the separation of molybdic anhydrid.

216. Separation of Iron and Aluminum Phosphates from the Calcium Compound.—There are many points of difference noted in the descriptions given by authors of the deportment of the iron and aluminum phosphates in presence of a large excess of the calcium salt. Especially is this true of the statements made by Hess and Glaser.³ The subject is of such importance, from an analytical point of view, as to merit a careful study.

In the laboratory of the Division of Chemistry a thorough investigation of the mutual deportment of these three phosphates has been made by Brown with the following results:⁴ When a mixture containing a known weight of the salts is treated exactly as Hess directs, in no case is there a complete separation of the iron aluminum phosphate from the calcium salt. In order to discover the cause of the failure, pure solutions of calcium and iron aluminum phosphates are treated under identical conditions by the necessary reagents. Fifty cubic centimeters of a solution of calcium phosphate, containing about one gram of the salt, are treated with 100 cubic centimeters of water and 50 cubic centimeters of the commercial ammonium acetate containing 150 grams

³ *Zeitschrift für angewandte Chemie*, 1894, **7** : 679, 701 ; 1889, **2** : 636.

⁴ Report to Author by W. G. Brown, 1894.

of the salt in a liter. An immediate precipitate is produced at ordinary temperatures, and on heating to 60° it becomes abundant. The addition of ammonium chlorid, phosphate, and nitrate in successive portions, does not prevent the precipitation. Making the solution more dilute lessens the difficulty. When 20 cubic centimeters of a 10 per cent. solution of ammonium phosphate are first added, followed by the usual quantity of ammonium acetate, a clear crystalline precipitate is sometimes observed. Experience also shows that the trouble is not due to an excess of the ammonium acetate.

In treating a solution of iron-aluminum phosphate, in similar circumstances, with the ammonium acetate, it is found that a complete precipitation takes place.

Since diluting the solution of the calcium salt diminishes its tendency to form a precipitate with the ammonium acetate, the true method of separation seems to lie in that direction. The calcium salt is held completely in solution when the separation is made in the following way:

The solution containing the mixed phosphates is diluted so as to contain not more than one gram thereof in half a liter. To this is added one drop of methyl orange, and afterwards ammonium hydroxid, until a very slight precipitate is formed. The mixture is heated to 70° and from 20 to 25 cubic centimeters of a 25 per cent. solution of acid ammonium acetate are added, enough to change the rose color of the indicator to orange. The iron-aluminum phosphate is separated by filtration and washed with a hot five per cent. solution of ammonium nitrate.

The washed precipitate shows no impurity due to calcium, as is proved by dissolving it, reprecipitating and filtering, adding ammonium hydroxid to the filtrate, and heating for a long time. Sometimes a slight troubling of the clear liquid may be observed which may be due to a slight solubility of the iron-aluminum phosphate in washing, an accident that may occur if the temperature be allowed to fall below 70° , but no weighable amount of material is obtained. If due to calcium phosphate, a greater dilution in the first precipitation will remove even this mere trace of that salt. In the above conditions the contamination of the

iron-aluminum precipitate with calcium phosphate may be entirely avoided. The problem of separating the phosphoric acid by the citrate method, followed by a destruction of the citric acid in the filtrate by combustion with sulfuric acid according to the kjeldahl process, and final separation of the iron and alumina in the residues was already under way when our attention was called to substantially the same process described by Jean.⁵ The method merits a further critical examination.

217. Methods of the German Fertilizer Association.—The methods of determining phosphoric acid and other constituents in mineral phosphates according to the directions prescribed by the Union of German Fertilizer Manufacturers differ only in unimportant details from other German methods described.⁶

Water-Soluble Phosphoric Acid.—This method is applied to superphosphate, phosphate precipitates and raw phosphates, but is not applicable to phosphatic slags. The extraction is performed upon 20 grams of superphosphate in a liter flask. The sample is covered with 800 cubic centimeters of water, shaken for 30 minutes and filled up to the mark. The ordinary shaking machine is used. In cases of double phosphates they should be previously boiled with nitric acid in order to convert any pyrophosphate into orthophosphate. It is recommended that the final precipitation of the phosphoric acid be conducted according to the usual molybdic acid method with only a few unimportant variations.

The Citrate Method.—In lieu of the molybdic acid method the Union of German Fertilizer Manufacturers also recommends the citrate method, which is carried out as has already been described, with unimportant variations.

Volumetric Method by Titration with Uranium Salts.—This method, although recognized as being a very old one, is recommended in cases where there are no large quantities of iron and alumina. The method as used does not differ in any marked respect from that already given.

Citrate-Soluble Phosphoric Acid.—The method of securing the

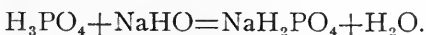
⁵ Journal de Pharmacie et de Chimie, 1895, [6], 1 : 99.

Chemisches Central-Blatt, 1895, 1 : 562.

⁶ Methoden zur Untersuchung der Kunstdüngemittel, 1903 : 2.

phosphoric acid which is soluble in a standard solution of citrate of magnesia is that of Wagner, which has already been fully described.

Free Phosphoric Acid.—Two methods are given for determining the free phosphoric acid which may be present in a fertilizer. The titration method is carried out as follows: The free phosphoric acid is extracted with the water-soluble as already described. An amount corresponding to one gram of the original substance is diluted to about 100 cubic centimeters and two or three drops of an aqueous solution of methyl orange made up in the proportion of one part of pure salt to 100 parts of water added. The titration is accomplished by means of soda lye of known strength until the red color is converted into yellow. In the standardizing of the soda lye a pure solution of phosphoric acid of known strength is used and in about the same dilution as that expected in the fertilizer. The change of color takes place immediately when the primary salt is formed from the phosphoric acid according to the following formula:



It is advisable to pass beyond the titration mark in the addition of a soda lye; afterwards separate the precipitate by filtration and titrate back the excess of alkali with a standard acid in an aliquot part of the filtrate. By this method the change of color can be more easily recognized. This back titration, however, is attended with an error due to the fact that a portion of the excess of soda lye may adhere to the precipitate and the more so in proportion as the amount of excess is greater. A slight correction, therefore, should be made, which is determined by experiments, in order to avoid obtaining too high a content of free acid by this method. In the second method the usual gravimetric process with molybdate solution is used.

Estimation of Iron and Alumina.—This is conducted according to the method of Glaser and Jones as has already been described.

Estimation of Fluorin.—For the purpose of determining fluorin the method of Fresenius and Richters is employed. There are two variations of the method, one for raw phosphate and the other for superphosphate. In the case of a raw phosphate five

grams are treated in a platinum dish with 20 cubic centimeters of a 20 per cent. acetic acid on a water bath until all the carbonic acid is eliminated. The mass is then evaporated to dryness and ignited in order to remove the moisture and any organic substance that may be present. The ignited mass is mixed with about 20 grams of pure ignited quartz sand, then placed in a dry flask of about 250 cubic centimeters capacity and treated with 40 cubic centimeters of pure concentrated monohydrate sulfuric acid. The flask is stoppered in such a way as to connect with it two U-tubes filled with water and is then heated for four hours to 140°. After the decomposition is completed a stream of warm air amounting in all to about one liter is drawn slowly through the apparatus. The contents of the U-tubes are poured into a beaker and the hydrofluosilicic acid is treated with one-half-normal soda-lye, using phenolphthalein as indicator. In case there are only small quantities of fluorin, namely, only one-half of one per cent., it is advisable to add some fluorid of calcium of known composition and the quantity of fluorin obtained is corrected by deducting the added fluorin from the total secured. In the case of superphosphate there is added to the five grams of substance a sufficient amount of milk of lime to produce a distinct alkaline reaction. The mixture is then evaporated and ignited as above. After cooling, the mass is rubbed with a pestle and poured through a dry funnel into the decomposition flask above mentioned. The platinum dish and funnel are repeatedly rinsed with finely ground, ignited quartz powder. The rest of the process is carried on as has just been described.

218. French Method for Mineral Phosphates.—The French official methods are adapted to determine phosphoric acid in various forms.⁷

First—Mineral phosphates composed chiefly of dry calcium phosphate mixed in a greater or less degree with carbonate of lime, silicious materials, etc., and in different degrees of fineness as secured by the usual mechanical means.

Second—Phosphate of fresh bone, phosphate of degelatinized bone, animal black, char from the sugar refining factories, etc.

⁷ Grandeau, *Traité d'Analyse des Matières agricoles*, 3d Edition, 1897, 1 : 443.

Third—Phosphate in products such as farm-yard manure, poudrette, guano, etc.

Fourth—Phosphates which have been treated by chemical processes producing superphosphates whether from bone or mineral phosphates, precipitated phosphates, ammoniaco-magnesium phosphates, etc.

Fifth—Phosphates which are produced in metallurgical operations, such as basic slag, etc.

The methods employed for these various processes are not essentially different from those which are already described. There are certain slight variations in the methods of preparation which are of interest but do not introduce any new principles or methods of procedure.

219. Method of Lasne.⁸—With ordinary phosphates, containing as much as three per cent. of alumina a convenient quantity to use is two grams. If the phosphate be poor in alumina, a larger quantity may be employed. The phosphate in a fine powder is dissolved in hydrochloric acid with or without the addition of nitric acid, as may be desired. The solution is evaporated to dryness, moistened several times with hydrochloric acid and again dried to render the silica totally insoluble. The soluble parts of the residue are taken up in dilute hydrochloric acid (one part strong acid to 20 of water) so as not to have more than 1.5 grams of HCl to each gram of phosphate. The solution may be either filtered and washed or made up to a known volume, filtered through a dry filter and an aliquot part of the filtrate employed for the subsequent analysis.

A convenient quantity of the filtrate to employ is one which corresponds to 1.25 grams of the original phosphate in case two grams have been taken.

Meanwhile, there should be prepared a solution of five grams of caustic soda free of alumina and silica. This is dissolved in a nickel dish with about 10 cubic centimeters of water. The quantity of soda to be employed is to be calculated as follows: Two grams per gram of the phosphate and one gram for each 100 cubic centimeters of the final volume employed. There is added

⁸ Bulletin de la Société chimique de Paris, 1896, [3], 15 : 6, 118, 146, 237.

to the liquor one gram of phosphate of soda containing about 20 per cent. of phosphoric acid. It is necessary to call attention to the fact that the liquor is to contain enough of phosphoric acid to completely saturate the lime and that the acid be in excess at least one decigram. It will be necessary, therefore, to increase a little the quantity indicated if the phosphate is very rich in carbonate. For certain chalky phosphates, it will be necessary to use as much as two grams of the phosphate of soda.

The soda liquor thus prepared is poured in a fine stream into the solution of the phosphate prepared as above, and its constantly stirred with a metal spatula. After the addition of the soda, the mixture is heated to about 100° for half an hour, but it is preferable to prolong the heating for an hour, stirring from time to time. After cooling, the mixture is placed in a flask marked at 250 cubic centimeters, and the volume completed with water to the mark.

To be able to take account of the volume of the precipitate, a half cubic centimeter of water, in addition, is added. The mixture is strongly shaken several times and left for half an hour in order to permit the complete diffusion of the liquid throughout the precipitate. The contents of the flask are next poured upon a dry filter and 200 cubic centimeters of the filtrate corresponding to one gram of the original phosphate, in case two grams have been used, employed for the estimation of the alumina.

It has been proved that by this treatment all the bases, except alumina, which can be present, have been retained as phosphates, while the phosphate of alumina has remained completely soluble.

The 200 cubic centimeters of the filtrate, obtained as above, are placed in an erlenmeyer and hydrochloric acid added until the precipitate at first formed is just dissolved. There are then added 25 cubic centimeters of a solution of ammonium chlorid containing 125 grams per liter. Ammonia is then added until there is formed a precipitate which persists. The mixture is next heated to near ebullition and with great care a solution of dilute ammonia is added. The heated mixture should not give off more than a feeble odor of ammonia, and it is highly important that the ammo-

nia be not added in excess. The mixture is then boiled for five minutes. It is allowed to rest for some moments and then filtered still hot. The precipitate is drained upon the filter and the filter and the precipitate in the erlenmeyer washed only once. The precipitate both on the filter and remaining in the erlenmeyer is then redissolved in from 20 to 25 cubic centimeters of hydrochloric acid diluted to one-twentieth and heated to 100° . The solution in the erlenmeyer and the wash-waters from the filter are united in an erlenmeyer and treated with 3.5 cubic centimeters of a 10 per cent. solution of ammonium phosphate. This solution should contain about 53.4 grams of phosphoric acid per liter. There is then 0.187 gram of phosphoric acid in excess, and this condition should be realized as nearly as possible. Ammonia is added until a light precipitate persists which is dissolved with great care in a few drops of dilute hydrochloric acid, in such a manner that the mixture clears up gradually after agitation. This having been accomplished, 1.5 grams of hyposulfite of ammonia are added, or 10 cubic centimeters of a solution of this salt containing 150 grams per liter. The volume of the mixture is completed to about 250 cubic centimeters, and afterwards it is carried to boiling, which is continued 30 minutes, the volume of water being kept up by occasional additions. At the end of this time the precipitation is easily completed. Nevertheless, in order to have a greater certainty, there should be added, after suspending the boiling for a moment, from four to five drops of a saturated solution of ammonium acetate. This salt, which in large quantities dissolves phosphate of alumina, has no influence in so small a quantity. The boiling is then continued for five minutes longer. After allowing to settle for a few minutes the liquor is filtered still hot. The precipitate does not adhere to the walls of the flask and is easily collected upon the filter where it is washed seven or eight times with boiling water. The collected precipitate, after drying, is incinerated and kept at a white heat for 15 minutes in the blow-pipe before weighing. The composition of this precipitate is exactly $P_2O_5Al_2PO_3$. The weight of the precipitate multiplied by 0.418 gives the weight of the alumina therein.

There is in the second precipitate mentioned above a slight loss of alumina which precise experiments have shown me to be 0.8 milligram. This is due to a solubility which depends only on the volume of the liquid and not upon the weight of the precipitate. Eight-tenths of a milligram should, therefore, be added to the weight of the alumina as determined above.

220. Comparison of Methods of Estimation of Iron and Alumina in Phosphates.—Blattner, in collaboration with Brasseur, at Lille, has made a comparative examination of some of the methods in use of determining the iron and alumina in natural phosphates. They have examined the following processes:

1. The process of Maret and Delattre, which is very extensively employed in France.
2. The method of E. Glaser.
3. The method of H. Lasne.
4. The method of J. Grueber.

The results of their studies are as follows:

1. The method of Maret and Delattre gives results which are not accurate, the quantities of iron and alumina being usually too small.
2. The method of E. Glaser, embracing separate determinations for the oxid of iron and alumina is able to give exact results, but if the phosphates contain manganese this substance goes also in the precipitate and is counted as alumina, and as a result the figures for alumina obtained by the method of Glaser are too high when manganese is present.
3. The method of Lasne gives results which are rigorously exact when conducted with reagents which are perfectly pure. It is the most exact method known up to the present time, and has been tried by the authors in the most minute detail. It can be regarded as a standard method.
4. The method proposed by Grueber appears to be an abridgement of the method of Lasne. The authors, however, prove that it does not give correct results. Grueber applied it to phosphates which were prepared by synthesis and which contained only certain of the matters, and not at all, which enter into the composition of natural phosphates. Where a great deal of lime

is present, by the modification of Grueber no alumina at all is obtained sometimes, when it may be present to the extent of half a per cent. The results of the investigation favor entirely the adoption of the method of Lasne to the exclusion of the others.⁹

221. The Estimation of Alumina and Ferric Oxid in Natural Phosphates.—The search for an accurate and rapid method for the determination of alumina and iron oxid in the presence of phosphoric acid has occupied the attention of analysts for years, and many methods have been proposed for this difficult operation. It may be said generally that even those methods that have stood the tests of extended use have not escaped severe criticism; they are only accurate within narrow and rigidly defined limits or they are tedious and time-consuming.¹⁰

Aside from its interest from the scientific point of view, this subject is of importance in its technical and commercial aspects. The value of raw mineral phosphates is judged largely by their content of alumina and iron.

In phosphatic slags the estimation of these oxids is more difficult, though possibly not so important.

Sources of Error in the Older Methods.—The Glaser alcohol, the acetate with its various modifications, and the caustic alkali methods as carried out by Lasne, Lichtschlag and Gladding, have all been criticised and the sources of error pointed out.

1. In the Glaser alcohol method the precipitation of manganese with the iron and aluminum phosphates and the solubility of the phosphates in the wash-water are important sources of error. Probably the manganese can be eliminated by a second precipitation in the presence of a large amount of ammonium chlorid. Possibly the presence of a large amount of ammonium sulfate may also affect the accuracy of this method, in those cases where the excess of ammonia is completely removed by boiling. Aluminum phosphate is noticeably soluble in a strong sulfate solution, which is neutral or faintly acid from SO_2 .

2. In the acetate method and its variations there is an error caused by the precipitation of the lime with the iron and alu-

⁹ Chemiker-Zeitung, 1897, 21 : 414.

¹⁰ Veitch, Journal of the American Chemical Society, 1900, 22 : 246.

minum phosphates, the solubility of aluminum phosphate in cold acetate solutions, and the solubility and dissociation of iron and aluminum phosphates in water.¹¹ Also when the phosphates are fused with sodium carbonate, and the iron determined by precipitation with ammonia, the contamination of the iron with calcium phosphate, which is not always entirely decomposed by fusion, is a source of error. Of these the most serious are the first and last mentioned.

3. In the caustic alkali methods there is danger of some of the aluminum being held by the voluminous precipitate produced by the alkali; there is also danger of alumina being precipitated if much carbon dioxide is absorbed. Lasne and Lichtschlag have shown that while the method is long, it gives accurate results if properly conducted. Blattner and Brasseur have investigated the more important methods and conclude:¹²

The acetate method should be discontinued; figures for alumina are nearly always too low.

The Glaser method (alcohol) gives accurate results in the absence of manganese.

The caustic soda method, as carried out by Lasne, gives exact results.

In view of these many sources of error in the conventional methods, considerable time has been devoted to the study of a method that, it is hoped, is free from most of the above mentioned objections. It is an adaptation, so far as possible, of the good points of the present best methods. From the precipitating reagent used, it may be designated the thiosulfate method.

The use of a soluble thiosulfate for the separation of alumina from iron and aluminum from several other metals seems to be due to Chancel.¹³ Later it was used by Stead and by Carnot; by the latter for the separation of aluminum as phosphate, in the presence of ammonium acetate, from iron.¹⁴ Lasne also uses it to precipitate aluminum phosphate in the presence of am-

¹¹ *Chemiker-Zeitung*, 1897, **21** : 264.

¹² *Bulletin de la Société chimique de Paris*, 1897, [3], **17** : 760.

¹³ *Comptes rendus*, 1858, **46** : 987.

¹⁴ Blair, *Chemical Analysis of Iron*, 6th Edition, 1905. : 196.

monium acetate, after removing iron, lime, etc., with caustic soda.¹⁵

The thiosulfate has nothing to do with the precipitation, except that it is an exact method of obtaining the desired neutrality. Thomson has devised a method in which he makes use of this principle, neutralizing with ammonia and using a delicate indicator to determine neutrality.¹⁶

Study of the Proposed Method.—One of the first problems presented in the study of any method for the determination of alumina as phosphate is the composition of the ignited phosphate. While there is a general agreement that the normal phosphate is only obtained in the presence of an excess of phosphoric acid, it is not certain that it is always obtained, even under these conditions.¹⁷

Wash Solutions.—It seems that the true solution of this problem can only be obtained by a study of the solutions used in washing the precipitate. Besides waters of all temperatures, solutions of various salts, such as five per cent. ammonium nitrate, ammonium chlorid, one per cent. ammonium nitrate plus 0.02 per cent. ammonium phosphate, and dilute ammonium acetate, have been proposed and used by many investigators. These various washes possibly account for the variations from the normal, so frequently noted. The recently precipitated phosphates of iron and aluminum, when freed from adhering salts, are slightly soluble, or rather are dissociated, in water of any temperature. Those who have apparently used water successfully as a wash probably did not wash enough, only three or four times, to remove the adhering salts. Cold ammonium or sodium acetate also slowly dissolves aluminum phosphate.

The effects of the following wash liquors have been studied:

Water at from 60° to 70° C.

Five per cent. ammonium nitrate at from 60° to 70° C.

One per cent. ammonium nitrate at from 60° to 70° C.

Five per cent. ammonium nitrate and 0.02 per cent. ammonium phosphate at from 60° to 70° C.

¹⁵ Bulletin de la Société chimique, de Paris, 1896. [3], 15 : 118.

¹⁶ Journal of the Society of Chemical Industry, 1896, 15 : 868.

¹⁷ Chemiker-Zeitung, 1897, 21 : 264.

Blair, Chemical Analysis of Iron, 6th Edition, 1906 : 196.

South Carolina Agricultural Experiment Station, Bulletin 2, 1891.

Method of Study.—Various quantities of the pure aluminum sulfate are placed in a 12-ounce beaker with a solution of two grams of ammonium phosphate, the resulting precipitate dissolved in hydrochloric acid, and 25 cubic centimeters of a 50 per cent. solution of ammonium chlorid added. The solution is made alkaline with ammonia and the precipitate just dissolved with hydrochloric acid, noting approximately the number of cubic centimeters required after the solution has become acid; the solution is diluted to about 250 cubic centimeters, and for each cubic centimeter of hydrochloric acid added to the acid solution five cubic centimeters of a 50 per cent. solution of ammonium thiosulfate were added dropwise, the beaker covered with a watch-glass, the solution boiled half an hour, filtered, washed, dried and ignited to constant weight.

Washing 20 times with five per cent. ammonium nitrate gives practically theoretical results. As many as 50 washings with this solution give results slightly low, but still good. The other solutions were rejected, as they showed a decided solvent effect, except the ammonium nitrates plus ammonium phosphate, upon prolonged washing. Twenty washings were required to free the precipitate from chlorids, sulfates, and ammonium phosphate. In all succeeding work five per cent. ammonium nitrate was used, washing 20 times. Long heating with the blast from 10 to 20 minutes was required to reduce to constant weight.

Composition of the Ignited Aluminum Phosphate.—The phosphoric acid in the aluminum phosphate, washed 20 times with five per cent. ammonium nitrate, was carefully determined by precipitation with molybdate solution, washing the precipitate of ammonium phosphomolybdate with dilute nitric acid, and washing the final precipitate free of chlorids.

The salt obtained under the above mentioned conditions seems to be the normal phosphate, AlPO_4 .

Effect of Iron Salts.—Five grams of ammonium ferric alum dissolved in water, two grams of ammonium phosphate added, and treated as for aluminum phosphate, precipitating while slightly warm, washing 20 times with ammonium nitrate, gave an

average of 1.2 milligrams of alumina. The iron, therefore, has a slightly disturbing effect when present in large quantities.

Solutions containing aluminum sulfate, ammonium phosphate and five grams of ammonio-ferric alum yielded apparently larger quantities of alumina, by the usual methods, than the theoretical amount. When these solutions, however, were previously treated with thiosulfate the theoretical amounts of alumina were obtained.

Effect of Calcium Salts.—The presence of calcium salts produces even less disturbance in the results than iron compounds. The addition of two grams of calcium phosphate gave no indication of alumina in the final results. When aluminum phosphate was present in the same quantity as the calcium salt, the theoretical yield of alumina was 74.3 milligrams instead of 70.5 milligrams, doubtless due to the mechanical entanglement of other compounds. When a second precipitation was employed, this error disappeared. There was obtained an average of 31.5 milligrams of alumina where the theoretical yield was 31.9 milligrams.

From the foregoing results the conclusion seems warranted that aluminum phosphate can be quantitatively separated by a soluble thiosulfate and ammonium chlorid reagent from a hydrochloric acid solution of iron, alumina, and lime phosphates containing only a small amount of sulfates. The statement of many observers, that theoretical results on aluminum phosphates can only be obtained in the presence of an excess of phosphoric acid, has been confirmed. The error produced by precipitating a second time without adding phosphoric acid amounted in some cases to two milligrams alumina.

The Effect of Magnesium, Sodium and Potassium Salts.—Salts of sodium, magnesium and potassium were added to the solutions containing alumina before precipitation as phosphate, and it was found that they exerted no disturbing influence on the results obtained.

The Effect of Sulfates.—In these cases the removal of silica is necessary and the property of the insolubility of silica in sulfuric acid was used as the basis of separation. The method of

Drown was employed.¹⁸ While the separation of silica by this method is satisfactory, it was found impossible to completely precipitate the aluminum phosphate in the presence of a thiosulfate.

The presence of more than 1.25 grams of sulfuric acid prevents the complete precipitation of aluminum phosphate, while 2.75 grams give a decided error.

The Effect of Fluorin.—The presence of a fluorid in a solution from which it is attempted to separate aluminum by this method, is as disastrous to the results as is the presence of sulfates.

In none of the current methods is the presence of fluorin mentioned as a disturbing factor.

The work so far done shows that alumina can be quantitatively separated as phosphate from a hydrochloric acid solution containing aluminum, iron, manganese, lime, magnesium, sodium and potassium, when only small quantities of sulfate are present; that the presence of silica in the solution produces a plus error too large to be neglected; and that the presence of large quantities of sulfates or the presence of fluorids prevents the complete precipitation of aluminum phosphate. Therefore, to obtain accurate results, silica and fluorin must be removed while sulfates, not more than the equivalent of 1.25 grams of sulfuric acid, may be present.

Proposed Method.—The following method for estimating alumina in phosphates is based upon the results of these experiments: Treat one gram of the substance in a platinum dish with from five to 10 cubic centimeters of hydrofluoric acid, let stand in the cold from two or three hours, heat on the water bath to complete dryness, add two cubic centimeters of concentrated sulfuric acid, running well around the sides, and heat at a low temperature until the substance no longer flows in the dish. By this process fluorin is completely expelled. Cool and add from 10 to 20 cubic centimeters of concentrated hydrochloric acid, and warm a few minutes to soften the mass; transfer to a small beaker, and boil until all aluminum compounds are surely dissolved (from 15 to 30 minutes); filter from undissolved residue,

¹⁸ Transactions of the American Institute of Mining Engineers, 1878-79, 7 : 346.

if any, washing the filter thoroughly, add 50 cubic centimeters of 25 per cent. ammonium chlorid solution and ammonia until alkaline, then hydrochloric acid until the precipitate just dissolves. Cool, dilute to about 250 cubic centimeters, and add 50 per cent. sodium thiosulfate solution, drop by drop, until the solution is colorless, adding in all 20 cubic centimeters; cover with a watch-glass, boil half an hour, filter, wash back into the same beaker, and dissolve in boiling hydrochloric acid; reprecipitate exactly as before, after adding two cubic centimeters of a 10 per cent. ammonium phosphate solution. Wash 20 times with five per cent. ammonium nitrate solution, and ignite to constant weight. For the second precipitation ammonium thiosulfate may also be used, but it is not necessary.

The greatest difficulty to be overcome in the execution of this method in the case of natural phosphates is the error produced by the presence of fluorin; hence it is necessary to heat the substance for a long time with sulfuric acid to insure the complete removal of fluorin before beginning the separation of the aluminum phosphate.

An attempt to overcome this source of error by adding an alkaline acetate before boiling with thiosulfate gave no satisfactory result.

Estimation of Ferric Oxid.—The determination of ferric oxid is made as follows: Dissolve one gram of the substance in 20 cubic centimeters of sulfuric acid, dilute, filter, washing the filter thoroughly, and if any organic matter is present add a little potassium chlorate and boil until chlorin is expelled. Reduce the iron with zinc, filter, and titrate at once with potassium permanganate solution, one cubic centimeter of which equals 0.0025 gram of ferric oxid.

222. Separation of Alumina from Iron by Phenylhydrazine.—This method of separation was proposed by Hess and Campbell and elaborated by Allen.¹⁹ It is based on the reduction of the iron by a sulfite and the precipitation of the alumina by phenylhydrazine.

223. General Conclusions.—It is evident from the foregoing

¹⁹ Journal of the American Chemical Society, 1899, **21** : 776.

Journal of the American Chemical Society, 1903, **25** : 421.

that many difficulties beset the separation of iron and alumina from the other substances occurring in phosphatic deposits. Veitch has called especial attention to these difficulties in view of the persistence with which ordinary precautions are disregarded.²⁰ The important points to be kept in view are that all the iron should be in solution in the ferric state, the solution should be free of silica, and should contain no more than 0.5 gram substance in 300 cubic centimeters. In these conditions the precipitation of the phosphates of iron and alumina is made in a five per cent. solution of ammonium chlorid, and the precipitate after washing several times with hot water, is dissolved in hydrochloric acid diluted to about 300 cubic centimeters and reprecipitated as before, with care to have always an excess of phosphoric acid over the amount required to unite with all the iron and alumina present. The precipitate is washed free of chlorid with a five per cent. ammonium nitrate solution and ignited to constant weight. With the precautions noted, concordant results may be obtained by precipitating with ammonium acetate and determining the phosphates thrown out. The aluminum may be separated from the iron with thiosulfate of ammonium or sodium, as pointed out by Veitch.²¹ The iron may afterwards be determined by titration.

The iron may be determined separately by reduction to the ferrous state and oxidizing by potassium permanganate or bichromate.

The solutions must in all cases be free of organic matter. If manganese titanium or vanadium be present the accuracy of the iron determination will be affected, and these elements must be separately determined where extreme accuracy is desired. The small quantities of these bodies usually found, although they deport themselves in the presence of phosphoric acid much in the same way as iron, do not introduce any material error into the percentage determination when weighed as iron phosphate, because they have approximately the same atomic weight as iron itself.

224. Estimation of Sulfuric Acid.—As a rule, sulfates are not

²⁰ Proceedings of the Fifth International Congress of Applied Chemistry, Berlin, 1903, 1 : 492.

²¹ Journal of the American Chemical Society, 1900, 22 : 246.

abundant in mineral phosphates. In case the samples are pyritiferous, however, considerable quantities of sulfuric acid may be found after treatment with aqua regia.

The acid is precipitated with barium chlorid, in the usual way, in an aliquot portion of the filtrate first obtained. The precipitate of barium sulfate is washed with hot water until clean, dried, ignited, and weighed. If the portion of the filtrate used represents half a gram of the original material, then the weight of barium sulfate obtained multiplied by 0.6858 will give the quantity of sulfur trioxid in one gram.

OCCURRENCE OF FLUORIN IN PHOSPHATES

225. Signification of Fluorin.—Fluorin is quite a constant constituent of organic phosphates of lime, as, for instance, bones and teeth, and occurs in considerable quantities in many deposits of such phosphates used for commercial purposes. It is the cause of much discomfort and annoyance in fertilizer factories.

The phosphates of pure mineral origin, and also sedimentary phosphates, contain uniformly considerable quantities of fluorin, in fact, in quite a definite proportion, and generally correspond in composition to apatite. Under the influence of living organs, of plants and animals, the fluorin tends to disappear.²²

The exact determination of fluorin, therefore, in phosphates, is of more than usual interest because its amount will throw much light on the origin of the sample under examination.

Free coproliths, that is, nodules of organic phosphates, are very rarely found. What are so called, preserve only the form. The original materials have been replaced by the fluorophosphates of more distinctly mineral nature. The fossil bones sometimes found in sedimentary phosphate deposits are only bones in form, just as fossil trees are only so in form. The analysis of the phosphatic material composing them shows them to be different from true bone. Only fossil phosphates unmetamorphosed exist in recent geological epochs and in guano deposits.

The almost universal presence of fluorin in natural phosphates makes of especial interest the methods for its exact estimation. The presence of fluorin is of little consequence from a practical

²² Lasne, *L'Engrais*, 1896, 11 : 1145, 1168.

point of view, except in the decomposition of phosphates with sulfuric acid, where the evolution of hydrofluoric acid or hydrofluosilicic acid may cause grave inconvenience to the workman and damage to the apparatus. It is important to know the exact content of a phosphate in fluorin before submitting it to the process of manufacture, by means of which phosphoric acid is rendered soluble in water and ammonium citrate. The principles upon which the estimation of the fluorin depend, comprise both the decomposition of the substance by fusion with the carbonate of soda and silica, and the estimation of the fluorin in the hydrofluosilicic acid evolved by the simultaneous action of concentrated sulfuric acid and silica upon the fluorin compound. The last method theoretically leads to the realization of the conditions necessary for an exact determination, but in practice it has been found to be attended with very great difficulties. The assumption that the hydrofluosilicic acid is evolved in the pure state is not always correct, since phosphates contain quite commonly some carbonates and organic matters, and even chlorids. When these compounds are treated with concentrated sulfuric acid, there is set free some sulfurous, carbonic, and hydrochloric acids, and these escaping in a gaseous form, are likely to carry with them also some water vapor. In the application of this method it has therefore been found necessary to previously ignite the phosphate, and this operation is also open to objections. In case calcination is practiced, it is necessary to carry it so far that there remains no trace of carbonic acid, or of carbon, for the presence of these bodies would interfere seriously with the subsequent determination of the fluorin. Even when this method can be successfully practiced with natural phosphates, it will be found extremely difficult of application in the estimation of any residual fluorin in superphosphates.

226. Estimation of Fluorin by the Method of Berzelius as Modified by Chatard.—The method of estimating fluorin as proposed by Berzelius has been found quite satisfactory in the laboratory of the Geological Survey, with the modifications given below.²³

²³ Transactions of the American Institute of Mining Engineers, 1892-93, 21 : 170.

Two grams of the phosphate are intimately mixed in a large platinum crucible with three grams of precipitated silica and 12 grams of pure sodium carbonate, and the mixture is gradually brought to clear fusion over the blast-lamp. When the fusion is complete the melt is spread over the walls of the crucible, which is then rapidly cooled (preferably by a blast of air). If this has been properly done, the mass separates easily from the crucible, and the subsequent leaching is hastened. The mass, detached from the crucible, is put into a platinum dish into which whatever remains adhering to the crucible or its lid is also washed with hot water. A reasonable amount of hot water is now put into the dish, which is covered and digested on the water bath until the mass is thoroughly disintegrated. To hasten this, the supernatant liquid may, after a while, be poured off, the residue being washed into a small porcelain mortar, ground up, returned to the dish and boiled with fresh water until no hard grains are left. The total liquid is filtered, and the residue is washed with hot water. The filtrate (which should amount to about half a liter) is nearly neutralized with nitric acid (methyl orange being used as indicator), some pure sodium bicarbonate is at once added, and the solution (in a platinum dish, if one large enough is at disposal, otherwise in a beaker) is placed on the water bath, when it speedily becomes turbid through separation of silica. As soon as the solution is warm it is removed from the bath, stirred, allowed to stand for two or three hours, and then filtered by means of the filter-pump and washed with cold water.

The filtrate is concentrated to about a quarter of a liter and nearly neutralized, as before, some sodium carbonate is added, and the phosphoric acid is precipitated with silver nitrate in excess. The precipitate is separated by filtration and washed with hot water, and the excess of silver in the filtrate is removed with sodium chlorid.

The filtrate from the silver chlorid (after addition of some sodium bicarbonate) is evaporated to its crystallizing point, then cooled and diluted with cold water; still more sodium bicarbonate is added, and the whole is allowed to stand, when additional silica will separate, and this is to be removed by filtration.

This final solution is nearly neutralized, as before; a little

sodium carbonate solution is added; it is heated to boiling and an excess of solution of calcium chlorid is added. The precipitate of calcium fluorid and carbonate must be boiled for a few minutes, when it can be easily filtered and washed with hot water. The precipitate is then washed from the filter into a small platinum dish and evaporated to dryness, while the filter, after being partially dried and used to wipe off any particles of the precipitate adhering to the dish in which it was formed, is burned, and the ash is added to the main precipitate. This, when dry, is ignited, and allowed to cool; dilute acetic acid is added in excess, and the whole is evaporated to dryness, being kept on the water bath until all odor of acetic acid has disappeared. The residue is then treated with hot water, digested, filtered on a small filter, washed with hot water, partially dried put into a crucible, carefully ignited, and weighed as calcium fluorid. The calcium fluorid is then dissolved in sulfuric acid by gentle heating and agitation, evaporated to dryness on a radiator, ignited at full red heat, and weighed as calcium sulfate. From this weight the equivalent weight of calcium fluorid should be calculated, and this should be very close to that actually found as above, but should never exceed it. The difference, which is generally about a milligram (sometimes more), is due to silica precipitated with the fluorid. The percentage of fluorin is, therefore, always calculated from the weight of the sulfate, and not from that of the fluorid obtained.

The main improvements in this method are the use of sodium bicarbonate to separate the silica, and the keeping of the earlier solutions as dilute as possible, which can not be done if ammonium carbonate be used for the separation of the silica. These changes make the fluorin estimation, although still tedious, far more rapid than before, and the results are very satisfactory.

227. Modification of Wyatt.—By reason of the tediousness of the method of Chatard given above, Wyatt has sought to shorten the process by the following modification.²⁴

The presence of fluorin having been established by a qualitative test, its estimation is secured as follows:

²⁴ *Phosphates of America*, 4th Edition, 1892: 149.

Five grams of the finely ground phosphate are fused in a platinum dish with 15 grams of the mixed carbonates of sodium and potassium and two grams of very fine sand. After fusing very thoroughly with a strong heat for a quarter of an hour, the dish is removed from the fire and cooled. Its contents, dissolved in hot water, are then put into a half-liter flask, and a considerable excess of ammonium carbonate is added to the liquid. All the soluble silica falls out of solution, and the flask, after cooling, is made up to the mark with distilled water, well shaken, and then set aside for 24 hours to settle. At the end of this time 200 cubic centimeters are carefully decanted through a filter; the filter is well washed, and the filtrate, after being nearly neutralized with hydrochloric acid, is treated with an excess of calcium chlorid solution.

The precipitate, consisting of phosphate, fluorid, and some calcium carbonate, is allowed to settle, and is then carefully washed with boiling water, first by decantation several times, and finally on the filter. After being properly dried in the gas-oven, calcined, and cooled, the residue is treated with acetic acid, placed upon the water-bath, and evaporated to complete dryness.

The calcium acetate is now well washed out by several treatments with boiling water, and the residue is brought upon a filter, dried, calcined, and weighed. The weight represents the calcium phosphate and fluorid contained in two grams of the original sample; and if the calcium phosphate in the residue be determined according to the usual methods, the difference will be calcium fluorid and may be thus estimated.

For this purpose the mixed phosphate and fluorid is placed in a platinum dish and the fluorin expelled by treatment with sulfuric acid. The residue is taken up with alcohol, 100 cubic centimeters, the undissolved portion washed with an additional 100 cubic centimeters of alcohol, and the phosphoric acid determined in the alcoholic solution by precipitation as ammonio-magnesium phosphate.

Example.—Assuming the calcined residue of calcium phosphate and fluorid in two grams of the original sample to have

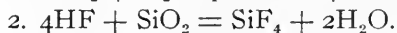
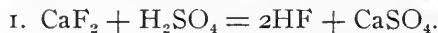
amounted to 1.6 gram and the calcium phosphate in this quantity to have been determined as 1.540 gram, the calcium fluorid is thus proved to be 0.060 gram, and, therefore, $2:0.060::100:x=3$ per cent. calcium fluorid, which, multiplied by 0.4897, gives 1.46 per cent. of fluorin.

The above method, while shorter, is not to be preferred to the former process when great accuracy is desired. All the soluble silica may not fall out of the solution as Wyatt says. Again, the method of separating the phosphoric acid can not be regarded as strictly accurate. Finally, the fluorin is calculated from small differences in the weight of very heavy precipitates, and all the error of the process may be found affecting the numbers for fluorin. For commercial purposes, however, the method has the merit of comparative brevity.

228. Method of Rose.—Clarke and Hillebrand recommend the Rose modification of the method just described, in which chromium and any residue of phosphoric acid are removed by silver nitrate.²⁵ The previous separation of silica and alumina by carbonate of ammonium is advised instead of nitrate or chlorid, to avoid loss of fluorin on evaporation. By whatever method the silica is thrown out, the alkaline carbonate must be converted into nitrate and not chlorid if chromium and phosphorus are present. The solution at the time the silver nitrate is added should contain enough of undecomposed alkaline carbonate to cause a copious precipitation of silver carbonate in order to take up the acid set free. After heating and filtering the excess of silver is to be removed by sodium or potassium chlorid, sodium carbonate added, and the fluorin precipitated by calcium chlorid in excess. No ammonium salts should be present in the solution when the calcium chlorid is added, for these tend to hold the fluorin in solution. The remaining part of the operation is conducted as above described. Attention is called to the fact that there is no very satisfactory qualitative test for the presence of fluorin. The usual method of heating the powdered substance by the blowpipe, with sodium metaphosphate on a platinum foil, is not always reliable.

²⁵ U. S. Geological Survey, Bulletin 148, 1897 : 57.

229. Burk's Modification of Carnot's Method.—Carnot's method is based on the digestion of a substance containing silica and a fluorid with sulfuric acid and conducting the silicon tetrafluorid evolved into a solution of potassium fluorid.²⁶ The reactions which take place are expressed by the following formulas:



The potassium fluosilicate separates in part and is completely precipitated by 90 per cent. alcohol. After standing, the precipitate is collected on a filter, washed free of potassium fluorid by 90 per cent. alcohol, and dried to constant weight.

Two-thirds of the fluorin in the dried product is derived from the mineral under investigation. The number representing the weight of the precipitate multiplied by 0.34511 gives the fluorin, and this multiplied by 2.0527 gives the weight of the calcium fluorid corresponding thereto. Burk describes the apparatus suited to the conduct of the work, and states the conditions under which it is accurate.²⁷ The chief sources of error are:

1. Moisture in the air or tubes through which the silicon tetrafluorid passes.
2. Fumes of sulfuric acid carried over in the air current or otherwise.
3. Insoluble addition products of potassium fluorid with the silica of the glass.

The methods of avoiding these sources of error are set forth in detail in the paper cited above.

230. Method of Lasne.—The difficulties which have been mentioned led Lasne to modify the method of separating the hydrofluosilicic acid in such a way as to render it practicable and exact.²⁸

The modification of Lasne consists essentially in removing the hydrofluosilicic acid evolved by the action of concentrated sulfuric acid on natural phosphate by a current of dry air conducted

²⁶ *Comptes rendus*, 1892, 114 : 750, 1003.

²⁷ *Journal of the American Chemical Society*, 1901, 23 : 825.

²⁸ *Bulletin de la Société chimique de Paris*, 1888, [2], 50 : 167.

Annales de Chimie analytique, 1897, 2 : 161, 182.

into a solution of caustic soda, where the fluorin is retained and ultimately estimated. It does not matter that the fluorin in this case is accompanied with other gases, and with vapor of water, since these impurities are absolutely without inconvenience in the subsequent proceedings. The phosphates can be treated without previous calcination or preparation in any form, and after mixing with sulfuric acid the temperature can be raised just to

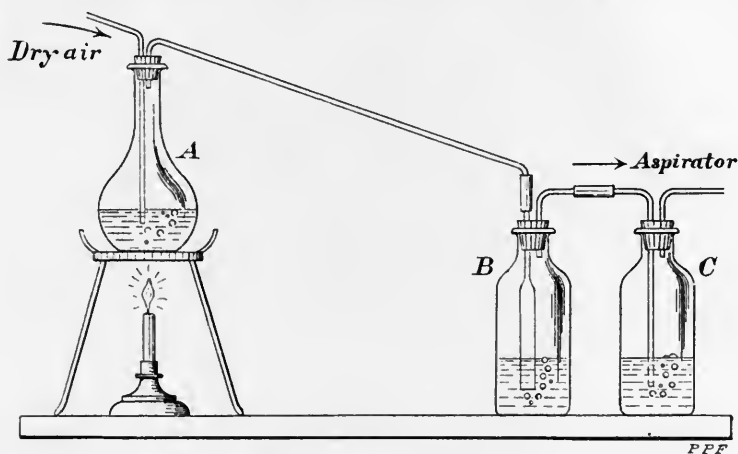


Fig. 12. Lasne's Apparatus.

the point of ebullition, which promotes very greatly the speed of the reaction and the perfect separation of the fluorin. The operation is conducted as follows:

A definite quantity of the phosphate or any other body whatever containing fluorin, provided it be decomposable by sulfuric acid, is introduced into a dry flask in which have been previously placed about 50 cubic centimeters of strong sulfuric acid and 10 grams of finely ground sand. The quantity of the phosphate employed should be such as to secure, if possible, an amount containing 0.1 gram of calcium fluorid. In phosphates which are very poor in fluorin it will be necessary to use from 10 to 20 grams. One of the great advantages of this process lies in the fact that it permits the employment of these great quantities of materials without in any way interfering with the accuracy of the analysis. The flask and receiving bottles employed in the

operation are illustrated by the accompanying Figure 12. The first receiving flask (B) contains two and one-half grams of caustic soda in 25 cubic centimeters, and the second (C) a half a gram in the same volume of water. The second flask is connected with the aspirator, by means of which the current of air is drawn through the whole apparatus. At the beginning of the operation the current of dry air is drawn through slowly and the flask (A) is moderately heated until its contents are brought to near the boiling point. During the heating the flask should be frequently shaken to secure the even distribution of the heat throughout the mass, and avoid danger of breakage. In this condition the evolution of the fluorin is terminated in about three hours. A blank experiment should show that the sulfuric acid and sand employed are free of fluorin. Sulfuric acid and sand entirely free from fluorin may be easily secured by heating one liter of the acid for two or three hours with 100 grams of finely ground sand, previously washed with hydrochloric acid. After cooling, the acid is decanted into a dry glass-stoppered flask, and the residual sand is washed and dried. These reagents are, when prepared in this way, both free from fluorin. When the fluorid of silica is entirely evolved from the mixture, which is easily determined by observing that the contents of the flask become limpid, the lamp is extinguished and the mass is allowed to cool until the flask can be easily handled. It is then removed and the delivery tube washed into a dish into which subsequently are poured the contents of the two receiving flasks, and their connecting tubes are washed with water. The solution obtained in this way should still be freely alkaline, as indicated by forming a red color with phenolphthalein. If it be not alkaline, a sufficient quantity of caustic soda should be added. The contents of the dish are heated for half an hour to 100° for the purpose of decomposing into hydrofluoric acid and silica the fluosilicate which has been formed at first. The total volume of the solution, in order to facilitate the operation, should be reduced by evaporation to about 100 cubic centimeters. After partial cooling the solution is saturated with carbon dioxide, the flask being covered meanwhile to prevent any loss by the projection of the liquor with the escaping gas. The residual liquor and the wash water

coming from the covered dish are introduced into a flask graduated to 125 cubic centimeters, which should not be completely filled. Some solid carbonate of ammonia is added and the mixture heated for half an hour to about 50° , adding from time to time a little of the carbonate. By this process the silica is, as a rule, completely precipitated. Nevertheless, as it is important that not the least trace of silica be in solution, it is recommended to finish the separation with oxid of zinc. For this purpose the volume of the mixture is completed to the mark and the contents of the flask filtered into a dried beaker. One hundred cubic centimeters of the filtrate are placed in a porcelain dish and 10 cubic centimeters of solution of oxid of zinc in ammonia, in all about 0.3 gram of oxid of zinc, are added. The solution is evaporated almost to dryness and some water added, and the evaporation repeated in this way two or three times. The precipitate of carbonate of zinc formed carries down the last traces of silica. The whole precipitate is finally collected upon a filter and washed. Since the quantity of carbonate of soda present is not exactly known, there are added to the solution a few drops of tropeolin, and carefully, afterwards, diluted hydrochloric acid, until a rose tint is produced, and without waiting 10 cubic centimeters of a solution of carbonate of soda containing 300 grams of the crystallized salt per liter. This quantity of carbonate of soda should be prepared in advance, so that it can be added instantly, as it is not safe to leave the solution acid, because it will attack the glass and bring a small quantity of silica into solution. After the addition of the carbonate of soda solution the mixture is boiled for 15 minutes. To the nearly boiling solution there is added a slight excess of calcium chlorid, say about 10 cubic centimeters of a solution containing 300 grams of the crystallized calcium chlorid per liter. Stir thoroughly and allow to settle for a short time and filter while still hot. Wash the precipitate, which is composed of calcium carbonate and calcium fluorid. The precipitate is dried and burned, the temperature being raised with great caution, so as to avoid a partial fusion, a phenomenon which is probably due to the existence of a fluocarbonate which has not yet been isolated. The ignition is conducted in a large platinum cruci-

ble. The capsule, after cooling, is covered with a funnel, and from 30 to 40 cubic centimeters of water are poured upon the ignited precipitate, followed by three cubic centimeters of glacial acetic acid. After the evolution of carbon dioxide is finished the funnel is removed and washed, the residual liquor is evaporated to near dryness, water added, and the evaporation repeated two or three times and finished by evaporating to dryness. The residue is taken up with 30 or 40 cubic centimeters of water containing one per cent. of acetic acid. After heating for a moment the fluorid of calcium which remains insoluble is collected and washed with water slightly acidulated with acetic. The washing is finished with pure water. The absence of sulfates in the last wash water should be ascertained by a careful test. It is rather difficult to filter the calcium fluorid, and some precautions to avoid a turbid filtrate will be found necessary. The precipitate is dried, ignited and the fluorid of calcium, obtained in a perfectly pure state, weighed. The purity of the residue can be determined by dissolving with concentrated sulfuric acid, afterwards diluting a little and precipitating by alcohol. The sulfate of lime obtained in this way should correspond, molecularly, to the original calcium fluorid. According to Lasne, this method, if carefully followed, gives results which are rigorously exact.

231. Carnot's Modification.—Carnot has proposed to shorten the method of Lasne in the following manner:

In place of receiving the fluorid of silicium in caustic soda, the gas is conducted into a solution of fluorid of potash, the delivery tube being plunged into mercury to avoid obstruction. There is thus formed a fluosilicate, which is precipitated by alcohol, collected upon a tared filter and weighed. Lasne considered this method to be, in fact, more rapid, but dangerous. It is always inconvenient, according to him, to use in determination a body of the same nature as that which is to be determined, a process which renders all final verification impossible.

Goutal has criticised the method of Lasne, preferring the shorter method of Carnot mentioned above.²⁹ His objections to the method of Lasne are based upon the following:

²⁹ *Annales de Chimie analytique*, 1897, 2 : 40r.

- (1) Five or six reagents are required.
- (2) Evaporations and ebullitions of alkaline liquids are carried on in glass vessels, which are subject to attack.
- (3) The precipitate weighs only a few centigrams.
- (4) The precipitate is mixed with silica.
- (5) The precipitate is soluble in the successive reagents employed.

These objections are answered by Lasne.³⁰

Lasne admits that if the phosphates in which fluorin is to be determined are previously ignited, many of the objections to the shorter method proposed by Carnot are removed, but he fears that there is danger of loss of fluorin, as well as of water, by calcination, and adds that the calcination of phosphates, and more particularly of bones, is an operation which is neither easy nor rapid, if it be desired to burn away the last traces of carbon.

232. Protection of Glassware in Working with Fluorin.—Carnot has proposed to coat the surfaces of flasks and tubes used in the determination of fluorin with gum-lac.³¹

According to Carnot, this lacquer protects completely the glass from the action of the solution of hydrofluoric acid.

233. Fluorin in Bones.—According to Carnot, the deposits of phosphates have been formed in the following manner:

(1) The accumulation of phosphatic animal débris, etc., along the banks of the ocean or in lakes or lagoons.

(2) The impregnation of these phosphates in the fluorid of calcium contained in the sea waters. Carnot has demonstrated the presence and determined the proportion of fluorin in the waters of the ocean, and has shown in the laboratory, by synthetic experiments, the gradual fixation of fluorin in bony deposits.

The fluorin which is a constituent of mineral phosphates is probably derived from bones. According to the researches of Carnot, there is often a considerable quantity of calcium fluorid in bones and teeth.³² In fossil bones very large quantities have been found, reaching as high as 6.21 per cent. of

³⁰ *Annales de Chimie analytique*, 1898, 3 : 6.

³¹ *Annales des Mines*, 1893, [9], 3 : 138.

³² *Comptes rendus*, 1892, 114 : 1189.

Annales de Chimie et de Physique, 1855, 1 : 47.

calcium fluorid in a fossil bone in a phosphate from the Charleston deposits. Gabriel has suggested a means of determining a minimum limit of fluorin in bones and teeth by the development of etchings in comparison with known quantities of pure calcium fluorid. The minimum quantity of calcium fluorid necessary to produce a distinct etching, in known conditions, having been determined, the test is applied to known weights of ignited bone or teeth. He concludes from his results that the ash of bones and teeth often contains less than one-tenth per cent. of fluorin. Since, however, there is a loss of fluorin from calcium fluorid on ignition, the whole of the fluorin may not have been available in the tests described.

234. Iodin in Phosphates.—The presence of iodin has been detected in many natural phosphates and is of interest in the discussion of the problem of their origin.⁸³ A sample of phosphate from Florida was found to contain 0.014 per cent. of iodin. This element has also been observed in the phosphates from other localities, as has been shown by Gilbert. A qualitative test for the detection of iodin may be applied in the following manner: Some finely ground phosphate is mixed with strong sulfuric acid and the gases arising from the reaction are aspired into some carbon disulfid or chloroform. The violet coloration arising indicates the presence of iodin. The gases carrying the iodin may also be brought into contact with starch-paste producing the well known blue color.

The quantity of iodin present in a phosphate is rarely more than one or two-tenths of one per cent. It can be determined as a silver salt, in the absence of chlorin or by any of the standard methods found in works on quantitative analysis.

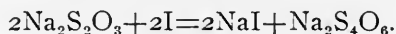
Iodin is quite a constant constituent of Florida phosphates. For a quantitative determination, the sample is treated with an excess of strong sulfuric acid in a closed flask and during the decomposition a stream of air is aspired through the flask and caused to bubble through absorption bulbs containing sodium or potassium hydroxid in solution.

The temperature of the decomposition may be raised to about 200°. After the distillation is complete the sodium iodid formed

⁸³ L'Engrais, 1895, 10 : 65.

is titrated by treating with potassium permanganate.³⁴ The reaction is represented by the equation: $\text{NaI} + 2\text{KMnO}_4 + \text{H}_2\text{O} = \text{NaIO}_3 + 2\text{KOH} + 2\text{MnO}_2$. The iodine also may be set free and determined in the usual way by titration with standard sodium thiosulfate solution.

The titration of free iodine is represented by the following reaction:



In this reaction thiosulfuric acid is converted into tetrathionic acid and the free iodine into hydriodic acid, both of which combine with the sodium present. The decinormal solution of sodium thiosulfate may be used. Grind the crystals of the salt to a fine powder, dry between blotting papers, and use 24.8 grams of the dried salt per liter. The quantity of iodine found in phosphates is so minute that it is hardly worth while to make a quantitative determination of it.

235. Occurrence of Chromium in Phosphates.—In some phosphates a small quantity of chromium has been found. In a sample of phosphate from the Island of Los Roques in the Caribbean Sea, Gilbert found three-fourths per cent. of chromium oxide (Cr_2O_3). The phosphates containing chromium have a greenish color and are characterized by great insolubility in solutions containing organic acids. The chromium is to be determined by the usual methods described in mineral analysis.

236. Estimation of Vanadium.—In the complete analysis of basic slags it becomes necessary to determine the presence of vanadic mixture with this solution until a drop of the clear liquor, the volumetric process of Lindemann.³⁵ It is conducted as follows: Dissolve four grams of the finely powdered slag in 60 cubic centimeters of dilute sulfuric acid (1 : 4), boil for a few minutes, cool, make the volume up to 100 cubic centimeters, filter and add decinormal potassium permanganate solution in slight excess to an aliquot part of the filtrate to secure the oxidation of the vanadium to vanadium pentoxide. Add, drop by drop, a weak solution of ferrous sulfate until the pink color just disappears. Prepare

³⁴ Sutton, *Volumetric Analysis*, 9th Edition, 1904 : 219.

³⁵ Ueber die quantitative Bestimmung des Vanadins in Eisenerzen, 1878. *Zeitschrift für analytische Chemie*, 1879, 18 : 99.

a ferrous sulfate solution by dissolving 2.183 grams of piano wire in sulfuric acid and making the volume to one liter. Titrate the vanadic mixture with this solution until a drop of the clear liquor, removed and brought in contact with potassium ferricyanid, shows a distinctive blue-green color.

One cubic centimeter of the ferrous sulfate solution is equivalent to 0.002 gram of vanadium, 0.002888 gram of vanadium di-oxid, and 0.003648 gram of vanadium pentoxid. The ferrous sulfate solution may also be made and standardized by any of the approved methods in common use.

The method described by Blair, designed especially for the estimation of vanadium in iron and steel, is conducted in the following manner:³⁶ Five grams of the drillings are dissolved in 50 cubic centimeters of nitric acid of 1.24 specific gravity. The solution is evaporated to dryness in a porcelain dish and heated thereafter until the nitrates are nearly decomposed. After cooling, the dried mass is transferred to a mortar and finely ground with 30 grams of dry sodium carbonate and three grams of sodium nitrate. The finely ground materials are placed in a platinum dish and fused for an hour at a high temperature. Spread the fused mass over the sides of the dish while cooling, and afterwards dissolve in hot water, filter, and wash until the volume is a little over half a liter. Add nitric acid to decompose carbonates, but not completely, and boil to get rid of carbon dioxide, being careful to keep the mass always slightly alkaline. Add nitric acid, drop by drop, until slightly in excess, and then sodium carbonate to marked alkalinity, boil, and filter. Add a slight excess of nitric acid to the filtrate, and the development of a yellow color will indicate the presence of vanadic acid. Add to the solution a small quantity of mercurous nitrate and then an excess of mercuric oxid, suspended in water to render the solution neutral and insure the complete precipitation of mercurous vanadate. The mercurous salt also precipitates phosphoric, chromic, tungstic, and molybdic acids which may be present. Boil, filter, and wash the precipitate with hot water, dry, and ignite. Fuse the residue with sodium carbonate and a little nitrate. Dissolve the fused mass, after cooling, in a little water

³⁶ The Chemical Analysis of Iron, 6th Edition, 1906 : 203.

and filter. Add to the filtrate ammonium chlorid in excess about 3.5 grams for each 10 cubic centimeters of the solution, and allow to stand, with occasional stirring, for some time. Ammonium vanadate, insoluble in a saturated solution of ammonium chlorid, separates as a white powder. It is necessary to keep the solution alkaline, and a drop of ammonia should be added from time to time for this purpose. The appearance of a yellowish tint at any time indicates that the solution has become acid, and this acidity must be corrected, or else the results will be too low. Separate the ammonium vanadate by filtration; wash first with a saturated solution of ammonium chlorid containing a little free ammonia, and then with alcohol. Dry, ignite, and moisten with a few drops of nitric acid; again ignite to obtain the compound as vanadium pentoxid, V_2O_5 . This compound contains 56.22 per cent. of vanadium.

The method of Rosenheim and Holverscheit may also be used.³⁷ It is based on the preliminary precipitation of the vanadic acid as a barium or lead salt. The substance supposed to contain vanadium is first brought into solution in such a manner as to secure it as vanadic acid, which is then precipitated with barium chlorid or lead acetate. The precipitate is boiled with hydrochloric acid and potassium bromid, and the liberated bromin determined by the quantity of iodine set free from potassium iodid. In the absence of bodies, such as molybdic acid, which are reduced by sulfurous acid or hydrogen sulfid the vanadic acid may also be determined by reducing it with one of these reagents and, after removing the excess by boiling, titrating the vanadium tetroxid with potassium permanganate. When vanadic and phosphoric acids occur together the former may be first reduced to tetroxid with sulfurous acid, and after expelling excess of this reagent, the phosphoric acid may be separated with molybdate solution and removed by filtration. When the amount of vanadic acid is large the phosphoric acid should be separated rapidly at 55° - 60° , using a considerable excess of the molybdate; or the vanadic acid may first be determined in the solution volumetrically by the bromine pro-

³⁷ Ueber Vanadinwolframsäure, Dissertation, Berlin, 1888.

Ueber die quantitative Bestimmung des Vanadins. Dissertation, Berlin, 1890.

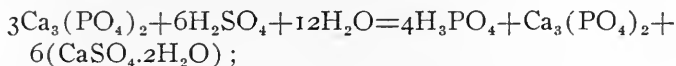
cess above described, and afterwards the phosphoric acid obtained by evaporating to dryness with a little sulfuric acid, taking the residue up with water, reducing the vanadic with sulfurous acid and precipitating the phosphoric acid with molybdate solution as described above.

CHEMISTRY OF SUPERPHOSPHATE MANUFACTURE

237. Chemical Changes in the Manufacture of Superphosphates.

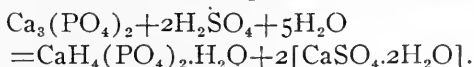
—In this country the expressions “acid” and “super” as applied to phosphates are used interchangeably. A more correct use of the terms would designate by “acid” the phosphate formed directly from tricalcium phosphate by the action of sulfuric acid, while by “super” would be indicated a similar product formed by the action of free phosphoric acid on the same materials. In Germany the latter compound is called “double phosphate.”

The reaction which takes place in the first instance is represented by the following formula:



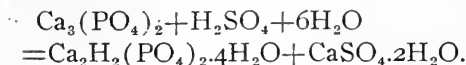
and $4\text{H}_3\text{PO}_4 + \text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O} = 3[\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$.

A simpler form of the reaction is expressed as follows:



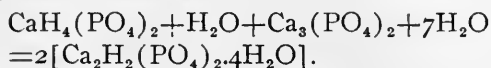
If 310 parts, by weight, of finely ground tricalcium phosphate be mixed with 196 parts of sulfuric acid and 90 parts of water, and the resulting jelly be quickly diluted with a large quantity of water, and filtered, there will be found in the filtrate about three-quarters of the total phosphoric as free acid. If, however, the jelly, at first, formed as above, be left to become dry and hard, the filtrate, when the mass is beaten up with water and filtered, will contain monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$.

If the quantity of sulfuric acid used be not sufficient for complete decomposition, the dicalcium salt is formed directly according to the following reaction:

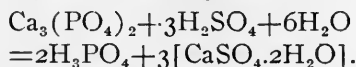


This arises, doubtless, by the formation, at first, of the regular

monocalcium salt and the further reaction of this with the tricalcium compound, as follows:



This reaction represents, theoretically, the so-called reversion of the phosphoric acid. When there is an excess of sulfuric acid there is a complete decomposition of the calcium salts with the production of free phosphoric acid and gypsum. The reaction is represented by the following formula:



The crystallized gypsum absorbs the six molecules of water in its molecular structure. While the above reactions represent the theoretical conditions, there is a wide divergence from them in actual manufacture. In the case of dissolved bone, especially, the actual quantity of sulfuric acid used is not so great as is indicated. The proportions of acid and raw materials are necessarily changed from time to time to meet the emergencies which may arise.

238. Reactions with Fluorids.—Since calcium fluorid is present in nearly all mineral phosphates, the reactions of this compound must be taken into consideration in a chemical study of the manufacture of acid phosphates. When treated with sulfuric acid the first reaction which takes place consists in the formation of hydrofluoric acid: $\text{CaF}_2 + \text{H}_2\text{SO}_4 = 2\text{HF} + \text{CaSO}_4$. Since, however, there is generally some silica in reach of the nascent acid, all, or a portion of it, combines at once with this silica, forming silicon tetrafluorid: $4\text{HF} + \text{SiO}_2 = 2\text{H}_2\text{O} + \text{SiF}_4$. This compound, however, is decomposed at once in the presence of water, forming hydrofluosilicic acid: $3\text{SiF}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$. The presence of calcium fluorid in natural phosphates is extremely objectionable from a technical point of view, both on account of the increased consumption of oil of vitriol which it causes, and also by reason of the injurious nature of the gaseous fluorin compounds produced. Each 100 pounds of calcium fluorid entails the consumption of 125.6 pounds of sulfuric acid, for which no economic return is secured.

239. Reaction with Carbonates.—Most mineral phosphates contain calcium carbonate in varying quantities. This compound is decomposed on treatment with sulfuric acid according to the reaction: $\text{CaCO}_3 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$. When present in moderate amounts, calcium carbonate is not an objectionable impurity in natural phosphates intended for acid phosphate manufacture. The reaction with sulfuric acid which takes place produces a proper rise in temperature throughout the mass, while the escaping carbon dioxide permeates and lightens the whole mass, assisting thus in completing the chemical reaction by leaving the residual mass porous, and capable of being easily dried and pulverized. Where large quantities of carbonate in proportion to the phosphate are present the sulfuric acid used should be dilute enough to furnish the necessary water of crystallization to the gypsum formed. For each 100 parts, by weight, of calcium carbonate, 80 parts of sulfuric anhydride are necessary, or 125 parts of acid of 1.710 specific gravity = 60° Beaumé.

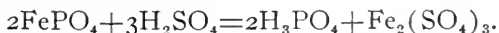
In some guanos a part of the calcium is found as pyrophosphate, and this is acted upon by the sulfuric acid in the following way: $\text{Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{SO}_4 = \text{CaH}_2\text{P}_2\text{O}_7 + \text{CaSO}_4$.

240. Solution of the Iron and Alumina Compounds.—Iron may occur in natural phosphates in many forms. It probably is most frequently met with as ferric or ferrous phosphate, seldom as ferric oxide, and often as pyrite, FeS_2 . The iron also may sometimes exist as a silicate. The alumina is found chiefly in combination with phosphoric acid, and as silicate.

Where a little less sulfuric acid is employed, as is generally the case, than is necessary for complete solution, the iron phosphate is attacked as represented below:

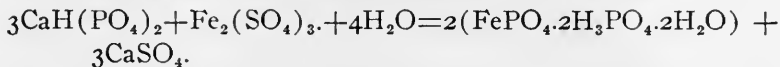


When an excess of sulfuric acid is employed, the formula is reduced to the simple one:



A part of the iron sulfate formed reacts with the acid calcium phosphate present to produce a permanent jelly-like compound, difficult to dry and handle. As much as two per cent. of iron

phosphate, however, may be present without serious interference with the commercial handling of the product. By using more sulfuric acid, as much as four or five per cent. of the iron phosphate can be held in solution. Larger quantities are very troublesome from a commercial point of view. The reaction of the ferric sulfate with monocalcium phosphate is as follows:

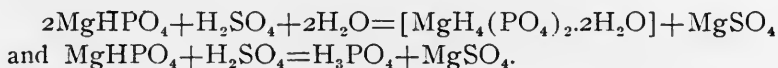


Pyrite and the silicates containing iron are not attacked by sulfuric acid and these compounds are therefore left, in the final product, in a harmless state. If the pyritic iron is to be brought into solution aqua regia should be employed.

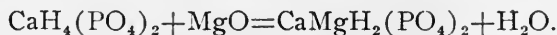
With sufficient acid the aluminum phosphate is decomposed with the formation of aluminum sulfate and free phosphoric acid:



241. Reaction with Magnesium Compounds.—The mineral phosphates, as a rule, contain but little magnesia. When present it is probably as an acid salt, MgHPO_4 . Its decomposition takes place in slight deficiency or excess of sulfuric acid, respectively, as follows:



The magnesia, when in the form of oxid, is capable of producing a reversion of the monocalcium phosphate, as is shown below:



One part by weight of magnesia can render three and one-half parts of soluble monocalcium phosphate insoluble.

242. Determination of Quantity of Sulfuric Acid Necessary for Solution of a Mineral Phosphate.—The theoretical quantity of sulfuric acid required for the proper treatment of any phosphate may be calculated from its chemical analysis and by the formulas and reactions already given. For the experimental determination the method of Rümpler may be followed.³⁸

Twenty grams of the fine phosphate are placed in a liter flask

³⁸ Käufliche Düngestoffe und ihre Anwendung, 4th Edition, 1897: 81.

with a greater quantity of accurately measured sulfuric acid than is necessary for complete solution. The acid should have a specific gravity of 1.455 or 45° B. The mixture is allowed to stand for two hours at 50°. It is then cooled, the flask filled with water to the mark, well shaken, and the contents filtered. Fifty cubic centimeters of the filtrate are treated with tenth-normal soda-lye, free of carbonate, until basic phosphate begins to separate and becomes permanent after shaking. The excess of acid is then calculated. Example: Twenty grams of phosphate containing 28.3 per cent. of phosphoric acid, 10.0 per cent. of calcium carbonate, 5.5 per cent. of calcium fluorid, and 2.4 per cent. of calcium chlorid were treated as above with 16 cubic centimeters of sulfuric acid containing 10.24 grams of sulfur trioxid. In titrating 50 cubic centimeters of the filtrate obtained as described above, 10.4 cubic centimeters of tenth-normal soda-lye were used, equivalent to 0.0416 gram of sulfur trioxid. Then $10.24 \times 50 \div 1000 = 0.5120 =$ total sulfur trioxid in 50 cubic centimeters of the filtrate, and $0.5120 - 0.0416 = 0.4704$ gram, the amount of sulfur trioxid consumed in the decomposition.

Therefore the sulfur trioxid required for decomposition is 47.04 per cent. of the weight of the phosphate employed. One hundred parts of the phosphate would, therefore, require 47.04 parts of sulfur trioxid equal to 73.6 parts of sulfuric acid of 1.710 specific gravity or 92.1 parts of 1.530 specific gravity.

A more convenient method than the one mentioned above, consists in treating a small quantity of the phosphate, from one-half to one kilogram, in the laboratory, or 50 kilograms in a lead box just as would be practiced on a large scale. A few tests with these small quantities, followed by drying and grinding, will reveal to the skilled operator the approximate quantity and strength of sulfuric acid to be used in each case. The quantities of sulfuric acid as determined by calculation from analyses and by actual laboratory tests agree fairly well in most instances. There is, however, sometimes a marked disagreement. The general rule of practice is to use always an amount of sulfuric acid sufficient to produce and maintain water-soluble phosphoric acid in the fertilizer, but the sulfuric acid must not be used in

such quantity as to interfere with the subsequent drying, grinding, and marketing of the acid phosphate.

For convenience, the following table may be used for calculating the quantity of oil of vitriol needed for the entire decomposition of each unit of weight of material noted.

ONE PART BY WEIGHT OF EACH SUBSTANCE BELOW REQUIRES :
Sulfuric Acid by Same Unit of Weight.

	At 48° B.	At 50° B.	At 52° B.	At 54° B.	At 55° B.
Tricalcium phosphate.....	1.590	1.517	1.446	1.382	1.352
Iron phosphate.....	1.630	1.558	1.485	1.420	1.390
Aluminum phosphate.....	2.025	1.930	1.839	1.756	1.721
Calcium carbonate.....	1.640	1.565	1.495	1.428	1.411
Calcium fluorid.	2.006	2.010	1.916	1.830	1.794
Magnesium carbonate.....	1.940	1.860	1.775	1.690	1.660

Example.—Suppose for example a phosphate of the following composition is to be treated with sulfuric acid; viz.,⁸⁹

Moisture and organic matter.....	4.00 per cent.
Calcium phosphate.....	55.00 “
Calcium carbonate	3.00 “
Iron and aluminum phosphate nearly all alumina	6.50 “
Magnesium carbonate.....	0.75 “
Calcium fluorid.....	2.25 “
Insoluble	28.00 “

Using sulfuric acid of 50° B., the following quantities will be required for the weights mentioned:

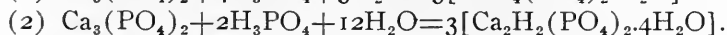
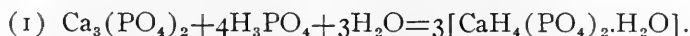
	Kilos of acid required.
Calcium phosphate, fifty-five kilos.....	83.44
“ carbonate, three and a half kilos	5.48
“ fluorid, two and a quarter “	4.52
Aluminum and iron phosphate, six and a half kilos.....	12.55
Magnesium carbonate, three-quarters of a kilo	1.40
Total 68 kilos.....	107.39

Since only a partial decomposition is attained in actual manufacture the quantity of 50° Beaumè acid required is often less than the weight of phosphate treated.

243. Phosphoric Acid Superphosphates.—If a mineral phosphate be decomposed by free phosphoric acid in place of sulfuric acid, the resulting compound will contain about three times as much

⁸⁹ Wyatt, *Phosphates of America*, 4th Edition, 1892: 128.

available phosphoric acid as is found in the ordinary acid phosphate. The reaction takes place according to the following formulas:



In each case the water in the final product is probably united as crystal water with the calcium salts produced. The monocalcium salt formed in the first reaction is soluble in water, and the dicalcium salt in the second reaction, in ammonium citrate. Where fertilizers are to be transported to great distances, there is a considerable saving of freight by the use of such a high-grade phosphate, which may, at times, contain over 40 per cent. of available acid. The phosphoric acid used in this process is made directly from the mineral phosphate by treating it with an excess of sulfuric acid.

244. Fixation of Phosphoric Acid in Basic Soils.—The problem of holding phosphoric acid in the soil probably does not come within the scope of this manual, except as incident to the character and time of its application. This subject has been studied by Crawley.⁴⁰

Experimentally, the determination of the holding powers of the soil for the phosphoric acid obtained, depends upon the same methods as are described for the absorption of salts by soils.⁴¹ In the irrigated soil with which Crawley worked, it was found that, when the application of fertilizer containing water-soluble phosphoric acid was followed immediately by irrigation, more than one-half of the soluble phosphoric acid remained in the first inch of the soil and more than nine-tenths in the first three inches, and practically the whole of it within the first six inches, of the surface. Crawley concludes from the results of his investigations that the water-soluble phosphoric acid does not become so widely distributed, in the case of heavy rains or irrigation beneath the surface, as has been expected. In this connection however, attention should be called to the fact that the Hawaiian

⁴⁰ Journal of the American Chemical Society, 1902, 24 : 1114.

⁴¹ Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 133.

soils on which Crawley worked, are very strongly basic and hence are in a condition better suited to fix and hold the phosphoric acid than the acidic soils with which the chemist is usually called upon to work. The obvious conclusion from an experimental work of this kind is that in determining the power of any particular soil for holding the phosphoric acid applied to it, its character, especially as regards its acidity or basicity, should be carefully considered.

245. Absorption of Phosphoric Acid of Superphosphates.⁴²—Mr. Joffre states that contrary to what is usually thought, the combinations soluble in water appear to be absorbed by vegetation. The proportion absorbed is, without doubt, very small, but it may have a very great importance because the absorption takes place at a moment when the plants have used up the material in the seed and have not yet developed sufficiently to evaporate the large quantity of water and to be able thus to extract from the soil the useful substances, difficultly soluble, which there exist.

This theory explains perfectly the results of the remarkable researches of Schloesing and Prunet who have found that, when fertilizers are planted in the rows, they produce greater effects than when they are mixed with the soil. This evidence depends upon the fact that when they are planted in rows, they become soluble less rapidly and the plants thus have more time to absorb the combinations of phosphoric acid soluble in water.

On page 698 of the same volume, Joffre continues the discussion of the subject. In this communication he has subjected to field experiments, the operations which he has previously conducted in the laboratory. He says: "Moreover, in the culture experiment made in pure sand where there was nothing which could produce insolubility of phosphate soluble in water and where it is seen that this body causes an increase in the crops, it is necessary to admit that the combinations of phosphoric acid soluble in water enter into the plant and are assimilated there. I have not said that insoluble phosphate is without utility in agriculture. It produces, indeed, in certain earth effects which are as

⁴² Bulletin de la Société chimique de Paris, 1895, [3], 13 : 522.

beneficial as the soluble phosphate, but in the greater part of soils, if it produces an action, this action is less than that of superphosphates and the inferiority of this action appears to be caused, at least in part, because no portion of it can enter immediately into the plant in a condition of aqueous solution.

“To resume, the whole of my experiment seems to make clear that the favorable action of superphosphate is not only caused by a greater dissemination of the combinations of phosphoric acid in the arable earth, but that it is also necessary to take into account the absorption in the form of combinations, soluble in water, of a portion of soluble phosphoric acid of superphosphates. If we desire to obtain a maximum result it is necessary to distinguish two sorts of soil; first, the soil analogous to those, of which numerous examples are found in Bretagne, in which insoluble phosphates succeed as well as superphosphates and where it is natural to employ phosphate simply ground. Second, the other soils which are far more numerous and in which the phosphoric acid fertilizers in combinations soluble in water are absolutely indispensable to obtain the maximum effect.”

246. Physical Condition of Availability.—In general it may be said that the physical state of subdivision of raw phosphates and basic slags is one of the most important factors in respect of their availability. This degree of fineness, however, depends for its efficiency largely on other conditions, especially where artificial means are employed for determining availability. For this reason it is advisable, when determining the availability of these materials by chemical means, to employ extremely dilute solutions. The method of Dyer depends on the use of an organic acid and of Moore upon the use of a mineral acid; both require great degrees of attenuation.⁴³ Only by the use of some such reagent can the conditions which occur in nature be simulated, yet it must not be considered that the same degree of attenuation must be present in the artificial means as in the natural. Otherwise the time of experimental determinations of the artificial means would have to continue over several months instead of several hours. It is possible that a revision of the common idea respect-

⁴³ Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 394, 459.

ing the action which takes place in the soil will show that the plant itself exudes no solvent material as has been assumed by many investigators, unless it be the excretion of carbon dioxide. The processes of solution which take place in the soil, from a study of all the conditions which obtain, must be regarded more as operations depending upon the soil itself than as largely influenced by the growing plant. At the present time, however, the solution of the problem, experimentally, in so far as fineness of subdivision is concerned, has perhaps been well answered and it is now clearly understood that in so far as the assimilation processes go on in the soil, they are favored more particularly by the fineness of the subdivisions than by any other factor. Even in soils which are not distinctly acid the fineness of subdivision greatly favors solution, and in regard to the other causes of solution and absorption of these bodies, excluding those due to weathering, it is probable that our ideas in the near future must undergo fundamental revision. Just at present we are unable to specify whether or not the frequent application of these partially insoluble phosphatic fertilizers is advisable or not. Some authors urge that when the crop is to be planted in the spring these fertilizers should be applied in the autumn, while some are of the opinion that equally good results are obtained by applying them at the time of sowing.⁴⁴

Reitmair concludes from his investigations that the extraction of bones in such a way as to remove practically all of their nitrogen does not unfit them for fertilizing purposes, since the residual phosphate of lime when reduced to a proper state of fineness is still valuable for its phosphoric acid.

⁴⁴ Reitmair, Wiener landwirtschaftliche Zeitung, 1905, 55 : 879, 889.

PART SECOND

NITROGEN IN FERTILIZERS, DRAINAGE WATERS, ETC.

247. **Kinds of Nitrogen in Fertilizers.**—Nitrogen is the most costly of the essential plant foods. It has been shown in the first volume that the popular notion regarding the relatively great abundance of nitrogen is erroneous. It forms only a minute part of the matter in and pertaining to the earth's crust. The great mass of nitrogen forming the bulk of the atmosphere is inert and useless in respect of its adaptation to plant food. It is not until it becomes oxidized by combustion, electrical discharges, or the action of certain micro-organisms that it assumes an agricultural value.

248. **States of Nitrogen.**—Having described the relation of nitrogen to the soil in the first volume, it remains the sole province of the present part to study it as aggregated in a form suited to plant food. In this function nitrogen may claim the attention of the analyst in the following forms:

1. In organic combination in animal or vegetable substances, forming a large class of bodies, of which protein may be taken as the type. Dried blood or cottonseed-meal illustrates this form of combination.

2. In the form of ammonia or combinations thereof, especially as ammonium sulfate, or as amid nitrogen.

3. In a more highly oxidized form as nitrous or nitric acid, usually united with a base of which Chile saltpeter may be taken as a type.

The analyst has often to deal with single forms of nitrogenous compounds, but in many instances may also find all the typical forms in a single sample. Among the possible cases which may arise, the following are types:

- a. The sample under examination may contain nitrogen in all three forms mentioned above.

b. There may be present nitrogen in the organic form mixed with nitric nitrogen.

c. Ammoniacal nitrogen may replace the nitric in the above combination.

d. The sample may contain no organic but only nitric and ammoniacal nitrogen.

e. Only nitric or ammoniacal nitrogen may be present.

249. Seeds and Seed Residues.—The proteid matters in seeds and seed residues, after the extraction of the oil, are highly prized as sources of nitrogenous fertilizers, either for direct application or for mixing. Typical of this class of substances is cottonseed-meal, the residue left after the extraction of the oil, which is accomplished at the present time mostly by hydraulic pressure but also by the use of a solvent. The residual cakes in the former case still contain some oil, but nearly half their weight consists of nitrogenous compounds. The following table gives the composition of a dry sample of hydraulic pressed cottonseed-meal:

Ash	7.60 per cent.
Fiber490 "
Oil	10.01 "
Protein	51.12 "
Digestible carbohydrates, etc.	26.37 "

While the above shows the composition of a single sample of the meal, it should be remembered that there may be wide variations from this standard due either to natural composition or to different degrees of the extraction of the oil.

The composition of the ash is given below:

Phosphoric acid, P_2O_5	31.01 per cent.
Potash, K_2O	35.50 "
Soda, Na_2O	0.57 "
Lime, CaO	5.68 "
Magnesia, MgO	15.19 "
Sulfuric acid, SO_3	3.90 "
Insoluble	0.69 "
Carbon dioxid and undetermined.	7.46 "

The cakes left after the expression of the oil from flaxseed and other oily seeds, are also very rich in nitrogenous matters; but these residues are chiefly used for cattle-feeding and only the undigested portions of them pass into the manure. Cottonseed

cake-meal is not so well suited for cattle-feeding as the others mentioned, because of the cholin and betain which it contains; often in sufficient quantities to render its use dangerous to young animals. The danger in feeding increases in proportion to the total quantity of the two bases and also the relative quantity of cholin to betain, the former base being more poisonous than the latter. In a sample of the mixed bases prepared by Maxwell from cottonseed cake-meal, the cholin amounted to 17.5 and the betain to 82.5 per cent. of the whole.⁴⁵

The nitrogen contained in these bases is also included in the total nitrogen found in the meal. The actual proteid value of the numbers obtained for nitrogen is, therefore, less than that obtained for the whole of the nitrogen by the quantity present as nitrogenous bases.

In the United States, cottonseed cake-meal is used in large quantities as a direct fertilizer, but not so extensively for mixing as some of the other sources of nitrogen. Its delicate yellow color serves to distinguish it at once from the other bodies used for similar purposes. No special mention need be made of other oil-cake residues. They are quite similar in their composition and uses, as well as in their manner of treatment and analysis to the cottonseed product.

250. Nitrogen in Sea-Weeds.—The waste available nitrogen finds its way sooner or later to the sea, and is recovered therefrom in many forms. Sea-weeds of all kinds are rich in organic nitrogen. Many years ago Forchhammer pointed out the agricultural value of certain fucoids.⁴⁶ Many other chemists have contributed important data in regard to the composition of these bodies.

Jenkins has shown from the analyses of several varieties of sea-weeds that in the green state they are quite equal in fertilizing value to stall manure, and are sold at the rate of five cents per bushel.⁴⁷ These data are fully corroborated by Goessmann.⁴⁸

Wheeler and Hartwell give the fullest and most systematic

⁴⁵ Maxwell, *American Chemical Journal*, 1891, **13** : 469.

⁴⁶ *Journal für praktische Chemie*, 1845, [1], **36** : 385.

⁴⁷ *Annual Report of the Connecticut Experiment Station*, 1890 : 72.

⁴⁸ *Annual Report of the Massachusetts Experiment Station*, 1887 : 223.

discussion which has been published of the agricultural value of sea-weeds.⁴⁹ Sea-weed was used as a fertilizer as early as the fourth century, and its importance for this purpose has been recognized more and more in modern days, especially since chemical investigations have shown the great value of the food materials therein.

To show the commercial importance of sea-weed, it is only necessary to call attention to the fact that in 1885 its value as a fertilizer in the State of Rhode Island was \$65,044, while the value of all other commercial fertilizers was only \$164,133. While sea-weed, in a sense, can only be successfully applied to marine littoral agriculture, yet the extent of agricultural lands bordering on the sea is so great as to render its commercial importance of the highest degree of interest.

251. Dried Blood and Tankage.—The blood and débris from abattoirs afford abundant sources of nitrogen in a form easily oxidized by the micro-organisms of the soil. Blood is prepared for use by simple drying and grinding. The intestines, scraps, and fragments of flesh resulting from trimming and cutting are placed in tanks and steamed under pressure to remove the fat. The residue is dried and ground, forming the tankage of commerce. The whole carcasses of animals condemned as unfit for food are reduced to tankage. Dried blood is richer in proteid matter than any other substance in common use for fertilizing purposes. When in a perfectly dry state it may contain as much as 14 per cent. of nitrogen, equivalent to nearly 88 per cent. of proteid or albuminoid matter. Tankage is less rich in nitrogen than dried blood, but still contains enough to make it a highly desirable constituent of manures.

252. Horn, Hoof and Hair.—These bodies, although quite rich in nitrogen, are not well suited to fertilizing purposes on account of the extreme slowness of their decomposition. Their presence, therefore, should be regarded in the nature of a fraud, because by the usual methods of analysis they show a high percentage of nitrogen, and therefore acquire a fictitious value. If these bodies be treated with sulfuric acid and rendered soluble their value as

⁴⁹ Rhode Island Experiment Station, Bulletin 21, 1893.



Fig. 13. Wild Ducks and Eggs on Layson Island.

a manure is greatly increased. The relative value of the nitrogen in these bodies as compared with the more desirable forms, has been a much disputed question.

253. Ammoniacal Nitrogen.—In ammonia compounds, nitrogen is used chiefly for fertilizing purposes as sulfate. Large quantities of ammonia are produced in the manufacture of coke and in other industrial operations. The ideal nitrogenous fertilizer is a combination of the ammoniacal and nitric nitrogen found in ammonium nitrate. The high cost of this substance excludes its use except for experimental purposes.

254. Nitrogen in Fish.—A large amount of nitrogen is also recovered from the sea in fishes. It is shown by Atwater that the edible part of fishes has an unusually high percentage of protein.⁵⁰ In round numbers about 75 per cent. of the water-free edible parts of fish are composed of albuminoids. Some kinds of fish, however, are taken chiefly for their oil and fertilizing value, as the menhaden, but the residue after the oil has been extracted is even richer in nitrogen than mentioned above. Squanto, an American Indian, first taught the early New England settlers the manurial value of fish.⁵¹

255. Nitrogen from Birds.—Immense quantities of waste nitrogen are further secured, both from sea and land, by the various genera of birds. The well known habit of birds in congregating in rookeries during the night and at certain seasons of the year tends to bring into a common receptacle the nitrogenous matters which they have gathered and which are deposited in their excrement and in the decay of their bodies. In former times the magnitude of these rookeries was probably much greater than now, but even at the present time they are of vast extent as shown by Fig. 13, a photograph of wild ducks on Layson Island. The feathers of birds are particularly rich in nitrogen, and the nitrogenous content of the flesh of fowls is also high. The decay of remains of birds, especially if it takes place largely excluded from the leaching of water, tends to accumulate vast deposits of nitrogenous matter. If the conditions in such deposits be favorable to the processes

⁵⁰ Report of the Commissioner of Fish and Fisheries, 1888 : 679.

⁵¹ Goode, American Naturalist, 1880, 14 : 473.

of nitrification, the whole of the nitrogen, or at least the larger part of it, which has been collected in this *débris*, becomes finally converted into nitric acid and is found combined with appropriate bases as deposits of nitrates. The nitrates of the guano deposits and of the deposits in caves arise in this way. If these deposits be subject to moderate leaching the nitrate may become infiltrated into the surrounding soil, making it very rich in this form of nitrogen. The bottoms and surrounding soils of caves are often found highly impregnated with nitrates.

256. Waste Nitrogen.—When nitrogen has played its role in vegetable and animal life it is broken down from the organic compounds it has formed by the action of organisms, or in the usual processes of decay, and is oxidized again to soluble forms, and may be even restored to its gaseous inorganic condition.

257. Soils Impregnated with Nitrogen.—While for our purpose, deposits of nitrates only are to be considered which are of sufficient value to bear transportation, or to warrant their concentration by leaching, yet much interest attaches to the formation of nitrates in the soil even when they are not of commercial importance.

In many of the soils of tropical regions not subject to heavy rain-falls, the accumulation of these nitrates is very great. Müntz and Marcano have investigated many of these soils to which attention was called first by Humboldt and Boussingault.⁵² They state that these soils are incomparably more rich in nitrates than the most fertile soils of Europe. The samples which they examined were collected from different parts of Venezuela and from valleys of the Orinoco, as well as on the shore of the Caribbean Sea. The nitrated soils are very abundant in this region of South America where they cover large surfaces. Their composition is variable, but in all of them carbonate and phosphate of lime are met with and organic nitrogenous material. The nitric acid is found always combined with lime. In some of the soils as high as 30 per cent. of nitrate of lime have been found. Nitrification of organic material takes place very rapidly the year round in this tropical region. These nitrated soils are everywhere

⁵² *Comptes rendus*, 1885, 101 : 65.

abundant around caves which serve as the refuge of birds and bats, as described by Humboldt. The nitrogenous matters, which come from the decay of the remains of these animals, form true deposits of guano which is gradually spread around, and which, in contact with the limestone and with access of air, suffers complete nitrification with the fixation of the nitric acid by the lime.

Large quantities of this guano are also due to the débris of insects, fragments of elytra, scales of the wings of butterflies, etc., which are brought together in those places by the millions of cubic meters. The nitrification, which takes place in these deposits, has been found to extend its products to a distance of several kilometers through the soil. In some places the quantity of the nitrate of lime is so great in the soils that they are converted into a plastic paste by this deliquescent salt.

258. Deposits of Nitrates.—The theory of Müntz and Marcano in regard to the nitrates of soils, especially in the neighborhood of caves, is probably a correct one, but there are many objections to accepting it to explain the great deposits of nitrate of soda which occur in many parts of Chile and other parts of the world. Another point which must be considered also, is this: That the process of nitrification can not now be considered as going on with the same vigor as formerly. Some moisture is necessary to nitrification, inasmuch as the nitrifying ferment does not act in perfectly dry soil, and in many localities in Chile, where the nitrates are found, it is too dry to suppose that any active nitrification could now take place.

The existence of these nitrate deposits has long been known.⁵³ The old Indian laws originally prohibited the collection of the salt, but, nevertheless, it was secretly collected and sold. Up to the year 1821, soda saltpeter was not known in Europe except as a laboratory product. About this time the naturalist, Mariano de Rivero, found on the Pacific coast, in the Province of Tarapacá, immense new deposits of the salt. Later the salt was found in equal abundance in the Territory of Antofogasta, and, further to the south, in the desert of Atacama, which forms the Department of Taltal.

⁵³ *Journal of the Royal Agricultural Society*, 1852, 13 : 349.

At the present time the collection and export of saltpeter from Chile is a business of great importance. The largest export prior to 1895, in any one year, was in 1890, when the amount exported was 927,290,430 kilograms; of this quantity 642,506,985 kilograms were sent to Europe and 86,124,870 kilograms to the United States. Since that time the imports of this salt into the United States have slowly increased.

The exportations from Chile during the years 1903, 1904 and 1905 were 1,445,000, 1,480,000 and 1,627,000 tons of 2204 pounds, respectively. During these three years there were imported directly into the United States 90,000, 75,000 and 117,000 tons, respectively.⁵⁴ The consumption of nitrate of soda in the United States is greater than the direct importation indicates, since considerable quantities come into the country from Europe. The total consumption in Europe in 1903 was 1,296,694 tons, and in the United States 259,993 tons. The total quantity of the salt exported from Chile from 1840 to 1903, inclusive, is 25,947,944 tons. The total quantity produced in Chile in 1905 was 1,733,644 tons, three-quarters of which were used as fertilizers. The quantity coming to the United States during that year was 353,177 tons. The total nitrate production of Chile in 1907 was 2,100,000 short tons of which 373,988 tons, valued at \$13,118,214 were directly or indirectly imported into the United States. The ratio of increase in exportation is rapidly decreasing, having fallen from 124 per cent. for the five years 1870-74 to 11.5 per cent. for the four years 1900-03.⁵⁵ In 1905 there were 78 factories in Chile engaged in the nitrate industry. In order to maintain prices a trust of the operators has been formed, regulating the amount which each factory may produce. About 55 tons of salt are produced annually for each laborer employed. The price per ton to wholesale American consumers ranges from \$45 to \$53. It is estimated that at the present rate of consumption, the supply from Chile will rapidly diminish in about 20 years.⁵⁶

According to Pissis these deposits are of very ancient origin.

⁵⁴ *L'Engrais*, 1906, 21 : 35.

⁵⁵ *American Fertilizer*, 1905, 22 : 5.

⁵⁶ *American Fertilizer*, 1905, 22 : 6.

This geologist is of the opinion that the nitrate deposits are the result of the decomposition of feldspathic rocks; the bases thus produced gradually becoming united with the nitric acid provided from the air.⁵⁷

According to the theory of Nöllner, the deposits are of more modern origin and due to the decomposition of marine vegetation.⁵⁸ Continuous solution of soils gives rise to the formation of great lakes of saturated water, in which occur the development of much marine vegetation. On the evaporation of this water, due to geologic isolation, the decomposition of nitrogenous organic matter causes generation of nitric acid, which, coming in contact with the calcareous rocks, attacks them, forming nitrate of calcium, which, in presence of sulfate of sodium, gives rise to a double decomposition into nitrate of sodium and sulfate of calcium.

The fact that iodine is found in greater or less quantity in Chile saltpeter, is one of the chief supports of this hypothesis of marine origin, inasmuch as iodine is always found in sea and not in terrestrial plants. Further than this, it must be taken into consideration that these deposits of nitrate of soda contain neither shells nor fossils, nor do they contain any phosphate of lime. The theory, therefore, that they are due to animal origin, is scarcely tenable.

Extensive nitrate deposits have been discovered in the U. S. of Columbia.⁵⁹ These deposits have been found extending over 30 square miles and vary in thickness from one to 10 feet. The deposits consist of a mixture of sodium nitrate, sodium chlorid, calcium sulfate, aluminum sulfate and insoluble silica, and contain from one to 13.5 per cent. of nitrate.

259. The Niter Deposits of California.—Many of the conditions which favor the deposition of niter in the soil are found in Southern California and Arizona, and it has been confidently predicted that niter deposits of value and of great extent would be found in these localities. The California State Mining Bureau

⁵⁷ Fuchs and de Launay, *Traité des Gîtes minéraux*, 1893, 1 : 425.

⁵⁸ Le Feuvre and Dagnino, *El Salitre de Chile*, 1893 : 12.

⁵⁹ Wiley, Presidential Address, *Journal of the American Chemical Society*, 1894, 16 : 20.

has made investigations of the deposits of niter in Southern California, and has collected practically all of the exact information that is available on the subject.⁶⁰ Nearly all of the niter deposits which have been discovered up to the present time are found in the northern part of San Bernardino County, and the beds are found particularly along the shore lines, or old beaches that mark the boundary of Death Valley as it doubtless appeared during the eocene times. The beds and clays contain the deposits which have been worn by erosive agencies into knobs, buttes and ridges that have been compared by some to haystacks and potato hills.

Until lately the principal value of the niter hills was supposed to lie solely in the surface coating. When this is removed, deposits which are full of other saline compounds are exposed. This top coating is, in accordance with the custom followed in Chile, called by the Spanish name "caliche." This caliche ranges in depth from a few inches to several feet. The surface caliche evidently owes its deposits of salt to the upward capillary flow of water from below, induced by the rapid evaporation at the surface in a region comparatively devoid of rains. The niter deposit is in the form of a soluble salt, which readily permeates the clay and separates into a white crystalline deposit. In Chile the colors of the caliche are usually yellow, pink and green, but in California a creamy yellow is the characteristic color; though pinks and greens are sometimes found. The quantity of niter contained in the caliche is extremely minute as compared with the more concentrated deposits of Chile, and hence it is evident that these extensive deposits in California will not become available commercially, until the more concentrated deposits in Chile and other similar localities are exhausted. The chief difficulty in the California deposits is that the niter is associated with other soluble salts, chiefly common salt, from which it is with some difficulty separated. The following table gives typical examples of the composition of the soluble salts of the caliche, not the representative or mean composition, but the extreme types of samples containing various proportions of niter:

⁶⁰ California State Mining Bureau, Bulletin 24, 1902 : 154.

	1	2	3	4	5
Niter (NaNO_3).....	7.28	14.50	27.40	46.50	61.20
Chlorid of Sodium	6.36	7.56	21.15	25.30	16.40
Sulfate of Sodium60	.70	2.05	5.30	3.10
Sulfate of Lime.....	.20	.10	1.04	.30	.20
Sulfate of Magnesium...	1.30	2.80	2.00	1.20	1.20
Insolubles.....	84.26	74.34	46.36	21.40	17.90
	100.00	100.00	100.00	100.00	100.00

It was found that the average composition of 104 samples of caliche, taken from as many different claims, was 9.54 per cent. of niter. The quantity of niter which has been located in Southern California is difficult to estimate. The following estimate comprises the whole amount of niter which is thought to exist in the small areas surveyed, but it does not indicate what can be commercially extracted. About 35,000 acres of the deposit have been examined, in which it is estimated that there exist about 22,000,000 tons of nitrate of soda. This, of course, is only a very rough estimate and is perhaps of little value in basing computations of the future supply.

In general, it may be said that the niter beds of California are at the present time of little importance from a commercial point of view. Not only is the amount of niter comparatively small, but the distance from markets and the cost of transportation are so great as to practically exclude the product from the markets of the world.

It is stated by Pennock that no commercial success has attended the exploitation of nitrate deposits in the United States.⁶¹ According to the same author the production of nitrate of soda is practically confined to Chile.

260. Functions of Sodium Nitrate.—Practically the only form of oxidized nitrogen which is of importance from an agronomic point of view is sodium nitrate, often known in commerce by the name Chile saltpeter. Ammoniacal compounds and nitrites are usually oxidized to nitric acid or its compounds before they are assimilated as plant foods. Applied to a growing crop, sodium nitrate at once becomes dissolved at the first rainfall or by the natural moisture of the soil. It carries thus to the rootlets of

⁶¹ Journal of the American Chemical Society, 1906, 28 : 1248.

plants a supply of nitrogen in the most highly available state. There is perhaps no other kind of plant food which is offered to the living vegetable in a more completely predigested state, and none to which a quicker response will be given. By reason of its high availability, however, it must be used with care. A too free use of such a stimulating food may have, in the end, an injurious effect upon the crop, and is quite certain to lead to the waste of a considerable portion of expensive material. For this reason sodium nitrate should be applied with extreme care, in small quantities at a time, and only when it is needed by the growing crop. It would be useless, for instance, to apply this fertilizer in the autumn with the expectation of its benefiting the crop to a maximum degree the following spring. Again, if the application of this salt should be made just previous to a heavy rain, almost or quite the whole of it would be removed beyond the reach of the absorbing organs of the plant.

When once the nitric acid has been absorbed by the living rootlet it is held with great tenacity. Living plants macerated in water give up only a trace of nitric acid, but if they be previously killed with chloroform, the nitric acid they contain is easily leached out.

The molecule of sodium nitrate is decomposed by dissociation or otherwise in the process of the absorption of the nitric acid. The acid enters the plant organism and the soda is left to combine with the soil acids. The nascent soda may thus play a rôle of some importance in decomposing particles of minerals containing potash or phosphoric acid. Some authorities say the decomposition of the sodium nitrate takes place in the cells of the absorbing plant organs, for it is difficult to understand how it could be accomplished externally. While the soda, therefore, is of no importance as a direct plant food, it can hardly be dismissed as of no value whatever in the process of fertilization. Many of the salts of soda, as, for instance, common salt, are quite hygroscopic and serve to attract moisture from the air and thus become carriers of water between the plant and the air in seasons of drought; and sodium nitrate itself is so hygroscopic as not to be suited to the manufacture of gunpowder.

To recapitulate: The chief functions of sodium nitrate are to give to the plant a supply of oxidized nitrogen ready for absorption into its tissues and incidentally to aid, by the residual soda, in the decomposition of silt particles containing potash or phosphoric acid and in supplying to the soil salts of a more or less deliquescent nature.

261. Commercial Forms of Chile Saltpeter.—The Chile saltpeter of commerce may reach the farmer or analyst in the lumpy state in which it is shipped, or as finely ground and ready for application to the fields. Unless the farmer is provided with means for grinding, the latter condition is much to be preferred. It permits of a more even distribution of the salt, and thus encourages economy in its use. For the chemist also it is advantageous to have the finely ground material, which condition permits more easily a perfect sampling, a process which, with the unground salt, is attended with no little difficulty.

262. Percentage of Nitrogen in Chile Saltpeter.—Chemically pure sodium nitrate contains 16.49 per cent. of nitrogen. The salt of commerce is never pure. It contains moisture, potash, magnesia, lime, sulfur, chlorin, iodine, silica and insoluble materials, and traces of other bodies. The value of the salt depends, therefore, not only on the market value of nitrogen at the time of sale, but also on its content of nitrogen. The nitrate of commerce varies greatly in its nitrogen content and is sold on a guaranty of its purity. The best grades range in nitrogen from 15 to 16 per cent. The content of nitrogen has long been estimated in the trade by determining the other constituents and counting the rest as nitrogen. This practice arose in former times when no convenient method was at hand for determining nitric nitrogen. The process is tiresome and unreliable, because all errors of every kind are accumulated in the nitrogen content, but inasmuch as the method is still required by many merchants, the analyst should be acquainted with it, and it is therefore given further along. The usual methods for determining nitric nitrogen may be applied in all cases where samples of sodium nitrate are under examination, but some special processes are described further on for convenience.

263. Adulteration of Chile Saltpeter.—The analyst, aside from

the honesty of the dealer, is the only protector of the farmer in guarding against the practice of adulteration of sodium nitrate. Even the honest dealer is compelled to protect himself against fraud, and therefore, the world over, commerce in this fertilizer is now conducted solely on the analyst's certificate. Happily, therefore, adulteration is almost unknown, because it is certain to be detected. Formerly, the saltpeter was adulterated with common salt, or low grade salts from the potash mines; but it is an extremely rare thing now to find any impurities in the salts other than those naturally present.

In every case the analyst may grow suspicious when he finds the content of nitrogen in a sample to fall below 13 per cent. It must not be forgotten, however, that some potassium nitrate may be present in the sample, and since that salt contains only 13.87 per cent. of nitrogen, its presence would tend to lower the value of the fertilizer; but although the potash itself is a fertilizer of value, it is not worth more than one-third as much as nitrogen. In all cases of suspected adulteration, it is advisable to make a complete analysis. The results of this work will, as a rule, lead the analyst to a correct judgment.

264. The Application of Chile Saltpeter to the Soil.—The analyst is often asked to determine the desirability of the use of sodium nitrate as a fertilizer and the methods and times of applying it. These are questions which are scarcely germane to the purpose of this work, but which, nevertheless, for the sake of convenience, may be briefly discussed. In the first place, it may be said that the data of a chance chemical analysis will not afford a sufficiently broad basis for an answer. A given soil may be very rich in nitrogen as revealed by chemical analysis, and yet poor in an available supply. This is frequently the case with vegetable soils, containing, as they do, large quantities of nitrogen, but holding it in practically an inert state. I have found such soils very rich in nitrogen, yet almost entirely devoid of nitrifying organisms. It is necessary, therefore, in reaching a judgment on this subject from analytical data to consider the different states in which the nitrogen may exist in a soil, and above all, the nitrifying power of the soil if the nitrogen be

chiefly present in an organic state. Culture solutions should therefore be seeded with samples of the soil under examination and the beginning and rapidity of the nitrification carefully noted. In conjunction with this the nitrogen present in the soil in a nitric or ammoniacal form should be accurately determined.

The quantities of Chile saltpeter which should be applied per acre vary with so many conditions as to make any definite statement impossible. On account of the great solubility of this salt, no more should be used than is necessary for the nutrition of the crop. For each 100 pounds used, from 14 to 15 pounds of nitrogen will be added to the soil. Field crops, as a rule, will require less of the salt than garden crops. There is an economic limit to the application which should not be passed. As a rule, 250 pounds per acre is a maximum dressing for field crops. The character of the crop must also be considered. Different amounts are required for sugar beets, tobacco, wheat, and other standard crops. It is rarely the case that a crop demands a dressing of Chile saltpeter alone. It will give the best effects, as a rule, when applied with phosphoric acid or potash. But this is a branch of the subject which cannot be entered into at greater length in this manual. The reader is referred to Weitz's work on Chile saltpeter for further information.⁶²

265. The Utilization of Nitrogen in the Air as a Fertilizing Material.—The only form of plant which has developed these tubercles to any extent is the legumes. It is, therefore, commonly understood that the nitrifying organisms of symbiotic forms are confined to leguminous plants. At the same time, mention is made in Volume I of the possible direct nitrifying of atmospheric nitrogen without the intervention either of any organic form thereof, or the activity of other symbiotic nitrifying activity. Some of the results of earlier workers in this field seem to indicate the existence of organisms which are capable of directly nitrifying atmospheric nitrogen and making it available as a fertilizing material. These earlier ideas which are mentioned in Volume I, have of late years received further investigation, with the result of establishing more firmly the belief that nitrification, indepen-

⁶² Der Chilisalpeter als Düngemittel, 1905.

dent of the processes commonly associated therewith, may sometimes take place.⁶³

The influence of oxid of iron in the soil in rendering available the nitrogen of the air, has received special attention. Bonnema has given to this subject careful consideration and has come to the conclusion that the so-called fixation of atmospheric nitrogen in the soil is dependent upon the presence of ferric hydroxid. This substance appears to have the property of oxidizing elemental nitrogen and changing it into nitrous acid, which is capable of conversion into nitric acid in the usual manner.

It appears from this investigation that the first step in the nourishment of a plant by atmospheric nitrogen is not necessarily one of biological chemistry, but rather one of a simple elementary process.⁶⁴

This problem has lately been studied more closely by Sestini.⁶⁵ It appears from the investigation made by Sestini that it is not the elemental nitrogen of the air, but the ammonia which is contained therein which is oxidized by ferric hydroxid into nitric acid. This is an important observation in view of the fact that it is generally supposed that the ammonia which enters the soil from the air is converted into nitrous acid through the activity of nitrifying ferments. The utilization of the oxid of iron, therefore, is not directed to the increase of the total quantity of assimilable nitrogen, but only to the change of the ammonia into an assimilable form. This has an important bearing upon the study of the chemical processes relating to fertilizing materials by reason of the relation of ammonia to fertility. The highly beneficial effects produced by the application of ammonia salts have long been recognized. Most observers claim that these salts are only useful when converted into nitric acid, and others that they are useful in the absence of ferments which can produce this change. In either case, however, it is evident, in view of the observations above mentioned, that ammonia is not directly assimilable even

⁶³ Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 568.

⁶⁴ Chemiker-Zeitung, 1903, 27 : 149.

⁶⁵ Die landwirtschaftlichen Versuchs-Stationen, 1904, 60 : 103.

in the cases last mentioned, but only after being converted into a more highly oxidized form by the activity of ferric hydroxid.

It seems to be established that ferric hydroxid at ordinary temperature, that is, from 15° to 25°, develops a catalytic influence on ammonia and ammonia salts, and that under this influence an assimilable form of nitrogen is developed in the soil independently of the activity of nitrifying ferments, even in the presence of large quantities of thymol or of corrosive sublimate up to two per cent., quantities which are entirely sufficient to inhibit the action of the ordinary nitrifying ferments. The ammonia of the air and of the soil may thus be converted into nitrous acid by the oxidation produced under the influence of the catalytic activity of ferric hydroxid.

266. The Utilization of Atmospheric Nitrogen by Other Plants Than Legumes.—The evidence which seeks to establish the fact that other plants than legumes are capable of utilizing atmospheric nitrogen is not wholly conclusive. Theoretically, it seems a rather strange provision of nature that only plants of the leguminous family should have the faculty, either symbiotically with nitrifying organisms or directly, to utilize atmospheric nitrogen as a source of plant food. Nevertheless, the greater number of carefully conducted experiments in which all sources of possible error are excluded, have led, as a rule, to negative results with other plants, so that it can scarcely be affirmed with any scientific certainty that this property of plants is a general or even a common one. On the other hand, in a review of this subject in connection with research work, Jamieson has reached the conclusion that the property of utilizing atmospheric nitrogen belongs to many other forms of plants besides the legumes.⁶⁶ In this report Jamieson undertakes to establish the fact that the legume tubercle theory is untenable, and that the nitrogen of the air is directly utilized by plants in general. In all the plants examined by him, structures which absorb free nitrogen from the air and transform it into the organic state were found. Seventeen forms of plants of widely different character are said by Jamieson to have been examined and found to possess the property indicated.

⁶⁶ Report of the Agricultural Research Association of the North-eastern Counties of Scotland, 1905 : 16.

The plants which are least capable of utilizing atmospheric nitrogen are the monocotyledons, and especially the cereals and grasses. According to Jamieson, the chlorophyll cell seems to possess in a high degree the property of transforming nitrogen, and the function of the green cell, in this particular, is analogous to that possessed by it of utilizing the carbon of the carbon dioxide in the air for the purpose of producing organic compounds. He claims to have established the fact, that the free nitrogen in the air is directly absorbed and transformed into organic compounds by these cells.

The number of these organs, their nature, and their aptitude to exercise their functions vary considerably from one plant to another. In particular, the monocotyledons such as the cereals and grasses are very poorly endowed with the organs from the point of view of the fixation of nitrogen. The form of these organs also varies greatly and the different forms observed by Jamieson are described in his work. These organs are called producers of protein, and are not met with in general except in the tender part of the very young leaves or their petioles. At the beginning of their formation they do not contain any protein. When these organs are completely developed the production of protein begins and the organs are sometimes gorged with protein, and this continues for a certain length of time. The plants which are most apt to fix a great deal of nitrogen do not have need of nitrogen fertilizers, provided they find at the beginning of their development favorable conditions that will permit the proper growth of the organs which produce the protein. Instead of buying nitrogenous fertilizers as a greater aid to the plants which are able to fix only little nitrogen, such as cereals and grasses, it will be sufficient to cultivate those plants which absorb and fix a great deal of nitrogen and thus to incorporate this nitrogen in the soil.

These observations are cited solely to call attention to them. If confirmed by future investigations, they will prove useful in practical agriculture in securing a more abundant supply of nitrogenous material for plant growth.

267. Accumulation and Utilization of Atmospheric Nitrogen in the Soil.—Interesting investigations have been made on this

point by Voorhees and Lipman.⁶⁷ The experiments conducted were so arranged as to bring out the relation of leguminous crops, such as cow peas, to soil and nitrogen and to determine, as far as practicable, the value of this leguminous crop as a source of nitrogen to subsequent non-leguminous crops. The soils selected contained an abundance of phosphoric acid and potash. The facts established by the investigation are of practical importance, in respect of the possibility of accumulating nitrogen in the soil directly from atmospheric nitrogen. The greater number of the investigations were of negative value, but a sufficient positive gain was found in some cases to indicate that further investigation may develop methods to promote the fixation of nitrogen in the soil. The authors admit that the probability of the continued fixation of nitrogen, in the manner in which the investigations were made, is not very great. Attention is called to the fact, however, that the present knowledge of bacteriological conditions in the soil is still so limited, that a general and successful inoculation with non-symbiotic nitrogen-fixing bacteria is out of the question. There is also a danger to be avoided in the attempt to increase the soil nitrogen by means of the inoculation of leguminous plants, where large quantities of leguminous material are incorporated in the soil, as shown by researches above mentioned. The nitrogen-decomposing bacteria can develop freely and the denitrifying organisms may set free more nitrogen than the nitrifying organisms fix.

Therefore, the practical problem of the utilization of atmospheric nitrogen as a fertilizing material is to be considered, and the conditions which determine the comparative rate of nitrification and denitrification are to be carefully studied in order that valuable results may be reached.

The authors also found that even under carefully controlled conditions there was no uniform gain of nitrogen due to the inoculation of soils with nitrifying ferments.⁶⁸

The investigation shows that there was no decided gain in nitrogen in the inoculated soil after the inoculation. There was,

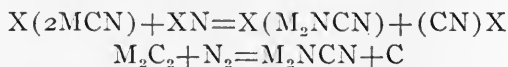
⁶⁷ *Journal of the American Chemical Society*, 1905, 27 : 556.

⁶⁸ *New Jersey State Agricultural Experiment Station, 25th Annual Report*, 1904 : 239.

in all cases, a loss of nitrogen during the summer when the soils were kept bare, and the losses were greatest where manure had been used.

These data show that the problem of increasing soil nitrogen in a uniform manner through the oxidation of atmospheric nitrogen is still unsolved. There is probably no other one problem of greater importance to agriculture. The nitrogenous fertilizers are of dominant importance, both by reason of their high cost and of the necessity of their presence in order that the other fertilizing materials in the soil shall be duly utilized. There are many indications, however, that in the near future the method for the utilization of atmospheric nitrogen by direct oxidation thereof in the field, either with or without the aid of growing plants, may be discovered and thus the farmer made more independent of the nitrogen now stored in various parts of the earth or produced by manufacturing operations.

268. Manufacture and Use of Cyanamid for Fertilizing Purposes.—Cyanamid has the general formula $H_2N:CN$. With univalent metals it yields metallic compounds corresponding to $M_2N:CN$. In investigating the manufacture of cyanids by means of carbids, Frank and Caro observed that if moist atmospheric nitrogen be passed through a retort heated to dull redness and containing a mixture of calcium and barium carbids, the nitrogen becomes fixed to the metal with formation of cyanid; besides cyanid, other nitrogenous compounds, *e. g.*, cyanamid, due in part to the action of the cyanid already formed and in part to the direct action of the reacting mass, as the following equations indicate, are formed:⁶⁹



The formation of cyanamid may be increased by giving the carbid a large surface thus allowing a large amount of nitrogen to act upon a small quantity of carbid. Frank and Caro's process is based on this observation.

The process of the Deutsche Gold und Silber Scheide Anstalt

⁶⁹ Robine and Lenglen, *The Cyanid Industry*, Translated by LeClerc, 1906, : 144.

for the preparation of cyanamid uses carbon in the solid state or in the form of hydrocarbon gas, and an alkali amid; or NH_3 brought in contact with a melted alkali metal and charcoal at $400^\circ\text{--}600^\circ$. In this way, alkali amid is formed which under the action of a portion of the charcoal becomes alkali cyanamid.⁷⁰

Calcium cyanamid (the formula of which when pure is CaCN_2) is a black powder, resembling basic slag in other properties and containing over 20 per cent. N, readily soluble in H_2O , besides more or less CaO , CaC_2 and C.

Gerlach found it to be equal in manurial value to NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ in pot experiments with barley and white mustard, though in field experiments its value fell to 74 ($\text{NaNO}_3 = 100$).⁷¹ With peaty soils, calcium cyanamid acts injuriously, due probably to the formation of dicyanodiamid by the organic acids, unless the application of the manure be made five or six weeks before sowing.

This early application causes a loss of nitrogen, which should be taken into account in reckoning its value.

Otto found it nearly as efficacious as sodium nitrate when used with spinach or cabbage, and better than nitrate or ammoniacal nitrogen in fertilizing maize.⁷²

Hall in comparing it with ammonium sulfate for fertilizing mangels, swedes and mustard, obtained favorable results.⁷³

The best way to determine the nitrogen in calcium cyanamid is to digest it with strong sulfuric acid by the usual kjeldahl process.

CaCN_2 decomposes in the soil into CaCO_3 and NH_3 ; this makes the soil alkaline; therefore it is better to use acid phosphate than disodium phosphate.⁷⁴

269. Cyanamid Compound as a Fertilizer.—Experiments have been conducted by Shutt and Charlton at the agricultural experiment station at Ottawa to determine the value of cyanamid compound as a fertilizer. The effect of the compound

⁷⁰ Robine and Lenglen, *The Cyanid Industry*, Translated by LeClerc, 1906: 176.

⁷¹ Biedermann's *Central-Blatt*, 1904, 33: 649.

⁷² *Chemisches Central-Blatt*, 1905, I: 117.

⁷³ *Journal of Agricultural Science*, 1905, 1: 146.

⁷⁴ Inamura, *Bulletin of the College of Agriculture*, Tokyo, 1906, 7: 53.

upon the vitality of seeds was first studied. The result of these experiments was to show that the cyanamid compound, except in very minute quantities, injuriously affected the vitality of the seed. As the amount is increased the toxic effect becomes more and more noticeable, not only in the retardation of germination, but also upon the health and vigor of the young plant. Wheat is better able to resist this action than peas. Nevertheless the wheat plants in the tests which contained the larger amount of cyanamid frequently turned black, withered and died after reaching a height of from three to five inches. It is believed that cyanamid compound in amounts not greater than five milligrams of nitrogen to 100 grams of soil, does not prove injurious to the germination of seed. Toxic effects were markedly noticeable, on the other hand, with amounts of cyanamid containing between 10 and 12 milligrams of nitrogen per 100 grams of soil. The potassium compound appears to be more injurious in action upon the life of the seed and young plants than the calcium salt. In regard to the value of cyanamid compound as a fertilizing material, the experiments were confined to the study of its degree of nitrification. It would seem from a consideration of the data secured that as the comparative amount of the cyanamid compound is increased in the soil there is a corresponding decrease in the rate of nitrification. This is probably due, as already indicated, to the toxic action upon the nitrifying organisms. It may be due partly also to denitrifying changes leading to a reduction of a part of the nitrogen to the free state. The conversion of the nitrogen of the cyanamid into available forms is probably continuous under favorable conditions, though not uniformly so. The first stage of the process may be considered possibly as purely chemical, since water at ordinary temperatures converts the nitrogen of cyanamid into ammonia. Further changes are brought about through the agency of living organisms, and are necessarily slower, depending for their activity on many factors, prominent among which is the relative proportion of the cyanamid compound present in the soil.⁷⁵

270. Later Experiments with Cyanamid.—Grandeau has sum-

⁷⁵ Chemical News, 1906, 94 : 150.

marized the latest results of the experimental value of nitrate and cyanamid of calcium produced by the electric process described later.⁷⁶ The compound used by him was produced by a factory in Norway, the term "Norwegian Nitrate" being used to distinguish it from the nitrate of Chile. The calcium cyanamid when subjected to the moisture of the soil produces ammonia.

The commercial product contains from 20 per cent. to 22 per cent. of nitrogen, while the sulfate of ammonia contains about 25 per cent. Pure calcium cyanamid CN_2Ca , contains 35 per cent. of nitrogen. The commercial cyanamid is a black powder, ground extremely fine, which owes its color to the carbon which it contains, in all about 17 per cent.

Practical experiments made by Cart, and reported to Grandeau, show that while the nitrate of lime acted very successfully as a fertilizer, the cyanamid of calcium was somewhat disappointing. There was difficulty in spreading this brown and black powder regularly, and in applying it to the soil the fine powder was extremely irritating to the face and hands. The effect upon the wheat after 24 hours was described as being similar to that produced by a solution of sulfate of copper, while the wheat treated with the nitrate took on a beautiful green tint and grew rapidly, and that which had received the cyanamid turned to a reddish tint, which was retained for at least a week.

The total amount of wheat harvested from the plot receiving the cyanamid was less than that receiving no nitrogenous fertilizer at all.

Müntz and Nottin conclude that the calcium cyanamid does not interfere with germination when employed in ordinary quantities, not exceeding 200 kilograms per hectare, and gives good results.

It is possible that the deleterious effects of the calcium cyanamid may be due to the fact which has been noticed by investigators that in the manufacture of cyanamid it may be associated with another compound, viz., dicyanamid, the poisonous properties of which for plants are well known. Perhaps the poisonous action noticed above by Cart may have been due to such an admixture. The matter needs further investigation.

⁷⁶ Journal d'Agriculture pratique, 1908, 72 : 229.

271. Utilization of Atmospheric Nitrogen.—In the first volume of this work attention has been called to the fixation and utilization of atmospheric nitrogen by the action of bacteria, especially those living in symbiosis with leguminous plants.⁷⁷ Berthelot in the first volume of his *Vegetable and Agricultural Chemistry*, has set out at great length the various methods in which atmospheric nitrogen may be rendered available for agricultural purposes.⁷⁸ It will prove convenient for the analyst and student to have a summary of the different methods described in which atmospheric nitrogen may be rendered useful for plant food.

The methods as set forth by Berthelot are as follows:

(1) Fixation of atmospheric nitrogen by means of microbes in the earth and upon vegetables.

(2) The continued fixation of free nitrogen by the organic compounds under the influence of atmospheric electricity of feeble tension.

(3) The fixation of nitrogen under the influence of slow oxidation.

There are many subdivisions made under these various heads but those represent in general the principal methods which Berthelot has studied. All these methods, it is noticed, are purely natural, that is, those which are going on constantly in nature, Berthelot not having taken up the study of the artificial production of nitrogen under strong electric influences in the first volume of his work.

272. Historical Development of the Fixation of Atmospheric Nitrogen by Means of Electricity.—The principal steps in the development of the investigation looking to the fixation of atmospheric nitrogen have been traced by Erlwein.⁷⁹ Attention is called to the researches of Crookes, Lord Rayleigh, Bradley, Lovejoy, Birkeland, Kowalsky, and Pauling in the research work and practical application of the principles discovered. Special attention is given to the work done by Siemens and Halske. These investigators studied the problem of the production of nitric acid by electrical discharges between

⁷⁷ Wiley, *Principles and Practice of Agricultural Analysis*, 2nd Edition, 1906, 1 : 521.

⁷⁸ *Chimie végétale et agricole*, 1899, 1.

⁷⁹ *Elektrotechnische Zeitschrift*, 1907, 14 : 41, 62. *Electrochemical and Metallurgical Industry*, 1907, 5 : 77.

heavy carbon electrodes. They also utilized the horn lightning arrester consisting of two vertical horns, the lower ends of which are near together, while upwards the two horns diverge from each other more and more. The arc is formed between the two lower ends of these electrodes and travels upwards, thereby enlarging its surface and causing it finally to be automatically broken. None of these methods, however, resulted in securing oxidized nitrogen on a commercial scale. The development of the cyanamid furnace is fully described in this paper and the fundamental reaction by which calcium cyanamid is produced is given as $\text{CaO} + 2\text{C} + 2\text{N} = \text{CaCN}_2 + \text{CO}$. When the price of calcium carbide fell to a point at which it could be commercially used it was found that the production of calcium cyanamid was more economically secured by starting with the carbide itself. The fundamental reaction in this case is $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$. The principle of the construction of the cyanamid furnace is based upon the utilization of a series of coal-fired retorts, closed air-tight, and partially filled with powdered calcium carbide. After the contents of the retort have reached a white heat nitrogen gas is introduced therein. In these conditions the carbide rapidly absorbs the nitrogen. The reaction is exothermic and the heat evolved promotes still more the activity of the combination. After the carbide is absorbed by the nitrogen the incandescent cyanamid is removed from the retorts, cooled under exclusion of the air and powdered and packed for shipping.

The commercial calcium cyanamid is a black powder, quite stable in the air and consists of 57 per cent. of calcium cyanamid 14 per cent. free carbon, to which the black color is due, 21 per cent. caustic lime, $2\frac{1}{2}$ per cent. of silicic acid, four per cent. of iron oxide, and small quantities of sulfur, phosphorus and carbonic acid. The average content of nitrogen is about 20 per cent. When placed in water calcium cyanamid dissolves, decomposing quickly, especially in hot water, and yielding caustic lime, and, by polymerization, a complicated compound called dicyanamid. Subjected to overheated steam calcium cyanamid gives off its nitrogen quantitatively in the form of ammonia. In aqueous solution, under the influence of certain acids, a series of synthetic organic compounds are produced, among which is found urea.

When fused with sodium carbonate, sodium chlorid or other similar materials, all of the nitrogen in the cyanamid is converted into cyanid nitrogen, in other words, the product is a mixture of calcium cyanid, and sodium cyanid. Erlwein draws the following conclusions from the present state of the art:

Cyanamid may be used directly as a fertilizer in agriculture. Those who are interested in the agricultural side of the problem will find interesting comparative pictures of the growth of plants under the fertilizing action of Chile saltpeter and calcium cyanamid, etc., in the original German paper.

2. Calcium cyanamid may be used for the production of ammonium sulfate, which is also consumed in large quantities for fertilizing purposes. The reaction yielding ammonia is $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$.

3. Cyanamid may be used for the manufacture of dicyanamid, a compound used in the manufacture of anilin dyes and gun powder. By suitable leaching with water and crystallization, this compound is obtained in the form of pretty white crystals. The chemical equation is $2\text{CaCN}_2 + 4\text{H}_2\text{O} = 2\text{Ca}(\text{OH})_2 + (\text{CNNH}_2)_2$.

4. Cyanamid may be used as the starting material for the commercial manufacture of sodium cyanid or potassium cyanid. According to a process devised by Freudenberg, the calcium is melted with sodium chlorid in excess and is thereby transformed almost completely into sodium cyanid. The product obtained in this way, which contains about 22 to 23 per cent. of sodium cyanid (corresponding to 30 per cent. of potassium cyanid), is either sold directly in this form as so-called "sodium-cyanid substitute" (Cyannatrium-Surrogat) for use in gold metallurgy, or is worked up into chemically pure sodium cyanid or potassium cyanid. Both brands will be made on a commercial scale as soon as a new factory is completed which is in course of erection near Berlin.

5. As a hardening material for iron and steel, calcium cyanamid has found a new sphere of application. This application is due to the ability of the cyanamid to give off carbon to the iron which is thereby hardened. This ability is enhanced by the addition of other compounds to the cyanamid and this product is

now sold under the trade name, of "Ferrodur." Dr. Reininger, chief chemist of the well-known tool-steel and machine works of Ludwig Loewe, first recognized this property of cyanamid and called attention to the extremely uniform action of this new hardening material, which proves useful especially at such temperatures at which a uniform introduction of carbon into iron heretofore met with difficulties.

6. For the manufacture of urea a small plant is already in operation in which the calcium cyanamid is treated in a suitable way with acids and immediately changed into solutions of urea, which may be easily crystallized.

273. Production of Nitric Acid by Electric Action.—This subject has been largely studied in many parts of the world, and in this country at Niagara Falls works of considerable magnitude have been erected for the production of nitric acid under electric influence, the electric power being generated by the water of Niagara Falls.^{79a}

The Atmospheric Product Company at Niagara Falls installed upon the methods of Bradley and Lovejoy gave, at first, apparently satisfactory results per kilowatt in the production of nitric acid. This method, however, necessitated apparatus of a very complicated character in order to insure its industrial success. For this reason, since the summer of 1904 it has not been operated for the production of nitric acid. The company had hoped to utilize 150,000-horse power furnished by Niagara Falls, and expected, therefore, to make a sufficient quantity of nitrate of soda for the world's supply. It is possible that the time may come when the utilization of 150,000-horse power will accomplish this result, but the experience so far obtained at Niagara does not bear out the hopes of its immediate fulfilment. While these experiments were conducted at Niagara Falls, Kowalski and Moscicki built a factory at Fribourg for the manufacture of nitric acid by electricity. They used alternating currents of very high tension, from 50 to 75 thousand volts. The electrodes employed were of aluminum. This factory, however, does not appear to have had very much greater success commercially than the one at Niagara Falls.

^{79a} Grandeau, *La Production électrique de l'Acide nitrique*, 1906.

In 1903 an improvement in the manufacture of nitric acid from the atmosphere was made by Birkeland and Eyde. Birkeland employed a continuous current produced by 40 amperes at 600 volts, which, in connection with other principles of the method, produced a magnetic field of very great intensity. This led to the invention and establishment of the apparatus which has been erected at Notodden, Norway. The furnaces now constructed comprise three of identical structure. The energy of the furnace has been carried from 500 to 700 kilowatts, that is from 700 to 1000 horse power, for each of them. It has been possible, in the very latest experiments to increase the energy of these furnaces to 1500 horse power. It is found, however, that the furnaces work more effectually and give better results at a uniform utilization of from 500 to 600 kilowatts. The electric energy necessary for the working of the factory at Notodden is furnished at a price of 32 francs per kilowatt-year. The electricity is furnished by a generator of two thousand kilowatts capacity of a triphase construction and at a tension of 5000 volts. The air sent into the furnace by the ventilators is used up at the rate of 25,000 liters per minute for each one, that is for the three furnaces 75,000 liters per minute. It at once reaches the magnetic field formed by the wall of the furnace made of fire clay. The air mixed with the nitric gas produced in the furnace leaves the apparatus through a tube kept at a temperature of from 500° to 700°, a temperature much higher than that in other apparatus destined to produce nitric acid. The gases pass first through a tubular boiler where they are cooled to about 200°. The steam which is produced in this boiler is utilized in the concentration of the solutions of nitrate of lime which are finally formed. From this boiler the gases are introduced into the cooling apparatus which rapidly reduces their temperature to 50° or 60°, a temperature which is the most favorable to the reactions which result in the formation of nitrous acid. In the magnetic field of the furnace it should be understood that there is formed only a single nitrogen combination; namely, oxid of nitrogen NO. Its proportion reaches about five per cent. of the total volume of gas. At a very high temperature of from 2000° to 2500° the elements of this oxid are separa-

ted and recombined incessantly in such a way that the total percentage of the oxid of nitrogen remains constant in the mixture.

274. Oxidation Towers.—These large reservoirs communicate with the electric furnaces by large tubes and are two in number. They are cylindrical in shape and in the interior are covered by a material which is not attacked by acids. In these towers the further oxidation of the oxid of nitrogen produced in the furnace takes place. In a short time in these towers the oxid of nitrogen (NO) is converted into NO_2 . Leaving the reservoirs, the nitrous gas produced is forced through a ventilator into the absorption towers where it is transformed into nitric acid. The transformation which takes place in these last towers, converts the nitrous oxid into nitric acid by means of water according to the formula, $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$. At the same time that the nitric and nitrous acids are formed there are produced lower oxids of nitrogen by the decomposition of nitrous acid according to the following equation: $2\text{HNO}_2 = \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$. These are reoxidized by the continuous fundamental reaction.

275. Absorption Towers.—These are prismatic in shape, having a section four meters square and 10 meters high. They contain, therefore, 40 cubic meters. They are placed along the sides of a hall in two parallel rows, each row embraces two towers in granite and two towers in sandstone, filled with pieces of quartz of the size of the thumb, two-thirds of their height. In the interior of these towers there are circulated in an inverse direction and in a continuous manner the gases and the water. This water, which constantly moistens the quartz, is charged progressively with the nitric acid which is formed. The other nitrous products, with the exception of the lower oxids, which accompany the formation of nitrous acid, are reoxidized in these towers in contact with the oxygen of the air, and give new quantities of nitrous acid, as has just been described. Finally, when the solution of nitric acid produced in the towers has attained by repeated contact with the gases and water a concentration of 50 per cent., that is, 50 kilograms of monohydrated nitric acid in 100 liters of liquid, it is received into ordinary vessels made of

granite and provisionally stored therein. From the towers in which the water and gases coming from the oxidation towers are circulated in an inverse direction, there is obtained the greatest part of the nitrate product transferred into monohydrate nitric acid and dissolved in water. It is, however, very important not to permit the loss of the nitric products which have escaped absorption in the system of towers and are found in notable quantities in the gases escaping from the last one of the vessels. In order to collect these gases an energetic absorbent is used, namely, milk of lime. For this purpose there is a fifth tower of wood of the same dimensions as the first four, and this is filled with bricks disposed in layers and over which circulates, methodically distributed, the milk of lime. The nitrous and nitric gases are retained by the lime and produce a mixture of nitrite and nitrate of lime. This mixture is afterwards broken up by the aid of nitric acid into the nitrate of lime and gaseous nitrous oxid, which is reintroduced into the absorbent system in the manner which has already been described. This breaking up of the compound by means of nitric acid is expressed by the following equation: $(\text{CaNO}_2)_2 + \text{HNO}_3 = (\text{CaNO}_3)_2 + \text{H}_2\text{O} + \text{NO}_2 + \text{NO}$.

Finally, in order to complete the operation and retain the rest of the nitric gases which still escape from the milk of lime vessel, these gases are made to traverse another vessel somewhat smaller in dimension than the other and containing quicklime. It is only in escaping from this last vessel that the gases which have traversed the whole system of oxidation since their entry into the electric furnace are allowed to escape into the atmosphere. The operations which have just been described permit the final transformation into pure nitric acid of 50 per cent. strength, of at least 95 per cent. of the oxid of nitrogen produced in the electric furnace, a remarkable result for an industrial operation.

276. Manufacture of Nitrate of Lime.—The solution of pure nitrate of lime, coming from the decomposition of mixtures of nitrates and nitrites described above, is conducted, together with the pure nitric acid of 50 per cent. strength, into a row of open vessels of granite containing pieces of carbonate of lime of from

13 to 20 centimeters in diameter. The carbonate of lime is employed in quantities suitable to neutralize completely the acid solution and to produce neutral nitrate of lime. This operation is conducted methodically in four superimposed vessels. Upon the fresh carbonate the solution which has been almost neutralized is brought. The fresh acid is placed in contact with the residue of lime which has not been dissolved by the first treatments with the partially saturated solution. By reason of their superposition the movement of the liquid in the vessels is operated automatically. Finally, there is obtained a solution of neutral nitrate of lime which is conducted into evaporation vessels. The concentration of the liquid is accomplished partially by the aid of steam coming from the boiler used for the cooling of gases escaping from the electric furnace, as has been previously described, and partially in a direct manner. The solution of nitrates is reduced to such a concentration that their boiling point rises to 145° , which gives a liquid containing from 75 to 80 per cent. of nitrate of lime, equivalent to from 15.2 to 15.5 per cent. of nitrogen. This viscous mixture is poured into vessels of 200 liters capacity and allowed to solidify by cooling. The nitrate can be shipped either in this state or after powdering.

Instead of evaporating the nitrate of lime until the liquid has obtained a boiling point of 145° , it may be allowed to crystallize after having been evaporated to 120° only. The crystals of nitrate of lime are then separated in a centrifugal. Finally there is manufactured at Notodden some basic nitrate of lime by adding to the hot solution a proper proportion of quicklime. After cooling, the product is broken up and passed through a sieve. The basic nitrate contains about 10 per cent. of nitrogen. It goes without saying that by the process just described there can also be manufactured nitrate of soda, or potash, in place of nitrate of lime. It is the cheapness of the lime, however, as compared with soda which has led the manufacturers at Notodden to transform the nitric acid into calcium nitrate.

The actual production of nitric acid at Notodden amounts to from 500 to 600 kilograms per kilowatt-year. The factory, which has been running since the 2d of May, 1905, has produced in one

year 730,000 kilograms of monohydrate nitric acid. The success of this enterprise, which has been so anxiously awaited throughout the whole world, should lead the farmers of the world to entertain the hope that even if the stores of nitric acid in Chile and other localities are exhausted there can be created a supply of this material, which may be said to be unlimited, obtained from the air and offered from an inexhaustible source, not only for agricultural needs, but also other industrial needs of man.

It is not likely that this process of Birkeland and Eyde has yet reached its limit of perfection. There is no reason why some similar process might not be conducted in connection with the great waterfalls of this country, which would lead to a supply of nitric acid even at a lower price than can now be secured from natural stores.

277. Absorption of Nitric Acid and Concentration of the Product.

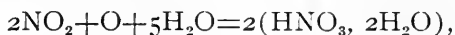
—This subject is discussed still further by Howles, especially in regard to the direct oxidation of nitric acid in the air by means of electric discharges and the production of nitric acid therefrom without the intervention of the calcium compounds. The conclusions reached by Howles in regard to this method of producing nitric acid are as follows:⁸⁰

After leaving the furnace, the air contains about two per cent. by volume of nitric oxid, which becomes rapidly converted, by means of the excess oxygen present into nitrogen peroxid. The mixed gases then pass on to absorption towers, which present no special features of construction and down which water or dilute acid flows. In the case of the last tower, milk of lime is used, as it is difficult to absorb the last traces of NO_2 by means of water alone. By this process there is obtained an acid of not more than 50 per cent. strength.

The preparation of a concentrated nitrous-free acid from the nitrous gases constitutes one of the most serious problems in connection with this process. The reaction represented by this equation, viz., $2\text{NO}_2 + \text{O} + \text{H}_2\text{O} = 2\text{HNO}_3$, does not take place in the absorption towers; such an equilibrium appears to exist only in the gaseous state. On condensation the right-hand side

⁸⁰ Electrochemical and Metallurgical Industry, 1907, 5 : 358.

of the equation is not produced. The most concentrated acid which has so far been obtained by the condensation of nitrous gases in water in the presence of oxygen corresponds to the formula $\text{HNO}_3, 2\text{H}_2\text{O}$, and possesses a density of 40.6° B. , representing 63.63 per cent. of anhydrous nitric acid. The formation of this acid takes place, according to the following equation, in the Lunge and Rohrmann plate towers:



from which acid of 40° to 41° B. is obtained. By passing the gases, however, through towers down which water flows, an equimolecular mixture of nitric and nitrous acids results, which at the most, can not attain a concentration greater than that obtained in the Lunge towers. Attempts at further concentration by the passage of nitrogen peroxid through the solution, simply result in an increase of nitric acid at the expense of the nitrous. The strongest acid is thus never free from nitrous acid, and each succeeding absorption tower contains less and less nitric acid, while at the same time the nitrous acid increases, for as the free oxygen in the gases becomes consumed the NO and NO_2 tend to react as N_2O_3 , yielding only nitrous acid. It is not possible to prepare much stronger acid by fractionating the 50 per cent. acid from the first absorption tower, since a product of minimum vapor pressure, boiling at 120° , and containing 68 per cent. of anhydrous acid, is obtained as residue.

Thus in order to prepare the most concentrated acid by the nitrogen combustion process it would be necessary to either add the 50 per cent. acid to concentrated sulfuric acid until a dilution of say 54° B. , is obtained (54° B. equals 120° Tw. equals 68.5 per cent. of H_2SO_4), and distill the nitric acid; or to prepare a salt of nitric acid, and distill in the usual way with sulfuric acid or a bisulfate.

An electrolytic method for concentrating and oxidizing the weak tower acid has lately been patented. The process consists in refrigerating the oxids of nitrogen evolved during electrolysis at the cathode, and leading them in the liquid state slowly to the anode compartment of the cell, where in presence of

the nascent oxygen there generated, a solution of pure nitric acid results, all nitrous acid undergoing oxidation. It is not stated if this process has proved a commercial success.

Thus, although the electrochemical production of nitric acid has attained a fair degree of efficiency in some of the processes described, the problem of directly manufacturing a 98 per cent. acid from the furnace gases has not yet been solved.

278. Method of Moscicki.—A further contribution to this interesting subject from an agricultural point of view has been made by Moscicki.⁸¹ In the system of Moscicki the principle of the magnetic deflection of the arc is used. The study of a quiet flame shows different zones within the flame. Only the hottest zone is used for the oxidation of the nitrogen. The oxidized nitrogen which is produced within this hot zone is more or less decomposed in passing into the parts of the arc of lower temperature. The important modification of Moscicki, therefore, consists in suppressing these cooler areas, and this is accomplished by a magnetic deflection of the flame. The magnetic attraction only sets those parts of the flame into motion which carry the electric current, while on account of the rapidity of the motion the influence of the cooler zones is eliminated.

279. Production of Nitric Acid in the United States from Atmospheric Nitrogen.—The present status of the industries relating to the oxidation of atmospheric nitrogen and the production of nitric acid, or some similar product therefrom, in the United States may still be described as a waiting one. There is no doubt of the importance of the problem under consideration, especially to agriculture, but the actual economical development of the industry is still in the future. Two general methods of experimental work have been followed. One class of experiments looks to the use of electric discharges through the air in order to produce the oxidation of the nitrogen and form the first products, which afterwards may be developed into nitric acid.⁸²

As has been before intimated the electric plant established at

⁸¹ *Electrochemical and Metallurgical Industry*, 1907, 5 : 491.

⁸² *Electrochemical and Metallurgical Industry*, 1907, 5 : 289.

Niagara Falls for the production of nitric acid from the air has been abandoned. The success of the experiments in Norway is promising, but attention is called to the fact that the process in Norway utilizes the moving arc method instead of the old spark method, and is dependent essentially on the exceedingly low prices of electric power in that country.

The second method of utilizing the atmospheric nitrogen, which is now under investigation, is that which starts with calcium carbide, the product of the electric furnace, and treats this compound later with nitrogen in such a way as to produce the calcium cyanamid. A company has been formed in the United States to operate a factory upon the above principle, and it is proposed to erect a plant of 20,000 metric tons annual capacity on the Tennessee River in Northern Alabama. In this locality there is abundant and cheap water power, as well as coal and coke. Labor is also abundant and reasonably cheap. The Tennessee River also furnishes water transportation of the cheapest character. It is near some of the great phosphate deposits, so that in the manufacture of the complete fertilizers a large part of the material would be derived from the same localities.

METHODS OF ANALYSIS

280. Classification of Methods.—In case a microscopic examination of the sample is required it should precede the chemical operations. In general, there are three direct methods of determining the nitrogen content of fertilizers. First the nitrogen may be secured in a gaseous form and the volume thereof, under standard conditions, measured and the weight of nitrogen computed. This process is commonly known as the absolute method. Practically it has passed out of use in fertilizer work, or is practiced only as a check against new and untried methods, or on certain nitrogenous compounds which do not readily yield all their nitrogen by the other methods. The process, first perfected by Dumas, whose name it bears, consists in the combustion of the nitrogenous body in an environment of copper oxid, by which the nitrogen, by reason of its inertness, is left in a gaseous state

after the oxidation of the other constituents; viz., carbon and hydrogen, originally present.

In the second class of methods the nitrogen is converted into ammonia, which is absorbed by an excess of standard acid, the residue of which is determined by subsequent titration with a standard alkali. There are two distinct processes belonging to this class, in one of which ammonia is directly produced by dry combustion of an organic nitrogenous compound with an alkali, and in the other ammonium sulfate is produced by moist combustion with sulfuric acid, and the salt thus formed is subsequently distilled with an alkali and the free ammonia resulting therefrom estimated as above described. Nitric nitrogen may also be reduced to ammonia by nascent hydrogen either in an acid or alkaline solution.

In the third class of determinations is included the estimation of nitric nitrogen by colorimetric methods. These processes have little practical value in connection with the analyses of commercial fertilizers, but find their chief use in the detection and estimation of extremely minute quantities of nitrites and nitrates. In the following paragraphs will be given the standard methods for the determination of nitrogen in practical work with fertilizing materials and fertilizers, and also the methods for the estimation of minute quantities of ammoniacal and nitric nitrogen.

281. Determination of the State of Combination.—Some of the sample is mixed with a little powdered soda-lime. If ammoniacal nitrogen be present free ammonia is evolved even in the cold and may be detected either by its odor or by testing the escaping gas with litmus or turmeric paper. A glass rod moistened with strong hydrochloric acid will produce white fumes of ammonium chlorid when brought near the escaping ammonia.

If the sample contain any notable amount of nitric acid it will be revealed by treating an aqueous solution of it with a crystal of ferrous sulfate and strong sulfuric acid. The iron salt should be placed in a test-tube with a few drops of the solution of the fertilizer and the sulfuric acid poured down the sides of the tube in such a way as to run under and not to mix with the other

liquids. The tube must be kept cold. A dark brown ring will mark the disk of separation between the sulfuric acid and the aqueous solution in case nitric acid be present. If water produces a solution of the sample too highly colored to be used as above, alcohol of 80 per cent. strength may be substituted. The coloration produced in this case is of a rose or purple tint.

Nitric nitrogen may also be detected by means of brucin. If a few drops of an aqueous solution of brucin be mixed with the same quantity of an aqueous extract of the sample under examination and strong sulfuric acid be added, as described above, there will be developed at the disk of contact between the acid and the mixed solutions a persistent rose tint varying to yellow.

To detect the presence of albuminoid nitrogen the sample is exhausted with water and heated with soda-lime, which gives rise to ammonia which may be detected as described above.

282. Microscopic Examination.—If the chemical test reveal the presence of organic nitrogen, the next point to be determined is the nature of the substance containing it. Often this is revealed by simple inspection, as in the case of cottonseed-meal. Frequently, however, especially in cases of finely ground mixed goods, the microscope must be employed to determine the character of the organic matter. It is important to know whether hair, horn, hoof, and other less valuable forms of nitrogenous compounds have been substituted for dried blood, tankage, and more valuable forms. In most cases the qualitative chemical, and microscopic examination will be sufficient. There may be cases, however, where the analyst will be under the necessity of using other means of identification suggested by his skill and experience or by the circumstances connected with any particular instance. In such cases the general appearance, odor, and consistency of the sample may afford valuable indications which will aid in discovering the origin of the nitrogenous materials.

283. Official Methods.—The methods adopted by the Association of Official Agricultural Chemists have been developed by more than 20 years of co-operative work on the part of the leading agricultural chemists of the United States. These methods should be strictly followed in all essential points by all analysts

in cases where comparison with other data is concerned. Future experience will doubtless improve the processes both in respect of accuracy and simplicity, but it must be granted that, as at present practiced, they give essentially accurate results.

284. Volumetric Estimation by Combustion with Copper Oxid.—This classical method of analysis is based on the principle, that by the combustion of a substance containing nitrogen in copper oxid and conducting the products of the oxidation over red-hot copper oxid and metallic copper, all of the nitrogen present in whatever form will be obtained in a free state and can subsequently be measured as a gas. The air originally present in all parts of the apparatus must first be removed either by a mercury pump or by carbon dioxid, or by both together, the residual carbon dioxid being absorbed by a solution of caustic alkali. Great delicacy of manipulation is necessary to secure a perfect vacuum, and, as a rule, a small quantity of gas may be measured other than nitrogen, so that the results of the analyses are often a trifle too high. The presence of another element associated with nitrogen, or the possible allotropic existence of that element, may also prove to be a disturbing factor in this long practiced, analytical process. For instance, if nitrogen be contaminated with another element, *e. g.*, argon, of a greater density, the commonly accepted weight of a liter of nitrogen is too great and tables of calculation based on that weight would give results too high.

First will be given the official method for this process, followed by a few simple variations thereof, as practiced in the laboratory of the Bureau of Chemistry.

285. The Official Volumetric Method.—This process may be used for nitrogen in any form of combination. Practically, it is no longer used in fertilizer analysis, but the method is inserted here because of its historic and scientific value.

The apparatus and reagents needed are as follows:

Combustion tube of best hard Bohemian glass, about 66 centimeters long and 12.7 millimeters internal diameter.

Azotometer of at least 100 cubic centimeters capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing paper.

Coarse cupric oxid, to be ignited and cooled before using.

Fine cupric oxid, prepared by grinding ordinary cupric oxid.

Metallic copper, granulated copper, or fine copper gauze, heated and cooled in a current of hydrogen.

Sodium bicarbonate, free from organic matter.

Caustic potash solution, a supersaturated solution of caustic potash in hot water. When absorption of carbon dioxide during the combustion ceases to be prompt, the solution must be replaced with a fresh portion.

Filling the tube.—Use from one to two grams of ordinary commercial fertilizers. In the case of highly nitrogenized substances, the amount to be used must be regulated by the amount of nitrogen estimated to be present. Fill the tube as follows: (1) About five centimeters of coarse cupric oxid. (2) Place on the small paper scoop enough of the fine cupric oxid to fill, after having been mixed with the substance to be analyzed, about 10 centimeters of the tube; pour on this the substance, rinsing the watch-glass with a little of the fine oxid, and mix thoroughly with a spatula; pour into the tube, rinsing the scoop with a little fine oxid. (3) About 30 centimeters of coarse cupric oxid. (4) About seven centimeters of metallic copper. (5) About six centimeters of coarse cupric oxid (anterior layer). (6) A small plug of asbestos. (7) From eight-tenths to one gram of sodium bicarbonate. (8) A large, loose plug of asbestos. Place the tube in the furnace, leaving about two and five-tenths centimeters of it projecting; connect with the pump by a rubber stopper smeared with glycerol, taking care to make the connection perfectly tight.

Operation.—Exhaust the air from the tube by means of the pump. When a vacuum has been obtained, allow the flow of mercury to continue; light the gas under that part of the tube containing the metallic copper, the anterior layer of cupric oxid (see (5) above), and the sodium bicarbonate. As soon as the vacuum is destroyed and the apparatus filled with carbon dioxide, shut off the flow of mercury and at once introduce the delivery

tube of the pump into the receiving arm of the azotometer just below the surface of the mercury seal, so that the escaping bubbles will pass into the air and not into the tube, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbon dioxide has very nearly or completely ceased, pass the delivery tube down into the receiving arm, so that the bubbles will escape into the azotometer. Light the gas under the 30 centimeter layer of oxid, heat gently for a few moments to drive out any moisture that may be present, and bring to a red heat. Heat gradually the mixture of substance and oxid, lighting one jet at a time. Avoid a too rapid evolution of bubbles, which should be allowed to escape at the rate of about one per second or a little faster.

When the jets under the mixture have all been turned on, light the gas under the layer of oxid at the end of the tube. When the evolution of gas has ceased, turn out all the lights except those under the metallic copper and anterior layer of oxid, and allow to cool for a few moments. Exhaust with the pump and remove the azotometer before the flow of mercury is stopped. Break the connection of the tube with the pump, stop the flow of mercury, and extinguish the lights. Allow the azotometer to stand for at least an hour, or cool with a stream of water until a permanent volume and temperature have been reached.

Adjust accurately the level of the potassium hydroxid solution in the bulb to that in the azotometer; note the volume of gas, temperature, and height of barometer; make calculation as usual, or read results from tables.

286. Note on Official Volumetric Method.—The determination of nitrogen in its gaseous state by combustion with copper oxid, has practically gone out of use as an analytical method. The official chemists rarely use it even for control work on samples sent out for comparative analysis. The method recommended differs considerably from the process of Jenkins and Johnson, on which it is based. The only source of oxygen in the official method is in the copper oxid. Hence it is necessary

that the oxid in immediate contact with the organic matter be in a sufficiently fine state of subdivision, and that the substance itself be very finely powdered and intimately mixed with the oxidizing material. Failure to attend to these precautions will be followed by an incomplete combustion and a consequent deficit in the volume of nitrogen obtained.

The copper oxid before using is ignited, and is best filled into the tube while still warm by means of a long pointed metal scoop, or other convenient method. The copper spiral, after use, is reduced at a red heat in a current of hydrogen, and may thus be used many times.

287. The Pump.—Any form of mercury pump which will secure a complete vacuum may be used. A most excellent one can be arranged in any laboratory at a very small expense. The pump used in the laboratory of the Bureau of Chemistry for many years answers every purpose, and costs practically nothing, being made out of old material not very valuable for other use.

The construction of the pump and its use in connection with the combustion tube will be clearly understood from the following description:

A glass bulb I is attached, by means of a heavy rubber tube carrying a screw clamp, to the glass tube A, having heavy walls and a small internal diameter, and being one meter or more in length. The tube A is continued in the form of a U, the two arms being joined by very heavy rubber tubing securely wired. The ends of the glass tubes in the rubber should be bent so that they come near together and form the bend of the U, the rubber simply holding them in place. This is better than to have the tube continuous, avoiding danger of breaking. A three way tube, T, made of the same kind of glass as A, is connected by one arm, a, with the manometer B, by a heavy rubber union well wired. The union is made perfectly air-tight by a tube filled with mercury held in place by a rubber stopper. The middle arm of the tee, a', is expanded into a bulb, E, branching into two arms, one of which is connected with A and the other with the delivery tube F, by the mercury-rubber unions, MM', just described. The in-

terior of the bulb E should be of such a shape, as to allow each drop of mercury to fall at once into F without accumulating in large quantity and being discharged in mass. The third arm of the tee, a", is bent upwards at the end and passes into a mercury sealing tube, D, where it is connected by means of a rubber tube with the delivery tube from the furnace. The flow of the mer-

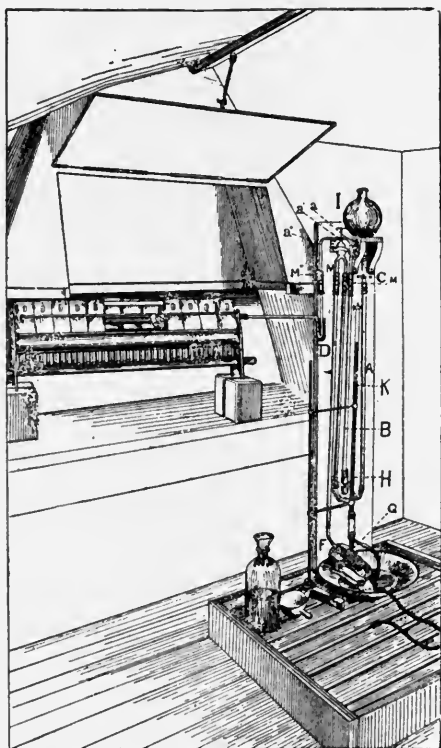


Fig. 14. Mercury Pump and Azotometer.

cury is regulated by the clamp C, and care should be taken that the supply does not get so low in I as to permit air bubbles to enter A. The manometer B dips into the tube of mercury H. A pump thus constructed is simple, flexible, and perfectly tight. The only part which needs to be specially made is the three way tube T, and the one in use here was blown in our own laboratory. The bent end of the delivery tube F may also be united to the main

tube by a rubber joint, thus aiding in inserting it into the V-shaped nozzle of the azotometer.

The azotometer used is the one devised by Schiff and modified by Johnson and Jenkins.⁸³

The V nozzles may be got separately and joined to any good burette by a rubber tube. The water-jacket is not necessary, but the apparatus can be left exposed until it reaches room temperature.

Any form of mercury pump capable of securing a vacuum may be used, but the one just described is commended by simplicity, economy, effectiveness, and long use.

288. The Pump and Combustion Furnace.—The pump and combustion furnace, as used in the above process, are shown in Fig. 14. The pump is constructed as just described, and rests in a wooden tray which catches and holds any mercury which may be spilled. The furnace is placed under a hood which carries off the products of the burning gas and the hot air. A well ventilated hood is an important accessory to this process, especially when it is carried on in summer. A small mercury pneumatic trough catches the overflow from the pump and also serves to immerse the end of the delivery tube during the exhaustion of the combustion tube.

The other details of the arrangement and connections have been sufficiently shown in the previous paragraph.

289. Volumetric Method of Bureau of Chemistry.—It has been found convenient to vary slightly the method of the official chemists in the following respects: The tube used for the combustion is made of hard refractory glass, which will keep its shape at a high red heat. It is drawn out and sealed at one end after being well cleaned and dried. It should be about 80 centimeters in length and from 12 to 14 millimeters in internal diameter. The relative lengths of the spaces occupied by the several contents of the tube are approximately as follows: Sodium bicarbonate, two; asbestos, three; coarse copper oxid, eight; fine copper oxid, containing sample, 16; coarse copper oxid, 25; spiral copper

⁸³ American Chemical Journal, 1880-81, 2 : 27.

gauze, 10 to 15; copper oxid, eight; and asbestos plug, five centimeters, respectively.

The copper oxid should be heated for a considerable time to redness in a muffle with free access of air before using, and the copper gauze be reduced to pure metallic copper in a current of hydrogen at a low red heat. The anterior layer of copper oxid serves to oxidize any hydrogen that may have been occluded by the copper. When a sample is burned containing all or a considerable part of the nitrogen as nitrates, the longer piece of copper gauze is used.

290. The Combustion.—The tube having been charged and connected with the pump, it is first freed from air by running the pump until the mercury no longer rises in the manometer. The end of the tube containing the sodium bicarbonate is then gently heated, so that the evolution of carbon dioxid will be at such a rate, as to slowly depress the mercury in the manometer, but never fast enough to exceed the capacity of the pump to remove it. The lamp is extinguished under the sodium carbonate and the carbon dioxid completely removed by means of the pump. The delivery tube is then connected with the azotometer, and the combustion tube carefully heated from the front end backwards, the copper gauze and coarse copper oxid being raised to a red heat before the part containing the sample is reached. When the nitrogen begins to come off, its flow should be so regulated by means of the lamps under the tube, as to be regular and not too rapid. From half an hour to an hour should be employed in completing the combustion. Since most samples of fertilizer contain organic matter, the nitrogen will be mixed with aqueous vapor and carbon dioxid. The former is condensed before reaching the azotometer, and the latter is absorbed by the potassium hydroxid. When the sample is wholly of a mineral nature it should be mixed with some pure sugar, about half a gram, before being placed in the tube. When bubbles of gas no longer come over, the heat should be carried back until there is a gradual evolution of carbon dioxid under the conditions above noted. Finally, the gas is turned off and the pump kept in operation until the manometer again shows a perfect vacuum, when

the operation may be considered finished. In the manipulation, our chief variation from the official method consists in connecting the combustion apparatus with the measuring tube before the heat is applied to the front end of the combustion tube. Any particles of the sample which may have stuck to the sides of the tube on filling, will thus be subject to combustion and the gases produced measured. Where it is certain that no such adhesion has taken place, it is somewhat safer on account of the possible presence of occluded gases to heat the front end of the tube before connecting the combustion apparatus with the azotometer.

291. Method of Johnson and Jenkins.—In the method of Johnson and Jenkins the principal variation from the process described consists in introducing into the combustion tube a source of oxygen whereby any difficultly combustible carbon may be easily oxidized and all the nitrogen be more certainly set free.⁸⁴ The potassium chlorate used for this purpose is placed in the posterior part of the tube, which is bent at a slight angle to receive it. The sodium bicarbonate is placed in the anterior end of the tube. The combustion goes on as already described, and at its close the potassium chlorate is heated to evolve the oxygen. The free oxygen is absorbed by the reduced copper oxid, or consumed by the unburned carbon. Any excess of oxygen is recognized at once by its action on the copper spiral. As soon as this shows signs of oxidation the evolution of the gas is stopped. Care must be taken not to allow the oxygen to come off so rapidly as to escape entire absorption by the contents of the combustion tube. In such a case the nitrogen in the measuring tube would be contaminated.

It is rarely necessary in fertilizer analysis to have need of more oxygen than is contained in the copper oxid powder in contact with the sample during the progress of combustion.

292. Calculation of Results.—The nitrogen originally present in a definite weight of any substance having been obtained in a gaseous form, its volume is read directly in the burette in which it is collected. This instrument may be of many forms but the essential feature of its construction is that it should be

⁸⁴ American Chemical Journal, 1880-81, 2 : 27.

accurately calibrated, and the divisions so graduated as to permit of the reading of the volume accurately to a tenth of a cubic centimeter. For this purpose it is best that the internal diameter of the measuring tube be rather small so that at least each 10 cubic centimeters occupies a space 10 centimeters long. The volume occupied by any gas varies directly with the temperature and inversely with the pressure to which it is subjected. The quantity of aqueous vapor which a moist gas may contain is also a factor to be considered. Inasmuch as the nitrogen in the above process of analysis is collected over a strong solution of potassium hydroxid capable of practically keeping the gas in a dry state, the tension of the aqueous vapor may be neglected.

293. Reading the Barometer.—Nearly all of the barometers in use in this country have the scale divided in inches and the thermometers thereunto attached are graduated in Fahrenheit degrees. This is especially true of the barometers of the Weather Bureau, which are the most reliable and most easy of access to analysts. It is not necessary to correct the reading of the barometer for altitude, but it is important to take account of the temperature at the time of observation. There is not space here to give minute directions for using a barometer. Such directions have been prepared by the Weather Bureau and those desiring it can get copies of the circular.⁸⁵

The temperature of a barometer affects its accuracy in two ways: First, the metal scale expands and contracts with changing temperatures; Second, the mercury expands and contracts also at a much greater rate than the scale. If a barometer tube holds 30 cubic inches of mercury, the contents will be one ounce lighter at 80° F. than at 32° F. The true pressure of the air is, therefore, not shown by the observed height of the mercurial column, unless the temperature of the scale and of the mercurial column be considered.

Tables of correction for temperature are computed by simple formulas based on the known coefficients of expansion of mer-

⁸⁵ Barometers and the Measurement of Atmospheric Pressure, 2nd Edition, 1901.

cury and brass. For barometers with brass scales the following formula is used for making the correction:

$C = - h \frac{t - 28.63}{1.113t + 10978}$. In this formula, $t =$ temperature in degrees Fahrenheit and $h =$ observed reading of the barometer in inches.

Example:—Temperature observed $72^{\circ}.5$

Barometer reading observed, 29.415 inches,
from which $C = 0.1165$, and this number, according to the conditions of the formula, is to be subtracted from the observed reading. The true reading in the case given is, therefore,

29.298 inches or	744.2 millimeters.
The observed reading	747.1 “
And the correction	$\frac{2.9}{2.9}$ “

Unless extremely accurate work be required, the correction for temperature is of very little importance in nitrogen determinations in fertilizers. Each instrument sent out by the Weather Bureau is accompanied by a special card of corrections therefor, but these are of small importance in fertilizer work. In order then to get the correct weight of the gas from its volume, the reading of the thermometer and barometer at the time of measurement must be carefully noted. However, after the end of the combustion, the azotometer should be carried into another room which has not been affected by the combustion and allowed to stand until it has reached the room temperature.

Every true gas changes its volume under varying temperatures at the same rate, and this rate is the coefficient of gaseous expansion. For one degree of temperature it amounts to 0.003665 of its volume. Representing the coefficient of expansion by K the volume of the gas as read by V , the volume desired at any temperature by V' , the temperature at which the volume is read by t and the desired temperature by t' , the change in volume may be calculated by the following formula:

$$V' = V[1 + K(t' - t)].$$

Example.—Let the volume of nitrogen obtained by combustion be 35 cubic centimeters, and the temperature of observation 22° . What would be the volume of the gas at 0° ?

Making the proper substitutions in the formula the equation is reduced to the form below :

$$V' = 35[1 + 0.003665(0^\circ - 22^\circ)]$$

$$\text{or } V' = 35(1 - 0.08063) = 32.18.$$

Thirty-five cubic centimeters of nitrogen, therefore, measured at 22° becomes 32.18 cubic centimeters when measured at 0° .

When gases are to be converted into weight, after having been determined by volume, their volume at 0° must first be determined; but this volume must also be calculated to some definite barometric pressure. By common consent, this pressure has been taken as that exerted by a column of mercury 760 millimeters in height. Since the volume of a gas is inversely proportional to the pressure to which it is subjected, the calculation is made according to that simple formula. Let the reading of the barometer, at the time of taking the volume of gas, be H , and any other pressure desired H' . Then we have the general formula :

$$V:V' = H':H; \text{ and } V' = \frac{HV}{H'}.$$

Example: Let the corrected reading of the barometer at the time of noting the volume of the gas be 740 millimeters, and the volume of the gas reduced to 0° be 32.18 cubic centimeters. What will this volume be at a pressure of 760 millimeters?

Substituting the proper values in the formula, we have :

$$V' = \frac{32.18 \times 740}{760} = 31.33.$$

Therefore, a volume of nitrogen which occupies a space of 35 cubic centimeters at a temperature of 22° , and at a barometric pressure of 740 millimeters, becomes 31.33 cubic centimeters at a temperature of 0° and a pressure of 760 millimeters.

One liter of nitrogen at 0° and 760 millimeters pressure weighs 1.25456 grams; and one cubic centimeter, therefore, 0.00125456 gram. To find the weight of gas obtained in the above supposed analysis, it will only be necessary to multiply this number by the volume of nitrogen expressed in cubic centimeters under the standard conditions; viz., $0.0125456 \times 31.33 = 0.039305$ gram.

If the sample taken for analysis weighed half a gram, the percentage of nitrogen found would be 7.85.

294. Tension of the Aqueous Vapor.—It has been shown by experience that when a gas is collected over a potash solution containing 50 per cent. of potassium hydroxid, the tension of the aqueous vapor is so far diminished as to be of no perceptible influence on the final result. To correct the volume of a gas for this slight tension would involve an unnecessary calculation for practical purposes. If a gas thus collected should be transferred to a burette over mercury, on which some water floats, then the correction should be made.

At 0° the tension of aqueous vapor will support a column of mercury 4.525 millimeters, and at 40° one 54.969 millimeters high.

The following table gives the tension of aqueous vapors in millimeters of a mercurial column for each degree of temperature from zero to 40.

Temperature.	Tension of vapor in millimeters.	Temperature.	Tension of vapor in millimeters.
0°	4.525	21°	18.505
1°	4.867	22°	19.675
2°	5.231	23°	20.909
3°	5.619	24°	22.211
4°	6.032	25°	23.582
5°	6.471	26°	25.026
6°	6.939	27°	26.547
7°	7.436	28°	28.148
8°	7.964	29°	29.832
9°	8.525	30°	31.602
10°	9.126	31°	33.464
11°	9.751	32°	35.419
12°	10.421	33°	37.473
13°	11.130	34°	39.630
14°	11.882	35°	41.893
15°	12.677	36°	44.268
16°	13.519	37°	46.758
17°	14.409	38°	49.368
18°	15.351	39°	52.103
19°	16.345	40°	54.969
20°	17.396		

When a gas is in contact with water the aqueous vapor is diffused throughout the mass, and the pressure to which the mix-

ture is subjected, is partly neutralized by the tension of the water vapor. The real pressure to which the gas, whose volume is to be determined, is subjected is, therefore, diminished by that tension. If, for instance, a gas in contact with water show a volume of 35 cubic centimeters at 22° and 740 millimeters barometric pressure, its volume is really greater than if it were perfectly dry. How much greater can be determined by inspecting the table; for at 22° the tension of water vapor is 19.675 millimeters of mercury. The real pressure to which the volume of gas is subjected is, therefore, $740 - 19.675 = 720.325$ millimeters.

If, therefore, in the example given, the nitrogen were in contact with water, the calculation would proceed as follows:

$$V' = \frac{32.18 \times 720.325}{760} = 30.5.$$

And $30.5 \times 1.25456 = 38.26$.

Millimeters tension of aqueous vapor for KOH solutions of

Temperature.	9.09 per cent.	16.66 per cent.	23.08 per cent.	28.57 per cent.	32.89 per cent.
10°.00	8.62	8.01	7.31	6.50	5.62
11°.00	9.21	8.56	7.82	6.95	6.01
12°.10	9.90	9.21	8.41	7.47	6.46
13°.00	10.50	9.77	8.92	7.93	6.86
13°.95	11.17	10.39	9.49	8.44	7.30
15°.15	12.06	11.22	10.25	9.11	7.86
16°.00	12.74	11.85	10.82	9.62	8.33
17°.00	13.57	12.63	11.54	10.26	8.88
18°.00	14.46	13.45	12.29	10.93	9.47
19°.00	15.39	14.33	13.09	11.65	10.09
20°.00	16.38	15.25	13.93	12.40	10.75
21°.00	17.42	16.22	14.82	13.20	11.44
21°.82	18.32	17.06	15.59	13.88	12.04
23°.00	19.68	18.32	16.75	14.92	12.94
24°.00	20.92	19.47	17.80	15.86	13.76
25°.00	22.19	20.67	18.91	16.85	14.62
26°.00	23.55	21.94	20.07	17.89	15.53
26°.98	24.95	23.25	21.27	18.96	16.46
27°.93	26.38	24.59	22.51	20.07	17.45
29°.00	28.08	26.18	23.96	21.38	18.59
30°.00	29.76	27.74	25.40	22.67	19.72
31°.00	31.51	29.38	26.91	24.03	20.91
32°.13	33.61	31.34	28.72	25.65	22.34
33°.00	35.30	32.93	30.18	26.97	23.50
34°.00	37.34	34.84	31.94	28.56	24.89

Hence, 38.26 milligrams of nitrogen correspond to 7.65 per cent., when half a gram of substance is taken for the combustion.

295. Aqueous Tension in Solutions of Potassium Hydroxid.—Even in strong solutions of potassium hydroxid the tension of aqueous vapor is not destroyed, but is reduced to a minimum, which is negligible in the calculation of the percentage by weight of the nitrogen in a sample of fertilizer. When dilute solutions of a caustic alkali are used, however, the neglect of the tension of the aqueous vapor may cause an error of some magnitude. In such cases the strength of the solution should be known and correction made according to the preceding table.⁸⁶

296. Use of Volumetric Method.—For practical purposes it may be said, that the volumetric determination of nitrogen in fertilizer analysis has gone entirely out of use. For control and comparison it is still occasionally practiced, but it has had to give way to the more speedy and fully as accurate processes of moist combustion with sulfuric acid, which have come into general use in the last two decades. The student and analyst, however, should not fail to master its details and become skilled in its use. There are certain nitrogenous substances, such as the alkaloids, which are quite refractory when subjected to moist combustion. While such bodies may not occur in fertilizers, except in rare cases such as nicotine in tobacco waste, it is well to have at hand a means of accurately determining their nitrogen content.

297. Tables for Calculating Results.—Where many analyses are to be made by the copper oxid process, it has proved convenient to shorten the work of calculating analyses by taking the data given in computation tables.⁸⁷ Before using these tables it must be known whether they are calculated on the supposition that the gas is measured in a moist state, partly moist, or wholly dry. Where the nitrogen is collected over water, a table must be used in which allowance has been made for the tension of aqueous vapor. In case a saturated solution of a caustic alkali be used in the azotometer, it is customary to take no account of the tension and the table employed must be con-

⁸⁶ Landolt and Börnstein, *Physikalisch-chemische Tabellen*, 2nd Edition, 1894 : 68.

⁸⁷ Battle and Dancy, *Conversion Tables*, 1885 : 34.

structed on this supposition. In point of fact even in the strongest alkali solution there is a certain amount of tension but this is so slight as only to affect the results in the second place of decimals. Since, as a rule, only a few analyses are made by this method, it will be found safer to use a caustic alkali solution of given strength and to calculate the results from the tables of aqueous tensions given above.

298. The Soda-Lime Process.—This process originally perfected by Varrentrap and Will, and improved by Peligot, was used very extensively by analysts until within the last two decades for the determination of nitrogen not existing in the nitric form. It is based on the principle that when nitrogen exists as a salt of ammonia, or as an amid, or as proteid matter, it is converted into gaseous ammonia by combustion with an alkali. This ammonia can be carried into a set solution of acid by a stream of gas free of ammonia and the excess of acid remaining after the combustion is complete can be determined by titration against a standard alkali solution. The results under proper conditions are accurate even when a small quantity of nitric nitrogen is present. When, however, there is any considerable quantity of this compound in the sample the method becomes inapplicable by reason of non-reduction of some of the nitrogen oxids produced by the combustion.

In bodies very rich in nitrogen, such as urea, all the nitrogen is not transferred directly into ammonia at the commencement of the combustion. A portion of it may unite with a part of the carbon to form cyanogen, which may unite with the soda to form sodium cyanid. With an excess of alkali, however, and prolonged combustion, this product will be finally decomposed and all the nitrogen be secured as ammonia.

The nascent hydrogen which unites with the nascent nitrogen during the combustion is also derived from the organic matter which always contains enough carbon to decompose the water formed in order to be oxidized to carbon dioxid. While at first, therefore, during combustion, the hydrogen may unite with the oxygen, it becomes again free by the oxidation of the carbon and in this condition unites with the nascent nitrogen to form ammo-

nia. In addition to carbon dioxide, ammonia, and free hydrogen there may also be found among the products of combustion marsh and olefiant gases and other hydrocarbon compounds which dilute, to a greater or less extent, the ammonia formed and help to carry it out of the combustion tube and into the standard acid.

299. The Official Method.—*Reagents and Apparatus.*—(1) *Standard solutions and indicator* the same as for the kjeldahl method.

(2) *Dry granulated soda-lime*, fine enough to pass a 2.5 millimeter sieve.

(3) *Soda-lime*, fine enough to pass a 1.25 millimeter sieve.

Soda-lime may be easily and cheaply prepared by slaking two and one-half parts of quicklime with a strong solution of one part of commercial caustic soda, care being taken that there is enough water in the solution to slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and, when cold, ground and sifted as above.

(4) *Sodium Carbonate and Lime or Slaked Lime.*—Instead of soda-lime Johnson's mixture of sodium and calcium carbonate, or slaked lime, may be used. Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water-oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda-lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analyzed than is the case with soda-lime.

(5) *Asbestos.*—The asbestos used should be ignited and kept in a glass-stoppered bottle.

(6) *Combustion Tubes.*—These are about 40 centimeters long and with an internal diameter of 12 millimeters, drawn out to a closed point at one end.

(7) *U-Tubes.*—Large-bulbed U-tubes with glass stop-cock, or Will's tubes with four bulbs.

Manipulation.—The substance to be analyzed should be powdered finely enough to pass through a sieve of one millimeter mesh; from 0.7 to 1.4 gram, according to the amount of nitrogen

present, is used for the determination. Into the closed end of the combustion tube put a small loose plug of asbestos, and upon it to the depth of about four centimeters, fine soda-lime. In a porcelain dish or mortar mix the substance to be analyzed, thoroughly but quickly, with enough fine soda-lime to fill approximately 16 centimeters of the tube, or about 40 times as much soda-lime as substance, and put the mixture into the combustion tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda-lime, which is to be put in on top of the mixture. Fill the rest of the tube to within about five centimeters of the end with granulated soda-lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda-lime should not be less than 12 centimeters deep. Lastly, put in a plug of asbestos about two centimeters long, pressed rather tightly, and wipe out the end of the tube to free it from adhering particles.

Connect the tube by means of a well-fitting rubber stopper or cork with the U-tube or Will's bulbs, containing 10 cubic centimeters of standard acid, and adjust it in the combustion furnace so that the end of the tube projects about four centimeters from the furnace suitably supporting the U-tube or Will's bulb. Heat the portion of the tube containing the granulated soda-lime to a moderate redness, and when this is attained extend the heat gradually through the portion containing the substance, so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Continue the combustion until gases have ceased bubbling through the acid in the bulbs, and the mixture of substance and soda-lime has become white, or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Extinguish the burners and when the tube has cooled below redness break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect the tube, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion tube.

It is found very advantageous to attach a bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent sucking back in case of a sudden condensation of steam in the bulbs.

300. The Official French Method.—The French chemists prefer to drive out the traces of ammonia remaining in the combustion tube by means of the gases arising from the decomposition of oxalic acid.⁸⁸ The operation is conducted by mixing about one gram of oxalic acid with enough of dry granular soda-lime to form a layer of four centimeters in length at the bottom of the tube. The rest of the tube is then charged substantially as directed above. At the end of the combustion, the oxalic acid is decomposed by heat, furnishing sufficient hydrogen to remove from the tube all traces of ammonia which it may contain. The French chemists employ for titration, either normal acids and alkalis or some decimal thereof, or else an acid of such strength as to have each cubic centimeter thereof correspond to 10 milligrams of nitrogen, thus making the computation of results exceedingly simple. Such an acid is secured when one liter thereof contains 35 grams of pure monohydric sulfuric acid or 45 grams of pure crystallized oxalic acid. The corresponding alkaline reagent should contain, in each liter, 40 grams of pure potassium hydroxid.

301. The Hydrogen Method.—Thibault and Wagner recommend that the combustion with soda-lime be conducted in an atmosphere of hydrogen; and Loges replaces this by common illuminating gas freed from ammonia by conducting it through a tube filled with glass balls moistened with dilute sulfuric acid⁸⁹⁻⁹⁰.

In these cases the combustion tube is left open at both ends

⁸⁸ Grandeau, *Traité d'Analyse des Matières agricoles*, 3me Edition; 1897, **1** : 427.

⁸⁹ *Zeitschrift für analytische Chemie*, 1884, **23** : 557.

⁹⁰ *Chemiker-Zeitung*, 1884, **8** : 649, 1741.

and the materials under the tube confined to the proper position by asbestos plugs. The gases used act in a merely mechanical manner and their use affords so few advantages over the method of aspirating air at the end of the combustion as to render it unadvisable.

302. Coloration of the Product.—It often happens, especially in the combustion of animal products, such as tankage and fish scrap, that the acid receiving the ammonia is deeply colored by the condensation of some of the other products of combustion. This coloration interferes, in a very serious way, with the delicacy of the indicator used to determine the end of the reaction. In this case the liquid may be mixed with an alkali and distilled, and the ammonia secured in a fresh portion of the standard acid as in the moist combustion process to be hereafter described.

303. General Considerations.—(1) *Preparation of the Sample.*—In the soda-lime method it is of great importance that the organic substances be in a fine state of subdivision so as to admit of intimate mixture with the alkali. In cases where fragments of hoof, horn, hair, or similar substances are to be prepared for combustion, it is advisable to first decompose them by heating with a small quantity of sulfuric acid. The excess of acid may be neutralized with marble dust and the resulting mixture dried, rubbed to a fine powder, and mixed with the soda-lime in the usual way. Care must be taken not to lose any of the ammonia from the sulfate, which may possibly be formed in mixing with the soda-lime in filling the tube.

(2) *Purity of Soda-Lime.*—The soda-lime employed must be entirely free of nitrogenous compounds, and blank combustions should be made to establish its purity or to determine the magnitude of the corrections to be made.

(3) *Temperature.*—The temperature of the combustion should not be allowed to exceed low redness. At very high temperatures there would be danger of decomposing the ammonia.

(4) *Aspiration of Air.*—Before aspiring a current of air through the tube to remove the last traces of ammonia, the gas should be put out under the furnace and the tube be allowed to

cool below redness to avoid any danger of acting on the nitrogen in the air.

304. The Ruffle Soda-Lime Method.—Many attempts have been made to adapt the soda-lime method to the determination of nitric nitrogen. Of these, the process devised by Ruffle is the only one which has proved successful.⁹¹ The method is founded on the action of sulfurous vapors on the nitrogen oxids produced during the combustion, whereby sulfuric acid is formed and the nascent nitrogen is joined with hydrogen to form ammonia. By this process all the nitrogen contained in the sample, even if in the nitric form, is finally obtained as ammonia. In the original method the reagents employed were sodium thiosulfate, soda-lime, charcoal, sulfur, and granulated soda-lime. Subsequently, the official chemists substituted sugar for the charcoal.⁹² The method was used for a long time by the official chemists and came into general favor until displaced by the simpler and cheaper processes of the moist combustion method adapted to nitric nitrogen. As finally modified and used by the official chemists, the process is conducted as described below.⁹³

305. The Official Ruffle Method.—*Reagents and Apparatus.*

—(1) The standard solutions and indicator are the same as in the kjeldahl method.

(2) A mixture of equal parts by weight of fine-slaked lime and finely powdered sodium thiosulfate dried at 100°.

(3) A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulfur.

(4) Granulated soda-lime, as described under the soda-lime method.

(5) Combustion tubes of hard Bohemian glass 70 centimeters long and 1.3 centimeters in diameter.

(6) Bulbed U-tubes or Will's bulbs, as described under the soda-lime method.

Manipulation.—(a) Clean the U-tube and introduce 10 cubic centimeters of standard acid.

(b) Fill the tube as follows: (1) A loosely fitting plug of as-

⁹¹ Journal of the Chemical Society, 1881, 39 : 87.

⁹² Division of Chemistry, Bulletin 16, 1887 : 51.

⁹³ Division of Chemistry, Bulletin 46, Revised Edition, 1899 : 19.

bestos, which has been recently ignited, is placed in the end of the tube to be attached to the absorption apparatus, and then 2.5 to 3.5 centimeters in depth of the thiosulfate mixture is added. (2) The portion of the substance to be analyzed is intimately mixed with from five to 10 grams of the sugar and sulfur mixture. (3) Pour on a piece of glazed paper or in a porcelain mortar a sufficient quantity of thiosulfate mixture to fill a depth of about 25 centimeters of the tube, add the substance to be analyzed, as previously prepared, mix carefully, and pour into the tube, shake down the contents of the tube, clean the paper or mortar with a small quantity of the thiosulfate mixture and pour into the tube, and fill up with soda-lime to within five centimeters of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube and close with a cork. (5) Hold the tube in a horizontal position and tap on the table until there is a gas-channel along the top of the tube. (6) Make connection with the U-tube containing the acid, aspirate and see that the apparatus is tight.

The Combustion.—Place the prepared combustion tube in the furnace, letting the ends project, so as not to burn the corks. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off at the rate of two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede toward the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker or porcelain dish; add a few drops of the cochineal solution, and titrate.

306. Observations.—In our experience we have found it much more satisfactory to adhere to the earlier directions for preparing the mixture of thiosulfate and alkali. We much prefer to make the mixture with soda-lime and without the previous drying of the sodium salt. Ruffle himself says that the sodium thiosulfate should be dry, but not deprived of its water of

crystallization.⁹⁴ The best method to dry the salt without depriving it of its crystal water is to press it between blotting papers.

As is seen from the above description the method is essentially a reduction process by the action of a powerful deoxidizer in the presence of an alkali. The crystals of the thiosulfate salt cannot be brought into direct contact with a pure alkali, like soda or potash, without forming at once a wet mass which would tend to cake and obstruct the tube. The soda-lime is, therefore, a mechanical device to prevent this fusion. Where many analyses are to be made, an iron tube, for economical reasons, may be substituted for the glass; but the glass tube permits a more intelligent observation of the progress of the analysis.

Since charcoal has very high absorbent powers it will be found always to contain a little nitrogen which may be in a form to generate ammonia during the combustion. The charcoal used should, therefore, be previously boiled with caustic soda or potash solution, dried, powdered, and preserved in well-stoppered bottles. Although pure sugar is practically free of nitrogen, even when it is used, it is advisable to occasionally make a blank determination and thus ascertain the correction to be made for possible contamination.

307. Boyer's Modification of Ruffle's Method.—The principle of the method rests on the observation that if nitrates be heated in a combustion tube with calcium oxalate and soda-lime, not more than two-thirds of the total nitrogen appear as ammonia; but if a certain proportion of sulfur be added the whole of the nitrogen is recovered.⁹⁵ The process may be divided into two steps; viz.:

(1) Action of the calcium oxalate upon the sodium nitrate in presence of soda-lime.

(2) The action of sulfurous acid and of calcium oxalate upon the sodium nitrate in presence of soda-lime.

The analysis is conducted as follows: Dry and pulverize one-half gram of nitrate and mix it intimately with 50 grams of the reducing compound containing approximately 10 per cent. sulfur,

⁹⁴ *Journal of the Society of Chemical Industry*, 1883, 2 : 21.

⁹⁵ *Comptes rendus*, 1891, 113 : 503.

22.5 per cent. neutral calcium oxalate, and 67.5 per cent. soda-lime. The combustion tube has a length of 55 centimeters and a diameter of 17 millimeters, and is charged as follows:

Two grams pulverized calcium oxalate.

Ten grams pulverized soda-lime.

Ten grams of the reducing compound.

The nitrate incorporated with 50 grams of the reducing mixture:

Ten grams of the reducing mixture.

Ten grams pulverized soda-lime.

The tube is then tightly closed with an asbestos plug and heated gradually from the front backwards, the calcium oxalate furnishing finally the gas necessary to drive out the last traces of ammonia.

The combustion should be terminated in 40 minutes and when completed, the acid, containing the ammonia, is placed in a beaker and boiled for two or three minutes to drive off the sulfurous and carbonic acids. The titration is then conducted in the usual manner.

The combustion can be carried on just as well in an iron tube as in a glass one. The reagents employed, especially soda-lime, being hygroscopic, a little water is disengaged in heating, which is condensed at the cold extremity of the tube, and which may absorb a little ammonia unless special precautions are taken to have the materials dry.

The process is equally applicable to the determination of nitrogen in all its forms or to mixtures thereof. The method has also been applied to the mixture of ammoniacal and organic nitrogen and to the mixture of ammoniacal, nitric, and organic nitrogen, the combustions having been made both in an iron and a glass tube. The amounts of material to be used vary from one-half gram to a gram, according to its richness in nitrogen.

THE MOIST COMBUSTION PROCESS

308. Historical.—As long ago as 1868 Wanklyn proposed to conduct the combustion of organic bodies in a wet way, using potassium permanganate as the oxidizing body.⁹⁶ About 10 years

⁹⁶ Journal of the Chemical Society, 1868, 21: 161.

after this he attempted to extend the method so as to estimate the quantity of proteid matter in a sample by treatment with an alkaline solution in presence of the permanganate salt. One gram of the finely pulverized sample was treated in a liter flask with one-tenth normal potash lye. According to the supposition of Wanklyn, pure albuminoid matters thus treated yielded 0.1 of their weight of ammonia, or about 50 per cent. of the total nitrogen appeared as ammonia. The ammonia content of the sample was determined by the colorimetric process devised by Nessler. It is needless to add that the process of Wanklyn proved to be of no practical use whatever, acting differently on different albuminoid matters, and even on the same substance. No other attempt was made to perfect the moist combustion process until Kjeldahl introduced the sulfuric acid method in 1883. The simplicity, economy, and adaptability of this method have brought it into general use. At first the process was only applied to organic nitrogenous compounds in the absence of nitrates, but especially by the modifications proposed by Asboth, Jodlbauer, and Scovell, it has been made applicable to all cases, with the possible exception of a few alkaloidal and allied bodies. The moist combustion process for determining nitrogen is now generally employed by chemists in all countries, not only for fertilizer control, but also for general work.

309. The Method of Kjeldahl.—The process originally proposed by Kjeldahl is applicable only to nitrogenous bodies free of nitric nitrogen. The principle of the process is based on the action of concentrated sulfuric acid at the boiling-point in decomposing nitrogenous compounds without producing volatile combinations and the subsequent completion of the oxidation by means of potassium permanganate. The original process has been modified by many analysts, but the basic principle of it has remained unchanged. It will, therefore, prove useful here to describe the process as originally given.⁹⁷

The substance is placed in a small digestion flask of resistant glass. Liquids which are not decomposed on heating are evaporated in a thin glass dish, which can be ground up and placed

⁹⁷ *Zeitschrift für analytische Chemie*, 1883, **22** : 366.

in the digestion flask with the desiccated sample. The strongest sulfuric acid is added in sufficient quantity, not less than 10 cubic centimeters in any case, to secure complete decomposition. The acid must be free of ammonia and be kept in such a way as not to absorb ammonia from the atmosphere of the laboratory. To guard against danger of error from such an impurity, frequent control determinations should be made. In control experiments one or two grams of pure sugar are used as the organic matter. If the acid employed contain traces of ammonia, the necessary corrections should be made in each analysis.

The flask having been charged is placed on a wire gauze over a small flame. The organic matter becomes black and tar-like, and soon there is a rapid decomposition, attended with the evolution of gaseous products, among which sulfur dioxide is found. To avoid danger from spurting, the digestion flask is placed in an oblique position. The flask should have a capacity of at least 100 cubic centimeters, and a long neck and be made of a kind of glass capable of withstanding the action of the boiling acid. Particles of the carbonized organic matter left on the sides of the flask by the foaming of the mass at first are gradually dissolved by the vapors of the boiling acid as the digestion proceeds. The action of the sulfuric acid is not entirely finished when gases cease to be given off, but the digestion should be continued until the liquid in the flask is clear and colorless, or nearly so. Usually about two hours are required to secure this result. When aided by the means mentioned below, the time of digestion can be very materially shortened. By adding some fuming sulfuric acid, or glacial phosphoric acid, the dilution caused by the formation of water in the combustion of the organic matter can be avoided. For albuminoid bodies it is hardly necessary to continue the combustion until all carbonaceous matter is destroyed. The full complement of ammonia is usually obtained after an hour's combustion, even if the liquid be still black or brown, but with other nitrogenous bodies the case is different, so that upon the whole it is safest to secure complete decoloration.

The temperature must be maintained at the boiling-point of

the acid or near thereto, since at a lower temperature, for instance, from 100° to 150° , the formation of ammonia is incomplete. Since all organic substances of whatever kind are dissolved by the boiling acid, the previous pulverization of the material need be carried only far enough to secure a fair sample. Many substances give up practically all their nitrogen as ammonium sulfate when heated with sulfuric acid, as, for instance, urea, asparagin, and the glutens. In most of the other organic bodies fully 90 per cent. of the nitrogen is likewise secured as the ammonium salt. In the aromatic compounds, or even in the form of amid in anilin salts, the nitrogen is more resistant to the action of sulfuric acid. In the alkaloids where the nitrogen is probably a real component of the benzol skeleton, the formation of ammonia is very incomplete. But even in the cases where the conversion of the nitrogen into ammonia is practically perfect, it is advisable to finish the process by completing the oxidation with potassium permanganate. The permanganate should be used in a dry powdered form and added little by little to the hot contents of the digestion flask, the latter being held in an upright position and removed meanwhile from the lamp. When carefully performed there is no danger of loss of ammonia, although the oxidation is at times so vigorous as to be attended with evolution of light. The permanganate must always be added in excess and until a permanent green color is produced. The flask is then gently heated for from five to 10 minutes over a small flame, but this is not important. The heating must not be too strong, or else a strong evolution of oxygen will take place, with a consequent reduction of the manganese compound. When this happens the liquid again becomes clear and there is a loss of ammonia.

After cooling, the contents of the flask are diluted with water, the green color giving place to a brown, with a rise of temperature. After cooling a second time, the whole is brought into a distillation flask of about three-quarters of a liter capacity and attached to a condenser which ends in a vessel containing titrated sulfuric acid. About 40 cubic centimeters of sodium hydroxid solution of 1.3 specific gravity are added and the stopper at once

inserted to prevent any loss of ammonia. To prevent bumping, some zinc dust is added, securing an evolution of hydrogen during the progress of the distillation. In this case the bumping is prevented until near the end of the operation, when it begins anew, probably by reason of the separation of solid sodium sulfate. After the end of the distillation, the excess of acid remaining in the receiver is determined by a set alkali solution, and thus the quantity of ammonia obtained easily calculated. Kjeldahl, however, preferred to titrate the solution after adding potassium iodate and iodid, a mixture which in the presence of a strong acid sets free a quantity of iodine equivalent to the free acid present. The iodine thus set free is titrated by a set solution of sodium thiosulfate, using starch as an indicator. The merits of this method are sharpness of the end reaction and the possibility of using only a small quantity of the nitrogenous body for the combustion. The sulfuric acid used in the receiver is made of the same strength as the thiosulfate solution; viz., about one-twentieth normal. Thirty cubic centimeters of this were found to be the proper amount for use with substances oxidized in such quantities as to produce ammonia enough to neutralize about half of it. The titration is carried on as follows: A few crystals of potassium iodid are dissolved in the acid mixture obtained after the distillation is completed, then a few drops of the starch-paste, and finally a few drops of a four per cent. solution of potassium iodate. The iodine set free is then oxidized by the addition of the one-twentieth normal sodium thiosulfate solution until the blue color disappears.

Example: Sulfuric acid used, 30 cc.
 Equivalent to sodium thiosulfate, 30 cc.
 Blank combustion required, 29.8 cc. thiosulfate solution.
 Combustion of 0.645 gram of barley required, 14.5 cc. " "
 Thiosulfate corresponding to barley, 15.3 cc.

In the computation it is more simple to multiply the corresponding number of cubic centimeters of thiosulfate by seven, half the atomic weight of nitrogen, and divide the product by the

weight of the substance, which will give the per cent. of nitrogen therein.

$$\text{Then } \frac{15.3 \times 7}{64.5} = 1.66 = \text{per cent. of nitrogen in sample.}$$

A more detailed description of the method of making the titration follows: After the distillation is finished the condensing-tube is rinsed with a little water, after which the sulfuric acid unneutralized in the receiver is determined. It is advisable first to test the reaction of the distillate with litmus paper before going any further; for if at any time all the acid should be found neutralized it will be necessary to add a sufficient quantity of one-twentieth normal sulfuric acid before adding the potassium iodid, etc., otherwise the determination will be irreparably lost. Add to the contents of the flask 10 cubic centimeters of the potassium iodid and two cubic centimeters of the potassium iodate solutions, described further on, and the sodium thiosulfate is then run in from a burette till the fluid, which is constantly kept agitated by shaking the flask, shows only a bare trace of yellow coloration from the iodine still present. Starch solution is then added, and the blue color obtained is at once removed by additional thiosulfate solution. When some experience has been gained, the eye is able to discern, with great certainty, even the slight coloration caused by only a small trace of free iodine.

In regard to the sensitiveness of the end reaction and the accuracy of the result, this method of titration leaves nothing to be wished for. The strength of the thiosulfate solution is determined in exactly the same manner, and with starch as an indicator. For this purpose, measure 10 cubic centimeters of one-twentieth normal sulfuric acid into an erlenmeyer, add 120 cubic centimeters of ammonia-free water, 10 cubic centimeters of potassium iodid solution, and two cubic centimeters of iodate solution; add thiosulfate solution till the fluid shows only the above mentioned light yellow tint, then add starch, and finally thiosulfate. In this way the strength of the thiosulfate is ascertained, which of course, must be occasionally redetermined, under exactly the same conditions as obtain in the nitrogen determinations, and

every possible error is thereby excluded. That the solution once decolorized within a short time again assumes a deep blue color, is a matter of no concern, inasmuch as both solutions are added in such a manner that the end reaction lies exactly at the point when the starch iodid reaction distinctly disappears.

310. Theory of the Reactions.—As has been seen above, the final product of heating a nitrogenous organic compound with sulfuric acid and an oxidizing body is ammonium sulfate. The various steps by which this is obtained have been traced by Dafert.⁹⁸

(1) The sulfuric acid abstracts from the organic matter the elements of water.

(2) The sulfur dioxid produced by the action of the residual carbon on sulfuric acid exercises a reducing effect on the nitrogenous bodies present.

(3) From the nitrogenous bodies produced by the above reduction ammonia is formed by the action of an oxidizing body.

(4) The ammonia formed is at once fixed by the acid as ammonium sulfate. According to the theory of Asboth, the hydrogen which is formed during the action of sulfuric acid on organic matter, when in a nascent state, also aids greatly in the production of ammonia. This idea is based on the fact that with those bodies which afford a deficit of hydrogen the formation of ammonia is imperfect.⁹⁹

311. Preparation of Reagents.—(1) *Pure Sulfuric Acid.*—As is well known, the so-called pure sulfuric acid in the market usually contains ammonia, a fact which compelled Kjeldahl to determine the quantity of nitrogen in the acid in every instance, and to make correction for the same in the analysis. An acid absolutely free from this impurity may, however, readily be prepared by the distillation of the commercial article in a small glass-retort holding easily about 400 cubic centimeters. To conduct this operation without danger it is only necessary to arrange the apparatus so that the heavy fluid is heated to boiling, not from the bottom of the retort, but from its sides, and that the upper

⁹⁸ Zeitschrift für analytische Chemie, 1885, 24 : 455.

⁹⁹ Chemisches Central-Blatt, 1886 : 165.

portion of the body and neck is kept sufficiently warm to prevent the sulfuric acid fumes from condensing and flowing back into the retort. Both these ends are attained by surrounding the retort with a piece of sheet iron, cylinder-shaped beneath, and with an oval upper part, having an opening of about one centimeter in diameter for the neck of the retort. To conduct the distillation, a burner is used with an arrangement for spreading the flame. To avoid with certainty all bumping of the sulfuric acid and the resulting danger therefrom, the lamp is so arranged that only the products of combustion go up between the retort and its iron hood, without allowing the flame itself to come into contact with the glass vessel. The retort should be filled about half full, or with 200 cubic centimeters of acid. By this device, without any danger whatever, about one liter of sulfuric acid may be distilled in a day. The retort will stand numerous distillations. Once begun, the distillation takes care of itself; it is necessary to discontinue it when only the bottom of the retort is covered with sulfuric acid, and to fill with fresh acid through a funnel when the retort has cooled off. The first 20 cubic centimeters of the distillate going over are collected by themselves and rejected. What comes over later is, as shown by experience, absolutely ammonia-free, and can be used without any correction for the nitrogen determinations according to Kjeldahl. The acid is kept in a stoppered bottle in a place not reached by ammonia fumes. The 10 cubic centimeter pipette used for measuring the quantity of sulfuric acid required for each determination is fastened in the perforated rubber stopper with which the bottle is kept closed, and is itself closed above by a small rubber tube with a plug of glass wool in it.

(2) *Potassium Permanganate*.—Crystals of this salt are crushed (not pulverized) with a pestle into small pieces of about one-half millimeter size, which are kept in a long glass tube of about ten millimeters diameter, closed with a stopper.

(3) *Ammonia-free Water*.—Common distilled water can not be used in the determination of nitrogen according to Kjeldahl, since it contains ammonia. Water may be obtained free from ammonia

by redistillation in a large glass retort with the addition of a few drops of sulfuric acid. All vessels used in the determination are rinsed out beforehand with this water.

(4) *Ammonia-free Soda-lye* is most conveniently prepared by adding 270 grams of common sodium hydroxid in sticks, little by little, to one liter of distilled water which is kept continually boiling, by means of a small flame, in a good-sized silver dish. The dish is kept covered with a glass plate. Care has to be exercised not to add the alkali too rapidly, nor in too large quantities at a time, for in this case the fluid will boil too violently at every addition of the alkali. After the operation is finished the lye is at once siphoned into a glass flask, and when cold is poured into a glass-stoppered bottle.

(5) *One-twentieth Normal Sulfuric Acid* is prepared from sulfuric acid and water, both absolutely ammonia-free, and is kept in a place where no fumes of ammonia can reach it, in a well-stoppered glass bottle, the stopper being smeared with vaseline.

(6) *Sodium Thiosulfate Solution*.—This should be of the same strength as the one-twentieth normal sulfuric acid. It is prepared by dissolving the salt in ammonia-free water and is compared with the acid, to which has been added potassium iodid and iodate, using starch as an indicator, in the manner described above. The solution is kept in a well-stoppered bottle, in the dark. When the salt and water used are perfectly pure, it will keep unchanged for a long time.

(7) *Potassium Iodid*.—Dissolve five grams of chemically pure potassium iodid in ammonia-free water and make the volume 100 cubic centimeters. Keep the solution in the dark and in a well-stoppered bottle. Ten cubic centimeters of this solution are used for each determination.

(8) *Potassium Iodate*.—Dissolve four grams of chemically pure potassium iodate in ammonia-free water and make the volume 100 cubic centimeters. Use two cubic centimeters of this solution for each determination.

(9) *Starch Solution*.—Digest pure starch for about a week with dilute hydrochloric acid, wash perfectly free from chlorin

by decantation, and finally dry it between filter-paper. The starch is then suspended in water with the aid of heat. Such a solution will keep for an indefinite time if it be saturated with common salt. Ten grams of this starch are dissolved in 1,000 cubic centimeters of ammonia-free water and one or two cubic centimeters used for each determination.

312. Modifications of the Kjeldahl Process.—It would be impracticable here to give even a summary of the many unimportant changes which the moist combustion process has undergone since the first papers of its author were published. These changes may be divided into three classes; viz.:

1. Those changes which refer solely to the quantities of substance used for analysis, to the composition of the acid mixture, to the duration of the digestion, to the form and size of the flasks, both for digestion and distillation, and to the manner of distillation and of titration. For references to the papers on these subjects the reader may consult Fresenius.¹ The most important of these minor changes are the following: Instead of the titration by means of separated iodine most chemists have had recourse to the simpler method of direct titration of the excess of acid by a set solution of an alkali. Ammonium, barium, sodium, and potassium hydroxids are the alkaline solutions most employed. This process permits of a larger quantity of the sample being taken for combustion and of the use of a larger quantity of acid in the receiver. It also implies the use of a larger digestion flask. In fact, it is now quite universal to make the digestion in a special glass flask large enough to be used also for the distillation. This saves one transfer of the material with the possible danger of loss attending it.

In the distillation it is a common practice, especially in Germany, to do away with the condensing worm and to carry a long glass tube from the distilling flask directly into the acid in the receiver. The only inconvenience in this method is the heating of the contents of the receiving flask, but this is attended with no danger of loss of ammonia and the distillate, on account of the high temperature it acquires, is left free of carbon dioxide.

¹ *Zeitschrift für analytische Chemie*, 1883 to date.

Many of these minor changes have tended to simplify the process, but without affecting the principle of the method in the least.

2. In the second place a class of changes may be mentioned in which there is a marked difference in the method of effecting the oxidation secured by the introduction of a substance, usually a metal, during the digestion for the purpose of accelerating the oxidation. In the original process the only aid to oxidation was applied at the end of the digestion in the use of potassium permanganate. In the modifications now under consideration a metallic oxid or metal is applied at the beginning of the digestion. Copper and mercury are the metals usually employed. A separate paragraph will be given to the description of this modification known as the process of Wilfarth.

3. The third class of changes is even more radical in its nature, having for its object the adaptation of the moist combustion method to oxidized or mineral nitrogen. The chief feature of this class of changes consists in the introduction of a substance rich in hydrocarbons, and capable of easily forming nitro compounds, for the purpose of holding the oxids of nitrogen which are formed during the combustion and helping finally to reduce them to the form of ammonia. The chief varieties of this class of changes were proposed by Asboth, Jodlbauer, and Scovell, and will be fully set forth in separate paragraphs.

313. Method of Wilfarth.—The basis of this modification as already noted rests on the fact that certain metallic oxids have the power of carrying oxygen and thus assisting in a catalytic way in the combustion of organic matter.² The copper and mercury oxids are best adapted for this purpose and experience has shown that mercuric oxid, or even metallic mercury gives the best results. The manipulation is carried out as follows:

From one to three grams of the sample, according to its richness in nitrogen, are heated with a mixture of 20 cubic centimeters of acid containing two-fifths fuming and three-fifths ordinary sulfuric acid. To this is added about seven-tenths gram of mercuric oxid prepared in the wet way from a mercury salt free of

² *Chemisches Central-Blatt*, 1885 : 113.

nitrogen. The combustion takes place in the usual kjeldahl flask. If the boiling be continued until the liquid is entirely colorless, final oxidation with potassium permanganate is unnecessary. To save time the combustion may be stopped when a light amber color is reached, and then the oxidation finished with permanganate. Before distilling, a sufficient quantity of potassium sulfid is added to precipitate all the mercury as sulfid and thus prevent the formation of mercurammonium compounds which would produce a deficit of ammonia. A convenient strength of the sulfid solution is obtained by dissolving 40 grams of potassium sulfid in one liter of water. Bumping at the end of the distillation is not usual, especially if potash-lye be used, but should it occur it may be stopped by the addition of zinc dust.

Only when a large excess of potassium sulfid is used is there an evolution of hydrogen sulfid, the presence of which, however, does not influence the accuracy of the results.

The presence of mercuric sulfid in the solution tends to prevent bumping during the distillation, but it is advisable, nevertheless, to use a little zinc dust. Other minor modifications consist of preparing the acid mixture with equal volumes of concentrated and fuming sulfuric acid containing in one liter 100 grams of phosphoric acid anhydrid, and using metallic mercury instead of mercuric oxid³; or a mixture of half a gram of copper sulfate and one gram of metallic mercury; or 0.05 gram of copper oxid and five drops of platinic chlorid solution containing 0.04 gram of platinum in a cubic centimeter.⁴

314. Kjeldahl Method as Practiced by the Holland Royal Experiment Station.⁵—*Necessary Reagents:* 1. Phosphosulfuric acid, made by mixing a liter of sulfuric acid of specific gravity 1.84 with 200 grams of phosphoric anhydrid.

2. Alkaline sodium sulfid solution, made by dissolving 500 grams of sodium hydroxid and six grams of sodium sulfid or eight and one-half grams of potassium sulfid in a liter of water.

3. Mercury.

³ Kulisch, *Zeitschrift für analytische Chemie*, 1886, **25** : 149.

⁴ Ulsch, *Chemisches Central-Blatt*, 1886 : 375.

⁵ *Methoden van Onderzoek aan de Rijkslandbouwproefstations voor het Jaar 1894.*

4. Paraffin in small pieces.
5. Dilute sulfuric acid and dilute potash solution, both of known strength.
6. Pieces of previously ignited pumice stone or of granulated zinc.
7. Neutral solution of rosolic acid or litmus.

Apparatus.—The necessary apparatus consists of oxidation flasks of about 200 cubic centimeters capacity and distillation flasks of about 500 cubic centimeters capacity, both of Bohemian glass. Copper may be used for the distillation flasks.

The Process.—A gram of the sample to be analyzed is placed in an oxidation flask, together with 20 cubic centimeters of phosphosulfuric acid and a drop of mercury (about 600 milligrams), and heated till the fluid becomes colorless. After cooling, dilute and wash the contents of the flask into a distillation flask. The resulting volume should be about 300 cubic centimeters. Add 100 cubic centimeters of the alkaline sodium sulfid solution and some pieces of ignited pumice stone or granulated zinc. Distil the ammonia, receiving the distillate in a flask containing a known volume of the standard sulfuric acid. Titrate with tenth-normal potash, using litmus or rosolic acid as indicator.

315. The Kjeldahl Method as Practiced at the Halle Station.—The method in vogue in the German stations of conducting the moist combustion process is well illustrated by the method of procedure followed at Halle.⁶ From 0.7 to 1.5 grams of the sample are used for analysis, according to its richness in nitrogen. Because of the fact that so small a quantity of the sample is used, it is of the highest importance that it be perfectly homogeneous throughout its entire mass. Otherwise, grave errors may arise. From the sample as sent to the laboratory the analyst should remove a subsample, and this should be rubbed to a fine powder and the part used for analysis carefully selected therefrom. If the sample be moist it may be rubbed up with an equal weight of gypsum, in which case a double quantity is employed for the determination. Substances like bone-meal,

⁶ Bieler und Schneidewind, Die agricultur-chemische Versuchsstation Halle a/S., 1892 : 34.

which do not keep well mixed, especially when occasionally shaken, should be intimately mixed before each weighing. The sample is placed in a glass flask of about 150 cubic centimeters capacity. The flask should be made of a special glass to withstand the conditions of the combustion. A globule of mercury weighing a little less than one gram is placed in the flask and also 20 cubic centimeters of pure sulfuric acid of 1.845 specific gravity. The mercury is conveniently measured by an apparatus suggested by Wrampelmayer. It consists of an iron tube holding mercury, and is conveniently filled, from time to time, from a supply vessel placed in a higher position and joined by means of a heavy glass tube and rubber tube connections. The lower end of the iron tube is provided with a movable iron stopper having a pocket just large enough to hold a globule of mercury, weighing a little less than a gram. On turning the stopper the pocket is brought opposite a discharge orifice and the measured

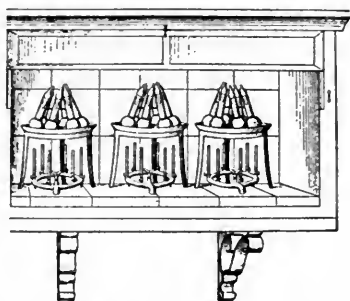


Fig. 15. Moist Combustion Apparatus of the Halle Agricultural Laboratory.

globule of mercury is discharged. With substances which tend to produce a strong foaming a little paraffin is used. The flasks after they are charged are placed on circular digesting ovens under a hood, as shown in Fig. 15.

At first the tripodal support of the flasks is so adjusted as to bring them between the lamps, and in this way a too rapid reaction is at first avoided. After half an hour the tripods are so turned as to bring each flask directly over the lamp, the flame of which is allowed to impinge directly against the glass. The flame is so regulated that after the evolution of the sulfur dioxide

has nearly ceased the contents of the flask are brought into gentle ebullition. The boiling is continued until the contents of the flask are colorless, usually about two hours. As a rule, such substances as cottonseed-meal and dried blood will take a longer time for complete combustion than other fertilizing materials. During the combustion the flasks are closed with an oblong loose-fitting unground glass stopper. When the oxidation is finished the contents of the flasks are allowed to cool, the stoppers are removed, and enough water is added to fill the flasks about three-quarters full. The flasks are gently shaken, and the possibility of breaking from the heat developed must not be overlooked. To avoid confusion, the flasks are all numbered before beginning the work and the numbers noted by the analyst in connection with the samples. The contents of each one are next poured into the distillation flask and the digestion vessels are washed with 100 cubic centimeters of water in three portions and the wash-water added to the liquid. Sometimes in washing out the digestion flask yellow basic mercury compounds separate on its walls, but this does not in any way influence the accuracy of the results. The distillation flasks should have about 600 cubic centimeters capacity. To avoid the transfer, the digestion may take place in the distillation flask, in which case the latter must be made of special glass as indicated.

To the liquid thus transferred are added 75 cubic centimeters of soda-lye, containing one and one-half times as much potassium sulfid as is necessary to combine with the mercuric sulfate present. The lye is of such a strength that 60 cubic centimeters are sufficient to neutralize the acid present. It has a specific gravity of 1.375 and contains 33 grams of potassium sulfid in a liter.

In order to avoid the bumping which may take place during the distillation, some granulated zinc should be added.

The distillation flask is closed with a rubber stopper carrying a bulb-tube which ends above in a glass tube about three-quarters of a meter long, bent at an acute angle and passing obliquely downward on a convenient support. This tube is connected by a rubber, with the end tube bent nearly at a right angle and dip-

ping into the standardized acid in the erlenmeyer receiver. The general arrangement of the distilling apparatus is shown in Fig. 16. Since the contents of the vessel are warmed by mixing with the soda-lye, the flame can be turned on at full head at once at the commencement of the operation. In about a quarter of an hour the liquid in the receiver will be at the boiling-point, and the boiling should be continued for five minutes more, making 20 minutes in all for the completion of the distillation. By this boiling the contents of the receiver are not charged with carbon dioxid, as might happen if a condenser were used. The receiver contains 20 cubic centimeters of a standardized sulfuric acid solution and about 50 cubic centimeters of water.

The acid used should contain 38.1 grams of sulfuric acid of 1.845 specific gravity in a liter; and it should be set by titration

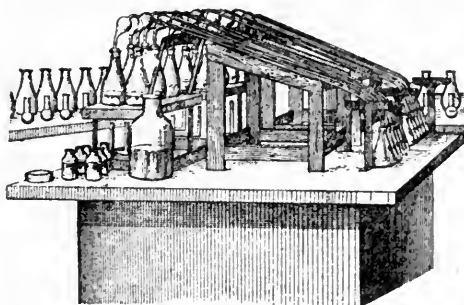


Fig. 16. Distillation Apparatus of the Halle Agricultural Laboratory.

with chemically pure sodium carbonate. For this purpose 0.7 gram of sodium carbonate is heated in a platinum crucible for two hours over a small flame, weighed, and placed in an erlenmeyer together with 20 cubic centimeters of the sulfuric acid, care being taken to avoid loss from the vigorous evolution of carbon dioxid. After boiling for 10 minutes all the carbon dioxid is removed from solution. After cooling, the excess of acid is determined by titration with a standardized barium hydroxid solution, using rosolic acid as indicator.

The solution of barium hydroxid is made as follows: Digest, with warm water, 260 grams of caustic baryta, $\text{Ba}(\text{OH})_2$, until it is nearly all dissolved, filter, and make up to a volume of 10

liters and keep in a flask free of carbon dioxid. A solution of barium hydroxid is to be preferred to the corresponding sodium compound for titration. If traces of carbonate be formed in the two liquids, the sodium salt will remain in solution while the barium compound will settle at the bottom of the flask.

The Indicator.—The indicator used to determine the end of the reaction is made by dissolving one gram of rosolic acid in 50 cubic centimeters of alcohol. From one to two drops are enough for each titration. The color reaction is less definite as the quantity of ammonia in the liquid increases. When the titration solutions have been prepared as above described it is found to require about 90 of the barium hydroxid to neutralize 20 cubic centimeters of the sulfuric acid.

By direct titration with sodium carbonate it is ascertained how many grams of nitrogen the 20 cubic centimeters of sulfuric acid represent.

Example.—Suppose the weight of the dried sodium carbonate prepared as above directed is 0.6989 gram.

$$\begin{array}{rcccl} & 1/2\text{Na}_2\text{CO}_3, & & 1/2\text{N}_2 & \\ \text{Then } 0.6989 & : 53 & = x & : 14 & \\ \text{Whence } x = & 0.184615 & \text{gram of nitrogen.} & & \end{array}$$

Suppose further that 20 cubic centimeters of sulfuric acid solution require 94 cubic centimeters of barium hydroxid for complete saturation and after treatment with the above amount of sodium carbonate, 10½ cubic centimeters of the barium solution to neutralize the remaining acid.

$$\text{Then } 94 - 10.5 = 83.5$$

$$\text{And } 0.184615 : 83.5 = x : 94.$$

Whence $x = 0.207830$ gram of nitrogen corresponding to 20 cubic centimeters of the sulfuric acid used.

Then $0.20783 \div 94 = 0.002211$ gram of nitrogen corresponding to one cubic centimeter of the barium hydroxid solution.

If then in the analysis of a fertilizer it is found that 60.5 cubic centimeters are required to neutralize the excess of sulfuric acid after distillation, the percentage of nitrogen in the sample is found as follows:

$$60.5 \times 0.002211 = 0.13377.$$

$$0.20783 - 0.13377 = 0.07406.$$

$0.07406 \times 100 = 7.406 =$ per cent. nitrogen in sample when one gram is used for the combustion.

316. The Official Kjeldahl Method. Not Applicable in the Presence of Nitrates.—In order to determine if the sample contains nitric acid or nitrates, apply the following test:⁷

Mix five grams of the fertilizer with 25 cubic centimeters of hot water and filter. To a portion of this solution add two volumes of concentrated sulfuric acid, free from nitric acid and oxids of nitrogen, and allow the mixture to cool. Add cautiously a few drops of concentrated solution of ferrous sulfate, so that the fluids do not mix. If nitrates are present the junction shows at first a purple, afterwards a brown color, or if only a very minute quantity be present, a reddish color. To another portion of the solution add one cubic centimeter of dilute solution of nitrate of soda (three grams to 300 cubic centimeters) and test as before to determine whether sufficient sulfuric acid was added in the first test.

Preparation of Reagents.—(1) *Acids.*—(a) *Standard hydrochloric acid*, the absolute strength of which has been determined by precipitating with silver nitrate, and weighing the silver chloride as follows:⁸

To any convenient quantity of the acid to be standardized, add a solution of silver nitrate in slight excess, and two cubic centimeters of pure nitric acid, of specific gravity 1.2. Heat to boiling-point, and keep at this temperature for some minutes without allowing violent ebullition, constantly stirring until the precipitate assumes the granular form. Allow to cool somewhat, and then filter the fluid through asbestos. Wash the precipitate by decantation, with 200 cubic centimeters of very hot water, to which have been added eight cubic centimeters of nitric acid and two cubic centimeters of dilute solution of silver nitrate containing one gram of the salt in 100 cubic centimeters of water. The washing by decantation is performed by adding

⁷ Division of Chemistry, Bulletin 49, 1897 : 19.

⁸ Division of Chemistry, Bulletin 46, Revised Edition, 1899 : 14.

the hot mixture in small quantities at a time, and beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all the time, but to keep out dust during the washing, the cover is only removed from the crucible when the fluid is to be added.

Put the vessels containing the precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove them from the receiver, and set aside to recover the excess of silver. Rinse the receiver and complete the washing of the precipitate with about 200 cubic centimeters of cold water. Half of this is used to wash by decantation and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chlorid being broken down with a glass rod. Remove the second filtrate from the receiver and pass about 20 cubic centimeters of 98 per cent. alcohol through the precipitate. Dry at from 140° to 150° . Exposure for half an hour is found more than sufficient, at this temperature, to dry the precipitate thoroughly. It has been proposed to modify this process somewhat by directing that the precipitate be washed several times by decantation instead of with 200 cubic centimeters of water, this quantity not being considered sufficient in all cases.

The above is the old method of standardizing the hydrochloric acid. The method now in use is as follows:⁹

By means of a preliminary test with silver-nitrate solution, to be measured from a burette, with excess of calcium carbonate to neutralize free acid and potassium chromate as indicator, determine exactly the amount of nitrate required to precipitate all the hydrochloric acid. To a measured and also weighed portion of the standard acid add from a burette one drop more of silver-nitrate solution than is required to precipitate the hydrochloric acid. Heat to boiling, cover from the light, and allow to stand until the precipitate is granular. Then wash with hot water through a gooch crucible, testing the filtrate to prove excess of silver nitrate. Dry the silver chlorid at 140° to 150° C.

(b) *Standard sulfuric acid*, the absolute strength of which has

⁹ Bureau of Chemistry, Bulletin 107, 1907 : 5.

been determined by precipitation with barium chlorid and weighing the resulting barium sulfate:

For ordinary work half-normal acid is recommended, *i. e.*, containing 24.52 grams sulfuric acid to the liter; for determining very small amounts of nitrogen, one-tenth normal acid is recommended. In titrating mineral acids against ammonia solutions, use cochineal as indicator.

(*c*) *Sulfuric acid*, specific gravity 1.84, free of nitrates and also of ammonium sulfate, which is sometimes added in the process of manufacture to destroy nitrogen oxids.

(*d*) *Standard alkali*, the strength of which, relative to the acid, has been accurately determined. One-tenth normal ammonia solution, *i. e.*, containing 1.7051 grams of ammonia to the liter, is recommended for accurate work.

(*e*) *Metallic mercury or mercuric oxid*, prepared in the wet way. That prepared from mercuric nitrate can not be safely used.

(*f*) *Potassium permanganate* finely pulverized.

(*g*) *Granulated zinc, pumice stone, or zinc dust* (one-half gram) is to be added to the contents of the flask during distillation, when found necessary, in order to prevent bumping.

In the laboratory of the Bureau of Chemistry, zinc dust is no longer used, since its use tends to break the flask. Pumice stone is also no longer used, since experience has shown that granulated zinc is best suited to secure the purpose intended.

(*h*) *Potassium sulfid*.—A solution of 40 grams of commercial potassium sulfid in one liter of water.

(*i*) *Soda*.—A saturated solution of sodium hydroxid free of nitrates.

(*j*) *Indicator*.—A solution of cochineal prepared as follows: Digest for a day or two at ordinary temperatures and with frequent agitation, three grams of pulverized cochineal in a mixture of 50 cubic centimeters of strong alcohol with 200 cubic centimeters of distilled water. The filtered solution is employed.

Apparatus.—(1) *Kjeldahl digestion flasks*, pear-shaped, round bottom, of hard, moderately thick, well-annealed glass: These flasks are about 22 centimeters long, having a maximum diame-

ter of six-centimeters and tapering out gradually in a long neck, which is two centimeters in diameter at the narrowest part, and flared a little at the edge. The total capacity is about 250 cubic centimeters.

(2) *Distillation flasks*.—For distillation, a flask of ordinary shape, of about 550 cubic centimeters capacity may be used. It is fitted with a rubber stopper and with a bulb-tube above to prevent the possibility of sodium hydroxid being carried over mechanically during distillation. The bulbs are about three centimeters in diameter, the tubes being of the same diameter as the condenser and cut off obliquely at the lower end, which is fastened to the tube of the condenser by a rubber tube.

(3) *Kjeldahl flasks for both digestion and distillation*.—These are pear-shaped, round-bottom flasks, having a total capacity of about 550 cubic centimeters, made of hard, moderately thick and well-annealed glass. When used for distillation the flasks are fitted with rubber stoppers and bulb-tubes, as given under distillation flasks.

Manipulation.—(1) *The Digestion*.—From seven-tenths to three and five-tenths grams of the substance to be analyzed, according to its proportion of nitrogen, are brought into a digestion flask with approximately seven-tenths gram of mercuric oxid or its equivalent in metallic mercury and 20 cubic centimeters of sulfuric acid. The flask is placed in an inclined position, and heated below the boiling-point of the acid for from five to 15 minutes or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required until the contents of the flask have become a clear liquid, which is colorless or, at least, has only a very pale straw color. The flask is then removed from the frame, held upright and, while still hot, potassium permanganate is dropped in carefully and in small quantities at a time until, after shaking, the liquid remains of a green or purple color. Respecting the time of boiling, it is suggested that the following be added to the official methods in place of the sentence beginning "no further attention, etc." "Boil for at least one hour or until the

in order to give a better view of the arrangement of the furnace. In the furnace there are three sets of eight digestion flasks. The neck of each flask is held by an opening into a lead tube of five inches diameter, connected with a ventilating flue concealed by the tube in the photograph. Any sulfuric acid which condenses in this tube is caught by a vessel placed under the lowest part of the lead tube; the volatile products escape in the flue.

318. The Distillation Apparatus in Use in the Laboratory of the Bureau of Chemistry.—In the nitrogen laboratory of the Bureau the distilling apparatus is arranged as shown in Fig. 18. The flasks are the same as are used in the digestion process. They are connected to the block tin condensers by the trap shown in Fig. 19. The block tin condensers are contained in an iron tube through which cold water flows during the distillation. The trap (Fig. 19) above the flask carries an emergent tube which extends to nearly the center of the trap and is bent laterally to avoid any danger of carrying over any alkali that may be projected into the trap during boiling. A small hole near the bottom allows any condensed steam to flow back into the distilling flask. The cold water enters the condensers through the pipe provided with a stop-cock shown in the center, and leaves by the two pipes shown at the sides of the apparatus. The boiling is continued usually for nearly an hour, or until bumping begins. The table on which the apparatus is placed is so arranged as to permit of easy access on all sides. The standard acid is held in erlenmeyers placed on wooden blocks so that the end of the condenser, which is a drawn-out glass tube, dips beneath the surface of the acid.

319. Patrick's Distilling Flask.—To avoid the expense and annoyance attending the breaking of the distilling flasks, Patrick has proposed to make them of copper.¹⁰ The size, about half a liter, made for the evolution of oxygen for experimental purposes, may be used. A little excess of potassium sulfid is used to make up for any of it which might be consumed by the copper. About 25 cubic centimeters of this solution are recommended. No zinc or pumice stone is required to prevent bumping,

¹⁰ Division of Chemistry, *Bulletin* 31, 1891 : 142.

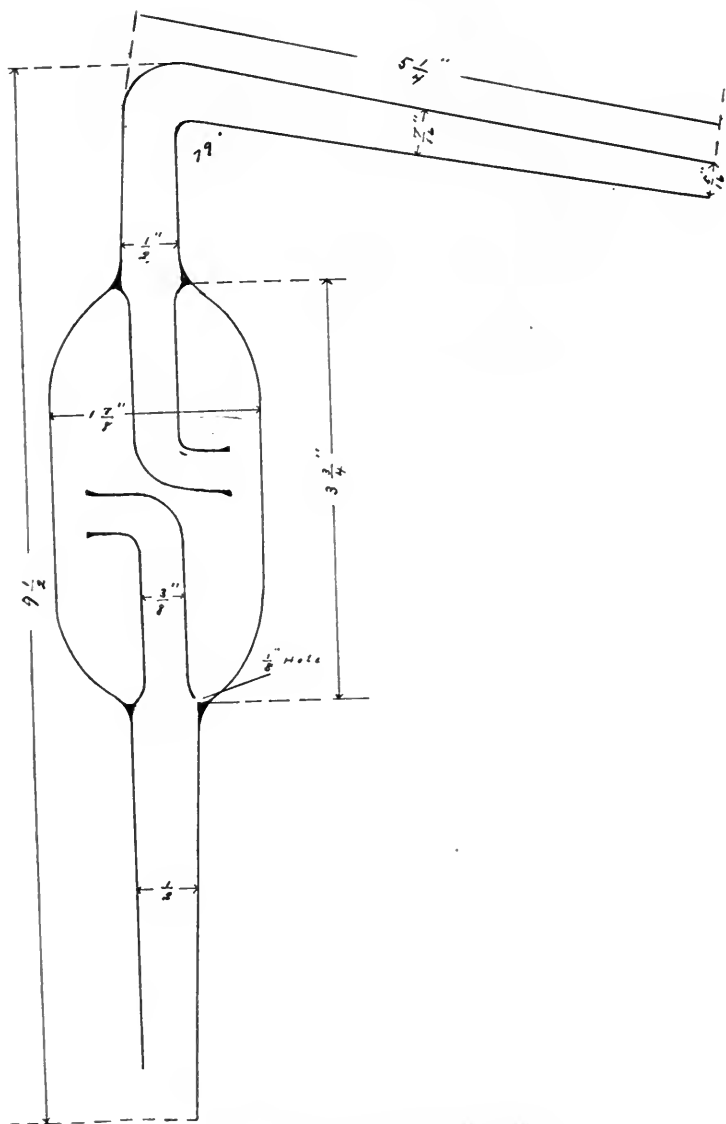


Fig. 19. Trap of Distilling Apparatus.

and the distillation may be finished within 30 minutes, thus securing a saving of time. There will doubtless be a slight corrosion of the flasks by the sulfid employed, but where the gunning oxidation process is practiced this danger would be avoided.

320. The Gunning Moist Combustion Process.—The modification proposed by Gunning was based upon the observation that in the ordinary kjeldahl process the excess of sulfur trioxid in the beginning of the operation soon escapes or unites with water in a form not easily decomposed.¹¹ During the progress of the combustion the acid diminishes in strength until it is below the concentration represented by the formula H_2SO_4 , and in this diluted condition the oxidation takes place more slowly. Gunning proposes to avoid this difficulty by mixing potassium sulfate with the sulfuric acid. This salt forms with the sulfuric acid, acid salts which, by heating, lose water easier than acid, and, as is well known, they not only act as decomposing and oxidizing media as well as sulfuric acid, but even in a higher degree, resembling the action of sulfuric acid at high temperatures and under pressure.

By heating this mixture of sulfuric acid and potassium sulfate with organic matters in an open vessel, not only the water originally present, but that which is formed during the oxidation, is driven off without loss of acid. For this reason instead of the oxidizing mixture becoming weaker, the acid becomes stronger, the boiling-point rises and this, combined with the fluidity of the mass, favors the decomposition and oxidation of the organic matter in a constantly increasing ratio.

The original mixture used by Gunning has the following composition; viz., one part of potassium sulfate and two parts of strong sulfuric acid. The substances are united by heat, and on cooling are in a semi-solid state, melting, however, easily on the application of heat and assuming a condition that permits them to be poured from vessel to vessel. The quantity of the sample should vary in proportion to its nitrogenous content from half a gram to a gram. The combustion takes place in flasks entirely similar to those used in the ordinary kjeldahl process. In the

¹¹ Zeitschrift für analytische Chemie, 1889, 28 : 188.

case of liquids, they should be previously evaporated to dryness before the addition of the oxidizing mixture. At the beginning of the combustion there is a violent foaming, attended with evolution of some acid and much water, and afterwards of stronger acid. This loss of acid should not be allowed to go far enough to produce too great concentration of the material in the flask. One of the best ways to avoid it, is to place a funnel in the flask covered with a watch-glass, which will permit of the condensation and return of the escaping acid. As soon as the foaming ceases, the flame should be so regulated as to permit of the volatilized acid being condensed upon the sides of the flask. In the end a colorless mass is obtained in which no metallic oxides are present, and this mass can at once be diluted with water, treated with alkali, and distilled. According to the nature of the substance, from half an hour to an hour and a half are required for the complete combustion.

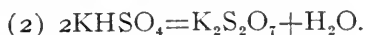
Modifications of the Gunning Method.—As in the case of the kjeldahl method, numerous minor modifications of the gunning method have been made, the most important of which relate to its application to substances containing nitrates. In general the same processes are employed in this case as with the kjeldahl method. One of the best modifications consists in the use of the mixture of salicylic and sulfuric acids, followed by the addition of sodium thiosulfate or of potassium sulfate or sulfid. These modifications will be given in detail under the official methods.

321. Reactions of the Gunning Process.—The various reactions which take place during the combustion according to the gunning method have been tabulated by Van Slyke.¹²

The first reaction to take place is the union of sulfuric acid and potassium sulfate to form potassium acid sulfate in accordance with the following equation:

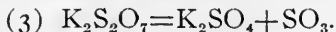


When heated, the potassium acid sulfate decomposes, forming potassium disulfate and water, thus:



¹² Division of Chemistry, Bulletin 35, 1892 : 68.

The potassium disulfate at a higher temperature decomposes, forming normal potassium sulfate and sulfur trioxid, thus:



At a sufficiently high temperature the two preceding reactions may take place in one, thus:



At the temperature at which these reactions take place, the water that is set free does not recombine with the sulfur trioxid nor with the sulfuric acid that is present in excess, but is expelled from the mixture; hence the mixture becomes more concentrated during the digestion. The sulfur trioxid set free acts upon the organic matter in the powerful manner peculiar to it, and the potassium sulfate, formed in the last reaction above, unites with another molecule of sulfuric acid, and the same round of reactions is repeated continuously so long as there is an excess of free sulfuric acid present in the mixture. As the liquid becomes more concentrated with the continuation of the digestion, the boiling-point increases so that the effect is the same as heating under pressure. The danger of too great concentration and risk of consequent loss of nitrogen is avoided by using increased proportions of sulfuric acid.

As compared with the kjeldahl, the gunning method presents the following advantages:

(1) The gunning method requires fewer reagents. As no form of mercury is used, no potassium sulfid is needed, and there is no risk of loss from the presence of mercurammonium compounds.

(2) The solution to which caustic soda is added is clear, so that in neutralizing it is an easy matter to avoid great excess of alkali, and so, in most cases, to avoid foaming and bumping in distillation.

(3) In the blank determinations less nitrogen is found in the reagents used in the gunning method. In only one case was more nitrogen reported in a blank by this method than in the other methods; in all the others the amount was considerably less.

322. The Official Gunning Method.¹³—In a digestion flask hold-

¹³ Bureau of Chemistry, Bulletin 107, 1907: 7.

ing from 250 to 550 cubic centimeters, place from 0.7 to 3.5 grams of the substance to be analyzed, according to its proportion of nitrogen. Add 10 grams of powdered potassium sulfate and from 15 to 25 cubic centimeters (ordinarily about 20 cubic centimeters) of concentrated sulfuric acid. Conduct the digestion as in the kjeldahl process, starting with a temperature below boiling-point and increasing the heat gradually until all frothing ceases. Digest until colorless or nearly so. Do not add either potassium permanganate or potassium sulfid. Dilute, neutralize, and distil as in the kjeldahl method. In neutralizing, it is convenient to add a few drops of phenolphthalein indicator, by which one can tell when the acid is completely neutralized, remembering that the pink color, which indicates an alkaline reaction, is destroyed by a considerable excess of strong fixed alkali. The distillation and titration are conducted as in the kjeldahl method. In distilling, the use of zinc or of some substance to prevent bumping or foaming is generally necessary. The amount of sulfuric acid recommended by Gunning is two grams for each gram of potassium sulfate; but Van Slyke has found that this mixture is so viscous as to cause troublesome foaming frequently, and after cooling it cakes in a hard mass, which may be difficult to redissolve.¹⁴ To avoid foaming and caking, he has found it an effective means to increase the amount of sulfuric acid used, using instead of two grams to one of potassium sulfate, three or four grams of acid to one of potassium sulfate. It is, therefore, suggested in carrying out the work, to use from five to 25 cubic centimeters (ordinarily about 20 cubic centimeters) of sulfuric acid for 10 grams of potassium sulfate. In case the potassium sulfate is not free from nitrogen compounds, one or two recrystallizations will make it pure.

CHANGES IN KJELDAHL METHOD TO INCLUDE NITRIC ACID

323. **Modifications of Asboth.**—In order to adapt the moist combustion process to nitric nitrogen Asboth proposed the use of benzoic acid.¹⁵ For half a gram of saltpeter 1.75 grams of ben-

¹⁴ Division of Chemistry, Bulletin 35, 1892 : 68.

¹⁵ Chemisches Central-Blatt, 1886 : 161.

zoic acid should be used. At the end of the combustion the residual benzoic acid is oxidized by means of potassium permanganate with a subsequent reheating. If the nitrogen be present as an oxid or as cyanid, one gram of sugar is added. The metallic element added is half a gram of copper oxid. Asboth also recommends that the soda-lye used in the distillation be mixed with sodium potassium tartrate for the purpose of holding the copper and manganese oxids in solution and thus preventing bumping. The alkaline liquor contains in one liter 350 grams of the double tartrate and 300 grams of sodium hydroxid.

The principle on which the use of benzoic acid rests is found in the fact that it easily yields nitro-compounds and thus prevents the loss of the nitrogen oxids, these readily combining with the benzoic acid. The nitro-compounds can be subsequently converted into ammonia by treatment with potassium permanganate.

The pyridin and chinolin groups of bodies do not yield all their nitrogen as ammonia by the above treatment.

The conclusions drawn by Asboth from the analytical data obtained are:

(1) Sugar should be used in the ordinary kjeldahl process in those cases where the nitrogen in the organic substance is present as oxids or as cyanogen.

(2) In the case of nitrates good results may be secured with benzoic acid but permanganate must be added at the end.

(3) The kjeldahl-wilfarth process can be applied with substances difficultly decomposed, *e. g.*, alkaloidal bodies.

324. Variation of Jodlbauer.—The benzoic acid method, although a step forward, is not entirely satisfactory in the treatment of nitrates by moist combustion. Jodlbauer has proposed to substitute for the benzoic, phenolsulfuric acid.¹⁶

From two- to five-tenths gram of a nitrate are treated with 20 cubic centimeters of concentrated sulfuric and two and a half of phenolsulfuric acid, together with three grams of zinc dust and five drops of a solution of platinic chlorid of the strength mentioned above. The phenolsulfuric acid is prepared by dis-

¹⁶ *Chemisches Central-Blatt*, 1886 : 433.

solving 50 grams of phenol in 100 cubic centimeters of strong sulfuric acid. The combustion is continued until the solution is colorless, which may take as much as five hours. If phosphoric anhydrid be used the time of the combustion may be diminished by one-half, but in such a case the glass of the combustion flask is strongly attacked and is quite likely to break.

When the substances used are very rich in nitrates, it is advisable to rub them first with dry gypsum.

The theory of the process rests on the fact that by a careful admixture of a nitrogenous substance diluted with land plaster with phenolsulfuric acid, it is possible to change the nitric acid into nitro-phenol, and by the reducing action of zinc dust to change the nitro-product formed into amido-phenol. This afterwards is transformed into ammonium sulfate by heating with sulfuric acid, by which process, at the same time, all other nitrogenous compounds present in the substance, as with Kjeldahl's method, likewise form ammonium sulfate, only with the difference that addition of mercury is here absolutely necessary for the complete transformation of the slowly decomposed amido-phenol, and this again brings about the necessity of decomposing the nitrogenous mercury compounds formed in the solution by potassium sulfid, which is added after or with the soda-lye.

325. The Dutch Jodlbauer Method.—The Royal Experiment Station of Holland directs that the jodlbauer process be carried out as indicated below.¹⁷

The reagents necessary are:

1. *Phenolsulfuric acid*, prepared by dissolving 100 grams of pure crystallized phenol in pure sulfuric acid (1.84) and making up the solution to a liter with the same sulfuric acid.

2. *Zinc*, carefully washed and thoroughly dried.

3. *Sodium hydroxid solution*, the same as is used in the kjeldahl method.

4. *Potassium sulfid solution*, made by dissolving 355 grams of potassium sulfid (K_2S), or sodium sulfid solution, made by dissolving 250 grams of sodium sulfid (Na_2S) in a liter of water.

¹⁷ Methoden van Onderzoek aan de Rijkslandbouwproefstations voor het Jaar, 1894.

Oxidation flasks holding about 200 cubic centimeters, and distillation flasks holding about 750 cubic centimeters, both of Bohemian glass are used.

Manipulation.—Moisten one gram of substance with water, dry and introduce into an oxidation flask. Cover with 15 cubic centimeters of phenolsulfuric acid and, after cooling, thoroughly mix by gently shaking. After five minutes add from two to three grams of zinc in small proportions, keeping the flask cool, then 20 cubic centimeters of sulfuric acid, and finally two drops of mercury. Boil the mixture till the fluid is colorless, cool and dilute. Wash into a distillation flask and add an excess of sodium hydroxid solution and 25 cubic centimeters of the sodium (or potassium) sulfid solution. Distil and titrate as in the kjeldahl method.

326. The Halle-Jodlbauer Method.—At the Halle Station it is the uniform practice to mix the nitrate with gypsum before the combustion.¹⁸ In the case of Chile nitrates 10 grams are rubbed with an equal amount of gypsum, and two grams of the mixture, equal to one gram of the nitrate, used for the determination. In the case of saltpeter mixtures which contain over eight per cent. of nitrogen, one gram of the mixture with gypsum is used, of guanos one and a half grams, and of lower forms of nitrates or mixtures thereof, from three to five grams.

The sample, as prepared above, is treated with 30 cubic centimeters of a mixture of phenolsulfuric acid and phosphoric anhydrid. The mixture is prepared by dissolving 66 grams of phenol and 250 grams of phosphoric anhydrid in strong sulfuric acid, and, after cooling, mixing the two solutions and making the volume up to 1650 cubic centimeters with pure sulfuric acid. The mixture contains, in 30 cubic centimeters, one and two-tenths grams of phenol and four grams of phosphoric anhydrid. In the use of phenolsulfuric acid the presence of phosphoric anhydrid is indispensable in keeping the sulfuric acid water-free and in absorbing the water produced by the combustion.

¹⁸ Bieler und Schneidewind, Die agricultur-chemische Versuchsstation Halle a/S, 1892 : 34.

The phenolsulfuric acid used contains only enough phenol to reduce half a gram of saltpeter.

The sample and acid mixture having been put in the combustion flask, the latter is heated and shaken, at intervals, for an hour and the contents cooled.

The conversion of the nitrates into nitro-phenol compounds is finished in this time, and the next step consists in reducing these bodies to the amido-phenol group. This is accomplished in the cold by nascent hydrogen produced by the addition of zinc dust to the mixture. From one to three grams of the dust are to be used in proportion to the quantity of nitrates originally present.

The flask should be placed in a cooling mixture and the zinc dust added in small portions to prevent a too violent evolution of hydrogen. After the reduction is ended, the flask is allowed to stand for two hours, after which the combustion, distillation, and titration are accomplished in the usual way. On cooling, after the end of the combustion, the contents of the flask become solid. They may be brought again into the liquid state by shaking and gentle warming.

327. The Salicylic Acid Method.—The introduction of the use of salicylic acid as the proper reagent to prevent the loss of nitrogen when a nitrate is acted on by sulfuric acid is due to Scovell. It was noticed that the action of phenol was too violent to protect the process from loss of nitrogen. After a careful trial of many organic compounds capable of forming nitro-compounds in those circumstances, salicylic acid was selected as the most promising reagent.¹⁹ Rigid trials by Scovell and others extending over many years have confirmed the propriety of this choice.²⁰ The method has also been found to be accurate in the presence of chlorids as well as of nitrates.

328. Use of Zinc Sulfid and Sodium Thiosulfate.—During the many analyses made by this modified method, it was noticed that on pure nitrates there was apparently a slight

¹⁹ Thesis for Degree of Doctor of Philosophy, University of Illinois, June, 1906, (Unpublished).

²⁰ Division of Chemistry, Bulletin 16, 1887 : 51.

Division of Chemistry, Bulletin 19, 1888 : 47.

New Jersey Agricultural Experiment Station Report, 1887, 169.

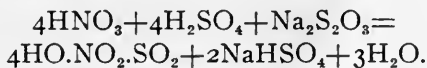
loss of nitrogen in adding the zinc dust. This was also a tedious part of the operation as the zinc dust had to be added gradually. Finely granulated zinc dust was tried, but in such cases the results were invariably low. The results were lower when using chemically pure zinc dust instead of the commercial article. An investigation showed that the commercial zinc dust which had hitherto been used contained some zinc sulfid. This suggested that hydrogen sulfid might complete the reduction as well if not better than nascent hydrogen. Working on this theory, Scovell and Peter made a series of experiments, using zinc dust in one set of experiments and zinc sulfid in another set.²¹ The results on pure potassium nitrate, containing a trace of water, and 13.83 per cent. of nitrogen were as follows:

Average.....	13.76
Theory.....	13.83

The advantage of zinc sulfid over zinc dust is: First, the liability of the loss of nitrogen is not so great. Second, the zinc sulfid can be added all at once, and, therefore, it is less troublesome and more rapid than when the zinc dust is used. Third, the oxidation is more rapid and, as less salts are present, the distillation is more quiet.

In 1893 sodium thiosulfate was substituted for zinc sulfid as the reducing agent in this method, not because better results were obtained, but because it was found to be difficult to get commercial zinc sulfid free from ammonia. The comparative results obtained by the different chemists using these two reducing agents were slightly in favor of zinc sulfid.²²

Otto Foerster gives the following as the reaction when sodium thiosulfate is used:²³



But it would be interesting to know whether hydrogen sulfid, which is also formed when salicylic acid and strong sulfuric acid

²¹ Division of Chemistry, Bulletin 24, 1890 : 91.

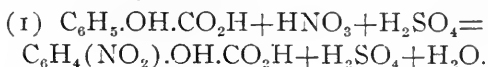
²² Division of Chemistry, Bulletin 38, 1893 : 34.

²³ Zeitschrift für analytische Chemie, 1889, 28 : 422.

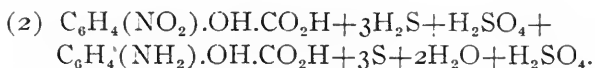
and nitrates are mixed, does not play at least a part in the reduction of the nitro into the amido compounds.

329. Theory of the Process.—The theory of the process by which salicylic acid converts nitrates to ammonia is as follows:

1. When salicylic acid and sulfuric acid are added to a nitrate, the sulfuric acid takes up water and one of the hydrogen elements of the salicylic acid is replaced by NO_2 , forming nitro salicylic acid. This reaction takes place without heat. It is probably mononitro and not dinitro salicylic acid that is formed. The reaction is probably as follows:



2. Subsequently when zinc sulfid is added the hydrogen sulfid liberated reduces the nitro salicylic acid to amido salicylic acid as follows:



3. The strong sulfuric acid and heat on the amido salicylic acid breaks it up and there is formed ammonium sulfate, carbonic acid, sulfur dioxide and water, as follows:



Similar reaction probably occurs when benzoic acid or phenol is used, but either nitro compounds are not as readily formed or they are not as easily converted into amido compounds, and probably the heat caused by the reaction when phenol is used is the cause of the loss of some nitric acid. Furthermore, phenol and benzoic acid do not break up as easily in the final reaction and, therefore, it takes longer to complete the oxidation than when salicylic acid is used.

Other nitro- and amido-forming compounds might be substituted for salicylic acid, but by the use of salicylic acid, the method is so simple and accurate that it is doubtful whether any substance other than salicylic acid would improve the method.

Other substances have been under observation, *e. g.*, pure potassium nitrate, using gallic acid in the place of salicylic acid, gave

6.68 per cent. of nitrogen; pyrogallic acid, 8.21 per cent.; phenol, 13.62 per cent.; benzaldehyde, 13.62 per cent.; phenyl salicylate, 13.72 per cent. It is interesting to note that phenyl salicylate gave satisfactory results; the oxidation, however, is not as rapid as when salicylic acid is used.

For ease in manipulation, rapidity of work, and accuracy of results the salicylic acid method is to be recommended.

330. The Official Kjeldahl Method for Nitric Nitrogen.—As has already been stated, the presence of certain organic compounds rich in hydrocarbons permits the reduction of nitric nitrogen to ammonia by combustion with sulfuric acid. Benzol, phenol, and salicylic acid have all been used for this purpose. The official chemists have adopted for their method the salicylic acid process first proposed by Scovell.²⁴

Besides the reagents and apparatus given under the kjeldahl method there will be needed:

(1) *Zinc dust*: This should be an impalpable powder; granulated zinc or zinc filings will not answer.

(2) *Sodium thiosulfate*.

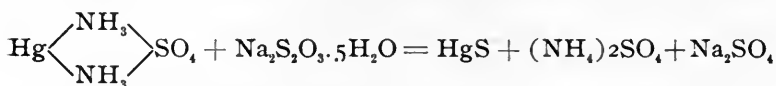
(3) *Commercial salicylic acid*.

It is found most convenient to prepare a solution of 33.3 grams of salicylic acid in one liter of the strongest sulfuric acid, and keep it for use rather than to mix it for each combustion.

The Manipulation.—Place from seven-tenths to three and five-tenths grams of the substance to be analyzed in a kjeldahl digesting flask, add 30 cubic centimeters of sulfuric acid containing one gram of salicylic acid, and shake until thoroughly mixed, then add five grams of crystallized sodium thiosulfate; or add to the substance 30 cubic centimeters of sulfuric acid containing two grams of salicylic acid, then add gradually two grams of zinc dust, shaking the contents of the flask at the same time. Finally place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly and the boiling continued until white fumes no longer escape from the flask. This requires about five or 10

²⁴ Division of Chemistry, Bulletin 16, 1887: 51.

minutes. Add now approximately 0.7 gram of mercuric oxid or its equivalent in metallic mercury, and continue the boiling until the liquid in the flask is colorless or nearly so. In case the contents of the flask are likely to become solid before this point is reached, add 10 cubic centimeters more of sulfuric acid. Complete the oxidation with a little potassium permanganate in the usual way, and proceed with the distillation as described in the kjeldahl method. The reagents should be tested by blank experiments. The object of adding the sodium thiosulfate is to prevent the development of the amido-mercurous salts which require to be subsequently broken up by the addition of a sulfid. The reaction which takes place is represented by the following formula:



+4H₂O. The sodium thiosulfate may also be added after the digestion instead of the sodium sulfid.²⁵

331. Gunning Method for Nitric Acid.—The essential features of this modification are due to Winton and Voorhees.²⁶ The modifications of the kjeldahl method, for similar purposes, furnished the material details for the gunning modified process. Winton reports good results from digesting for two hours from half a gram to a gram of the sample with 30 cubic centimeters of sulfuric containing two grams of salicylic acid, in a flask of half a liter capacity. Two grams of zinc dust are then slowly added, with constant shaking, and the flask heated, at first gently, until, after boiling a few minutes, dense fumes are no longer emitted. Three grams of potassium sulfate are next added and the boiling continued until the solution is colorless, or, if iron be present, until a light straw color is produced. On cooling, when the mixture begins to solidify, water is added with caution, and afterwards sodium hydroxid, and the ammonia is obtained by distillation.

In the process, as conducted by Voorhees, about one gram of

²⁵ Neuberger, Beiträge zur chemischen Physiologie und Pathologie, 1902, 2 : 214.

²⁶ Connecticut Agricultural Experiment Station, Bulletin 112, 1892 : 3. Division of Chemistry, Bulletin 35, 1892 : 86.

the sample is digested with 10 grams of potassium sulfate and 30 cubic centimeters of sulfuric containing one gram of salicylic acid, and three grams of zinc sulfid. The heat is kept down until frothing ceases, and then the mass kept in gentle ebullition until clear. The distillation is accomplished with the usual precautions. The voorhees process is superior to that recommended by Winton in adding the potassium sulfate at the beginning of the combustion.

332. Official Gunning Method Modified to Include the Nitrogen of Nitrates.²⁷—In a digestion flask holding from 250 to 500 cubic centimeters place from 0.7 to 3.5 grams of the substance to be analyzed, according to the amount of nitrogen present. Add from 30 to 35 cubic centimeters of salicylic acid mixture; namely, 30 cubic centimeters of sulfuric to one gram of salicylic acid, shake until thoroughly mixed, and allow to stand from five to 10 minutes, with frequent shaking; then add five grams of sodium thiosulfate and 10 grams of potassium sulfate. (It is suggested that after adding the sodium thiosulfate, the solution be heated for five minutes, cooled and the potassium sulfate added. This variation prevents foaming). Heat very gently until frothing ceases, then strongly until nearly colorless. Dilute, neutralize, and distil as in the gunning method.

DETERMINATION OF NITROGEN IN DEFINITE FORMS OF COMBINATION

333. Introductory Considerations.—In the foregoing pages has been given a summary of the methods most in vogue for the estimation of nitrogen in fertilizers and fertilizing materials. There are many cases in which the analyst may have to deal with a definite chemical compound, and where a modified or shorter method may be used. There are other cases in which the nitrogen may be present in two or three definite forms, as in artificially mixed fertilizers, and where it is desirable to show the proportions in which the various forms are present. For these reasons it is necessary to be able to use methods by which the percentage of nitrogen in its various forms may be relatively,

²⁷ Bureau of Chemistry, Bulletin 107, 1907 : 8.

as well as absolutely, determined. Such a case would be presented for instance, in that of a fertilizer containing dried blood, sodium nitrate, and ammonium sulfate. It is evident here that the total nitrogen could be determined by the volumetric method by combustion with copper oxid, or by the moist combustion process adapted to nitric nitrogen, but the method of determining the percentage of each constituent has not yet been described.

We have to deal here with a case entirely similar to that of phosphoric acid in a superphosphate. There is no doubt whatever of the uneven assimilability of the different forms of nitrogen. A nitrate, for instance, is already in condition for assimilation by plants. An ammoniacal salt is only partly changed to a state suited to plant nutrition, while organic nitrogen is forced to undergo a complete transformation before it becomes available to supply the needs of the growing plant. It is important, therefore, equally to the analyst, the merchant and the agronomist, to know definitely the forms of combination in which the nitrogen exists and the relative proportion of the different combinations.

334. Nitrogen as Ammonia.—The most frequent form in which nitrogen as ammonia is used for fertilizing is as sulfate. The method of determination to be described is, however, equally applicable to all ammonia salts. When no other form of nitrogenous compound is present the ammonia can be easily and directly determined by distillation with soda- or potash-lye, as described in the final part of the moist combustion process.

335. Determination of Ammonia.—To one gram of the ammonia salt add from 200 to 300 cubic centimeters of water and 30 grams of the soda-lye used in the moist combustion process; distil, collect the ammonia, and titrate the excess of sulfuric acid exactly as there described.

Fresenius recommends that the ammonia expelled by distillation be taken up by a standard solution of sulfuric (hydrochloric, oxalic) acid, the excess of which is titrated with a standard solution of soda or other alkali, using litmus as an indicator.²⁸ If the distillate, on examination, be found to contain thiocyanate, soda-

²⁸ *Chemical Quantitative Analysis, Cohn's Translation, from the Revised 6th German Edition, 1904, 1 : 254.*

lye can not be used for the expulsion of ammonia, but in its place caustic magnesia is applied.

In all cases where organic matter containing nitrogen is present, caustic magnesia must be substituted for the soda solution. The magnesia must be added in sufficient excess and the distillation continued a little longer than is necessary when soda-lye is used. Otherwise the details of the operation are the same.

In a mixed fertilizer containing organic nitrogen and ammonia salts, the total nitrogen can be determined by the moist combustion process, and the ammoniacal nitrogen by distillation with magnesia. The difference between the two results will give the nitrogen due to the organic matter.

To avoid any danger whatever of decomposing organic nitrogenous compounds, the ammonia may be determined in the cold by treatment with soda-lye, under a bell-jar containing some set sulfuric acid. The operation must be allowed to continue for many days. Even at the end of a long time it will be found that some ammonia is still escaping. It may, therefore, be finally inferred that all the nitrogen as ammonia is not obtained by this process, or that even magnesia may gradually convert other nitrogenous compounds into ammonia. In this connection the methods of determining ammonia in soils in paragraphs 450, 451 and 452, Volume I, may be consulted.

336. Method of Boussingault.—The official French method is essentially the original method of Boussingault with slight modifications. It is conducted as follows:²⁹ In case the sample is ammonium sulfate, about half a gram is placed in a flask of half a liter capacity, together with 300 cubic centimeters of distilled water and two grams of caustic magnesia. The flask is connected with a condenser of glass or metal which ends in a tube drawn out to a point and dipping beneath the set acid in the receiver in the usual way. The acid is colored with litmus or lacmoid tincture. The distillation is continued until about 100 cubic centimeters have gone over. The receiver is then removed with the usual precautions and the residual acid titrated. Suppose 20 cubic centimeters of normal acid have been employed

²⁹ Guide pour le Dosage de l'Azote : 14.

and $12\frac{1}{2}$ cubic centimeters of normal alkali be necessary to neutralize the excess of the acid. Then the nitrogen is found by the following equations: $20.0 - 12.5 = 7.5$ and $7.5 \times 0.014 = 0.105$ gram = weight of nitrogen found. Then $0.105 \times 100 \div 0.5 = 21$ = per cent. of nitrogen found.

The distilling apparatus of Aubin is preferred by the French chemists, an apparatus so arranged with a reflux partial condenser that nearly all the aqueous vapor is returned in a condensed state to the flask, while the ammonia, on account of its great volatility, is carried over into the receiver. To avoid the regurgitation which might be caused by the concentrated ammonia gas coming in contact with the acid, the separable part of the condensing tube is expanded into a bulb large enough to hold all the acid which lies above its mouth. By means of this apparatus the ammonia is all collected in the standard acid without greatly increasing its volume and the titration is thus rendered sharper. The employment of caustic magnesia has the advantage of not decomposing any organic matters or cyanids that may be present.

If the sample under examination hold part of its ammonia as ammonium magnesium phosphate, it will be necessary first to treat it with sulfuric acid in order to set the ammonia free, and then to use enough of the magnesium oxid to neutralize the excess of the sulfuric acid and still supply the two grams necessary for the distillation. When the sample contains a considerable quantity of organic matter it sometimes tends to become frothy towards the end of the distillation. This trouble can be avoided by introducing into the flask one or two grams of paraffin.

Where carbon dioxid is given off during the distillation, the contents of the receiver must be boiled before titration, or else lacmoid must be used as an indicator instead of litmus.

337. Determination of Thiocyanates in Ammoniacal Fertilizers.—The extended use of ammonium sulfate as a fertilizer renders it important to determine the actual constituents which may be present in samples of this material. The following bodies have been found in commercial ammonium sulfates: Sulfuric acid, chlorin, ammonia, thiocyanic acid, potash, soda, lime and

iron oxid. These are found in the soluble portions. In the insoluble portions have been found silica, sulfates, lime, magnesia and iron oxid. A sample of commercial ammonium sulfate analyzed by Jumeau contained the following substances:³⁰

	Per Cent.
Moisture	10.5109
Ammonium sulfate.....	67.8453
Ammonium thiocyanate.....	9.3935
Sodium sulfate.....	9.2429
Potassium sulfate.....	0.9774
Calcium sulfate.....	0.6800
Iron thiocyanate.....	0.5000
Magnesium chlorid	traces
Silica	0.0830
Undetermined	0.7670

The determination of the thiocyanic acid in the thiocyanate is generally made by the oxidation of the sulfur to sulfuric acid and its subsequent weighing in the form of barium sulfate. Jumeau has modified the method by determining the amount of the thiocyanate by means of a titrated liquid. The method is practiced as follows:

A solution of ammonium thiocyanate is prepared, containing eight grams of this salt per liter, and its exact content of thiocyanate is rigorously determined by titration with silver nitrate or by the weight of the barium sulfate produced after the oxidation of the sulfur. Ten cubic centimeters of the titrated liquor are diluted with water to about 100 cubic centimeters and 10 cubic centimeters of pure sulfuric acid added. Afterward, drop by drop, a solution of potassium permanganate is added, containing about 10 grams of that salt per liter. The permanganate is instantly decolorized. There is an evolution of hydrocyanic acid as the thiocyanate passes to the state of sulfuric acid. A single drop in excess gives to the mixture the well-known rose coloration of the permanganate solution which persists for several hours. The number of cubic centimeters necessary to produce the persistent rose tint is noted and the same operation is carried on with from one-half to one gram of the unknown product which is to be assayed. A simple proportion indicates the

³⁰ Revue de Chimie analytique appliquée, 1893, 1 : 51.

content of the thiocyanate in the unknown body. The process is of great exactitude and permits the rapid determination of thiocyanic acid in the presence of chlorids, cyanids, etc., which remain without action upon the permanganate. In case chlorids and cyanids are absent the thiocyanate can be determined directly by silver nitrate either by weighing the precipitate or by the process of Volhardt, based upon the precipitation of the silver by thiocyanate in the presence of a ferric salt. The end of the reaction is indicated by the red coloration which the liquid shows when the thiocyanate is in excess.

338. Separation of Proteid from Amid and Other Forms of Nitrogen in Organic Fertilizers.—It may be of interest to the dealer, farmer, and analyst to discriminate between the proteid and other nitrogen in fertilizers, such as oil-cakes, etc. The final value of the nitrogen for plant nourishment is not greatly different, but the immediate availability for the use of plants is a matter of some importance. The most convenient process in such a case is the copper hydroxid separation process as improved by Stutzer.³¹ The process is conveniently carried out in accordance with the method prescribed by the official chemists.³²

Total Crude Protein.—Determine nitrogen as directed for nitrogen in fertilizers and multiply the result by 6.25 for the crude protein.

Determination of Albuminoid Nitrogen.—To 0.7 gram of the substance in a beaker add 100 cubic centimeters of water, heat to boiling, or, in the case of substances rich in starch, heat on the water bath 10 minutes, and add a quantity of cupric hydroxid mixture containing one-half gram of the hydroxid; stir thoroughly, filter when cold, wash with cold water, and put the filter and its contents into the flask containing the concentrated sulfuric acid for the determination of nitrogen. The filter papers used must be practically free of nitrogen. Add sufficient potassium sulfid solution to completely precipitate all copper and mercury, and proceed as in the moist combustion process for nitrogen. If

³¹ Journal für Landwirtschaft, 1880, 28 : 103.

Chemiker-Zeitung, 1880, 4 : 360.

³² Bureau of Chemistry, Bulletin 107, 1907 : 38.

the substance examined consists of seed of any kind, or residues of seeds, such as oil-cake or anything else rich in alkaline phosphates, add a few cubic centimeters of a concentrated solution of alum free from ammonia just before adding the cupric hydroxid, and mix well by stirring. This serves to decompose the alkaline phosphates. If this be not done, cupric phosphate and free alkali may be formed, and the protein-copper precipitate may be partially dissolved in the alkaline liquid.

Cupric Hydroxid.—Prepare the cupric hydroxid as follows: Dissolve 100 grams of pure cupric sulfate in five liters of water, and add 2.5 cubic centimeters of glycerol; add a dilute solution of sodium hydroxid until the liquid is alkaline; filter, rub the precipitate up with water containing five cubic centimeters of glycerol per liter, and wash by decantation or filtration until the washings are no longer alkaline. Rub the precipitate up again in a mortar with water containing 10 per cent. of glycerol, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per cubic centimeter of this mixture.

Amid Nitrogen.—The albuminoid nitrogen determined as above subtracted from the total gives that part of the organic nitrogen existing in the sample as amids and in other allied forms.

339. Separation of Nitric and Ammoniacal from Organic Nitrogen.—The nitrogen being present in three forms, viz., organic, ammoniacal and nitric, the separation of the latter two may be accomplished by the following procedure:³³ One gram of the fertilizer is exhausted on a small filter with a two per cent. solution of tannin, using from 30 to 40 cubic centimeters in small portions. This is sufficient to dissolve all the nitrates and the greater portion of the ammoniacal salts, while the tannin renders insoluble all the organic nitrogenous compounds. The filter and its contents are treated for nitrogen by the kjeldahl process. When the distillation and titration are completed the solution obtained by the aqueous tannin is added to the distilling flask and the operation continued. This represents the ammoniacal nitrogen.

³³ Aubin et Quenot, Bulletin de la Société chimique de Paris, 1890, [3], 8 : 324.

The nitric acid is estimated by the ferrous iron or other appropriate method, to be described further on, in another portion of the substance.

340. Method of French Commission for Determining Nitrogen.—Several methods are proposed by this commission for the determination of nitrogen.³⁴ The old method of combustion with soda-lime which is conducted according to the general principles is described in full. When the nitrogen is to be determined in substances which are not homogeneous and which it is difficult to reduce to a powdered state, a modification of the process, due to Grandeau, is employed. Such substances are, for instance, pieces of cloth, leather, wool, horns and hair. It is almost impossible to obtain a homogeneous mixture of such bodies. Large quantities of them are, therefore, according to this method, treated with sulfuric acid and then heated until the decomposition is complete and they are easily reduced to a homogeneous mass. This is best secured by adding some finely powdered gypsum. When the decomposition is completed and a homogeneous mass is secured, the rest of the process is conducted by the usual methods.

The French commission also recommends the common method already described for the determination of nitrogen in an organic state by the process of Kjeldahl, and of nitrogen in the nitric state and of sulfate of ammonium by the methods usually employed.

341. Method of Determining Nitrogen Adopted by the Union of German Fertilizer Manufacturers.—*Nitric Nitrogen.*—The nitrogen in the form of nitrates is determined by the method of Ulsch and Devarda.³⁵

Ammoniacal Nitrogen.—This is determined in the usual way by titration with an alkali. Freshly burned magnesia hydrate is employed as an alkaline reagent, although lime may also be used where little or no organic matter is present, and the ammonia is mostly in the form of ammoniacal salt. Soda-lye should

³⁴ Grandeau, *Traité d'Analyse des Matières agricoles*, 3d Edition, 1897, 1 ; 427.

³⁵ *Methoden zur Untersuchung der Kunstdüngemittel*, 1903 : 15.

only be used when it is certain that no organic nitrogen is present. The ammonia is collected in set sulfuric acid, and, as an indicator, it is recommended to use paranitro-phenol solution in the proportion of one to 10 of alcohol. Tincture of cochineal or congo red in water is also permitted.

Organic Nitrogen.—The method of Kjeldahl, with its modern modification for the inclusion of nitric nitrogen, is recommended.

342. Estimation of Perchlorate in Chile Saltpeter.—Attention is called to the occasional occurrence in Chile saltpeter of potassium perchlorate. The method employed depends upon the determination of the chlorin content of the material under investigation both before and after the decomposition of the perchlorate. The conversion of perchlorate of potassium is secured by simple ignition or by ignition after the addition of different reagents, as, for instance, metallic lead, caustic lime, sodium carbonate, magnesium oxid, etc. The following method is recommended as satisfactory and easily carried out.³⁶

In this method five grams of Chile saltpeter, in which the amount of chlorin has been determined, is placed in a porcelain crucible of about 40 to 50 cubic centimeters capacity with from 15 to 20 grams of lead borings and submitted to a gradually increased heat. When the salt and the lead are melted, the mass is vigorously stirred with a copper wire with a regulation of the heat so as not to secure a too rapid evaporation of the mass. When the mass begins to thicken and only a few bubbles of gas are escaping, the heat is raised to a dark red on the bottom of the crucible and held at this temperature for one or two minutes. After cooling, the melt, which now contains nitrate and chlorate, is softened with hot water and washed into a beaker. Three or four grams of carbonate of soda are added and the mixture gradually warmed. After filtration nitric acid is added to the filtrate to acidity, and the chlorin estimated in the usual way with the nitrate of silver.

From the amount of chlorin obtained, that which was originally present is subtracted and the difference is the chlorin due to

³⁶ Selckmann, *Zeitschrift für angewandte Chemie*, 1898, 11 : 101.

perchlorate. One equivalent of silver nitrate corresponds to one equivalent of potassium perchlorate.

343. Method of Blattner-Brasseur.³⁷—In this method five grams of saltpeter, which has been freed from moisture by heating to 150°, are treated with from seven to eight grams of pure chlorine-free calcium hydrate in a porcelain or platinum crucible of about 25 to 30 cubic centimeters capacity and the covered crucible heated for 15 minutes over a bunsen. The ignited mass is dissolved and neutralized with nitric acid and the chlorine titrated with nitrate of silver or estimated by the gravimetric method as above described.

THE NITRIC ACID PROCESS

344. Occurrence of Highly Oxidized Nitrogen.—The nitrogen of fertilizers, soil waters, etc., often exists in a highly oxidized state as nitrous or nitric acid or compounds thereof. The following paragraphs are devoted to the description of methods employed for estimating nitrogen in these states of combination and the principles on which they are based. The processes for estimating nitrogen by combustion with copper oxid and by moist combustion with sulfuric acid have both been used for the determination of the quantity of nitrogen existing in a highly oxidized state. These processes have been fully discussed under their proper heads. In the case of soil extracts, drainage waters, etc., it will be sufficient to discuss, for the present, only those processes adapted especially to a quick and accurate estimation of oxidized nitrogen when occurring in relatively small quantities.

345. Method of Schloesing.—The principle of the method of Schloesing depends on the decomposition of nitrates in the presence of a ferrous salt and a strong mineral acid.³⁸ The nitrogen in the process appears as nitric oxid, the volume of which may be directly measured, or it may be converted into nitric acid and titrated by an alkali.

³⁷ Chemiker-Zeitung, 1900, **24** : 767.

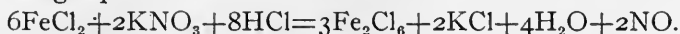
³⁸ Annales de Chimie et de Physique, 1854, [3], **40** : 479.

Zeitschrift für analytische Chemie, 1870, **9** : 24.

Die landwirtschaftlichen Versuchs-Stationen, 1869, **12** : 164.

Journal of the Chemical Society, 1880, **37** : 468; 1882, **41** : 345; 1889,

The typical reactions which take place are represented in the following equation:



346. Schloesing's Modified Method.—The schloesing method as now practiced by the French chemists is conducted in the apparatus shown in Fig. 20.³⁹ The carbon dioxide is generated by the action of the hydrochloric acid in F on the fragments of marble in A. After passing the wash-bottle, the gas enters the small tubulated retort, C, which contains the nitrate in solution. When the quantity of nitrate is small, as in ordinary soils, 100 grams are placed in an extraction flask, plugged with cotton, and

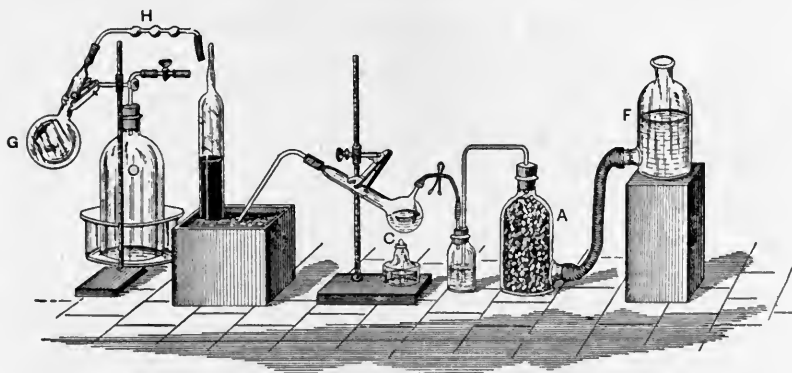


Fig. 20. Schloesing's Apparatus for Nitric Acid.

a layer of the same material is placed over the soil for the purpose of securing an even distribution of the extracting liquid. This liquid is distilled water containing in each liter one gram of calcium chlorid. The purpose of using the calcium chlorid is to prevent the soil from becoming compacted, which would render the extraction of the nitrate difficult. The extracting liquid is allowed to fall, drop by drop, from a mariotte bottle until the filtrate amounts to 500 cubic centimeters. This volume is concentrated on a sand-bath until it is reduced to 10 or 15 cubic centimeters, when it is transferred to a flat-bottomed dish and the evaporation finished over steam, care being taken not to allow the temperature to exceed 100°.

³⁹ *Encyclopédie chimique*, 1888, 4 : 151.

Another and more rapid method for dissolving the nitrate may also be practiced. In a flask holding about one liter, place 220 grams of the soil and 660 cubic centimeters of distilled water and shake vigorously, or enough water to make 660 cubic centimeters together with the moisture remaining in the air-dried sample taken. All the nitrates pass into solution. Throw the contents of the flask into a filter and use 600 cubic centimeters of the filtrate, which will contain all the nitrates in 200 grams of the sample taken. This filtrate is evaporated as described above.

In the flat dish containing the dried nitrates pour three or four cubic centimeters of ferrous chlorid solution and stir with a small glass rod until complete solution of the nitrates takes place. By means of a small funnel the solution is poured into C, and the capsule and funnel are well rinsed with two cubic centimeters of hydrochloric acid. The washing is repeated three times, as above described, and once with one cubic centimeter of water, which is added cautiously so as to form a layer over the surface of the heavier liquid. The tubulated flask is then connected with the carbon dioxid apparatus, previously freed from air, and the gas allowed to flow evenly until the whole of the interior of the apparatus is completely air-free. The other details of the method are essentially the same as those adopted by the Commission of French Agricultural Chemists, which will be given below.

347. The French Agricultural Method.—The Schloesing method, as practiced by the French agricultural chemists, is very slightly different from the procedure just described.⁴⁰ The process with soils and fertilizers poor in nitrogen is carried on as follows:

Five hundred grams of the sample are introduced into a flask of about two liters capacity and shaken thoroughly with a liter of distilled water. The whole of the nitrates of the soil is thus brought into solution. The solution is filtered and 400 cubic centimeters of the filtrate are used, which correspond to 200 grams of the soil. This liquid is evaporated in a flask, adding a fragment of paraffin to prevent foaming, until its volume is reduced to 15 or 20 cubic centimeters. It is afterwards transferred through

⁴⁰ *Annales de la Science agronomique*, 1891, 1 : 263.

a filter into a capsule with a flat bottom, in which the evaporation is finished on a steam-bath, taking care that the temperature does not exceed 100°. An important precaution is not to allow the contact of the water with the soil to be too prolonged, to avoid the reduction of the nitrates which could take place under the influence of the denitrifying organisms which are developed with so great a rapidity in moist earth. The apparatus in which the transformation of the nitrates into nitric oxid takes place is essentially that already described (Fig. 20). The carbon dioxid generator is connected by means of a rubber tube and a small wash-bottle to the small retort in which the reaction takes place, and from which the exit tube leads to a mercury trough. The gas which is disengaged is received under a jar drawn out to a fine point in its upper part, which carries about 15 cubic centimeters of potash solution containing two parts of water to one of potash.

The operation is conducted as follows:

Into the small capsule which contains the dried matter, three or four cubic centimeters of ferrous chlorid are poured. By means of a stirring rod the residue sticking to the sides of the capsule is detached with care, and all the matter is thus collected in the bottom. By means of a small funnel the contents of the capsule are introduced into the retort. About two cubic centimeters of hydrochloric acid are used for washing out the materials, and this acid is also introduced into the retort. The washing with hydrochloric acid is repeated three or four times, and finally the apparatus is washed with one cubic centimeter of water, which is also poured in by the small funnel with great care, so that this water may form a layer over the surface of the liquid. The apparatus is now connected and filled completely with carbon dioxid. Since it is necessary that this gas should be completely free of air, the flask which generates it is first filled with the acidulated water from the acid flask, and the air is thus almost totally displaced by the liquid. The evolution of carbon dioxid gas which follows, completely frees the apparatus from air. When this is accomplished the retort is connected with the rest of the apparatus and the gas allowed to pass for

about two minutes until the air is completely driven out of all the connections. The current is arrested for a moment by pinching the rubber tube which conducts the carbon dioxide into the retort, and the vessel which is to receive the gas is then placed over the delivery tube, this vessel being filled with mercury and a strong solution of potash. The communication between the retort and the carbon dioxide flask is broken and the flask is heated slightly by means of a small lamp. The first bubbles of gas evolved should be entirely absorbed by the potash. This will be an indication of the complete absence of the air. When the liquid is in a state of ebullition the nitrogen dioxide is set free. The boiling is regulated in such a way that the evolution is regular and the liquid of the retort may not, by a too violent boiling, pass into the receiver. The boiling is continued until the larger part of the liquid is distilled and only three or four cubic centimeters remain in the retort. At this time a few bubbles of carbon dioxide are allowed to flow through in order to cause to pass into the receiver the last traces of nitric oxide. The gas received is left for some minutes in contact with the potash.

Afterward, in a small flask, G, the neck of which is drawn out to a fine point, and carrying a bulb-tube, H, and a piece of rubber tubing, there are boiled 25 or 30 cubic centimeters of water for five or six minutes in order to drive all the air out of the flask, and while the boiling is continued the rubber tubing is fastened to the drawn-out part of the jar containing the nitric oxide. Within the rubber tubing the drawn-out point is broken and the vapor of water is forced into the jar and drives before it the solution of potash which has filled the capillary part of the drawn-out tube. As soon as the point is broken, the boiling of the flask is stopped and by its cooling the nitric oxide passes into it. It is necessary to press the rubber tubing with the fingers in order that the passage of the gas into the flask be not too rapid. As the solution of potash rises in the bell-jar which contains the nitric oxide near to the point where the rubber tubing covers its drawn-out portion, the fingers are removed and a clamp put in their place. There still remains a little nitric oxide in the flask, and to drive this out it is necessary to introduce five or six cubic

centimeters of pure hydrogen, which are allowed to pass over into the receiving flask by releasing the clamp in the same way as for the nitric oxid. The hydrogen being introduced in successive portions, finally carries all the nitric oxid into the flask without allowing any of the potash to enter.

The flask containing the nitric oxid is now connected with a reservoir of oxygen. The oxygen is allowed to enter, bubble by bubble, meanwhile cooling the flask by immersion in water. The transformation of nitric oxid into nitric acid is not entirely complete until after 24 hours. It is necessary, therefore, to wait so long after the introduction of the oxygen before determining the amount of nitric acid produced.

The contents of the flask are placed in a titration-jar, the flask being washed two or three times and a few drops of tincture of litmus being added. The nitric acid is then determined by a standard solution of calcium hydroxid or some other standard alkali. From the titration the content of nitric acid is calculated.

The French committee further suggests that this method may be modified in the way of making it more rapid by collecting the nitric acid in a graduated tube filled with mercury and containing some potash. The volume of the gas is determined and the pressure of the barometer together with the temperature are observed; then the usual calculations are made to reduce the volume to zero and to a pressure of 760 millimeters of mercury. Each cubic centimeter of nitric oxid thus measured corresponds to 2.417 milligrams of nitric acid. The presence of organic matter does not interfere with the determination of nitric acid by either of the methods given above.

348. Method of the French Sugar Chemists.—The nitrogen in Chile saltpeter is estimated by the French chemists according to the method of Schloesing. In order to avoid the trouble of calculating the results from the volume of nitric oxid obtained, a determination is first made with a pure salt, sodium or potassium nitrate. The volume of gas obtained is read directly without correction and used for direct comparison, which is made as follows:

The solutions of the pure salts and of the sample to be analyzed are made of such a strength as to contain 66 grams of sodium nitrate, or 80 grams of potassium nitrate, in a liter. Five cubic centimeters of such a solution will yield a little less than 100 cubic centimeters of nitric oxid under usual conditions. Let the volume of gas obtained with the pure salt be v , and that with the sample be v' . The calculation is then made from the equation : $\frac{v'}{v} = \frac{x}{100}$.

Example.—Let 95 cubic centimeters be the volume of gas from five cubic centimeters of the pure salt (sodium nitrate), and 91.5 cubic centimeters be the volume of gas from five cubic centimeters of the sample; then $\frac{91.5}{95} = \frac{x}{100}$, whence $x = 96.31$.

Hence the sample analyzed contains 96.31 per cent. of sodium nitrate. Since the pure sodium nitrate contains 16.47 per cent. of nitrogen, the sample under examination would contain $\frac{16.47 \times 96.31}{100} = 15.86$ per cent.

It is evident that this comparative method is quite easy of application when the sample under examination has no other nitrate in it except that combined with the one base.

349. Method of Schloesing-Wagner.—The schloesing-wagner method for estimating nitrogen in the nitrates of fertilizers is carried out at the Halle experiment station as follows:⁴¹

A flask, Fig. 21, of about 250 cubic centimeters capacity, is provided with a rubber stopper with two holes. Through one of them is passed the stem of a funnel carrying a glass stop-cock. The other carries a delivery tube leading to the receiving vessel. The end of the delivery tube is bent so as to pass easily under the mouth of the measuring burette and is covered with a piece of rubber tubing.

Fifty cubic centimeters of saturated ferrous chlorid solution and the same quantity of 10 per cent. hydrochloric acid are placed in the flask. The ferrous chlorid solution is obtained

⁴¹ Bieler and Schneidewind, Die agricultur-chemische Versuchsstation, Halle a/S, 1892 : 51.

by dissolving nails or other small pieces of iron in hot hydrochloric acid and it is kept in glass stoppered flasks, of about 50 cubic centimeters capacity, entirely filled. The content of one flask is enough for about 12 determinations and by using the whole content of a flask as soon as possible after opening, any danger of oxidation, which would take place in a large flask frequently opened, is avoided.

The contents of the flask are boiled until all the air is driven off. The delivery tube is then placed under the measuring tube, which is filled with 40 per cent. potash-lye. The measuring tube is previously almost filled with potash-lye and then a

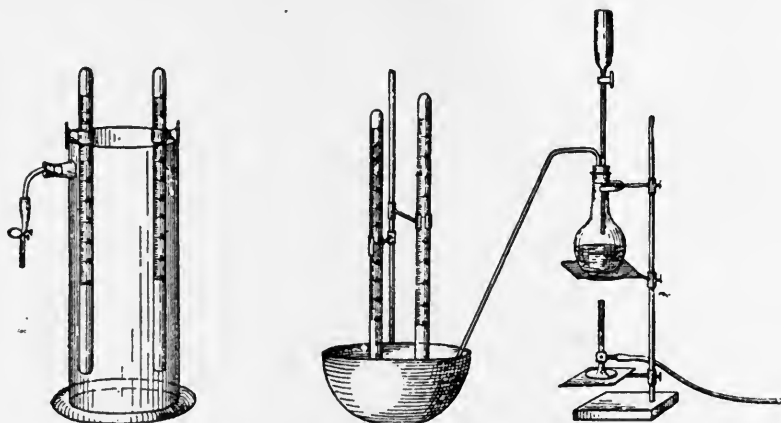


Fig. 21. Schloesing-Wagner Apparatus.

few drops of water added and the tube covered with a piece of filter paper. By a careful and quick inversion the measuring tube can be brought into the vessel receiving it without any danger of air entering. The boiling is continued for some time and when no more air escapes, the end of the delivery tube is brought into another freshly filled measuring tube and the estimation is commenced.

Ten cubic centimeters of a normal saltpeter solution, containing two and a half grams of pure sodium nitrate in 100 cubic centimeters are placed in the funnel and, with continued boiling, allowed to pass, drop by drop, into the flask. When almost all has run out the funnel is washed three times with 10 cubic cen-

timeters of 10 per cent. hydrochloric acid and this is allowed to pass, drop by drop, into the flask. When no more nitric oxid is evolved the measuring tube is transferred to a large jar filled with distilled water.

The solution of the substance to be examined should be used in such quantity as will give about the same quantity of gas as is furnished by the 10 cubic centimeters test nitrate solution before described; viz., about 70 cubic centimeters. Eight or 10 determinations can be made, one following the other, and finally another determination with normal sodium nitrate solution should be made as a check. At the end of the opera-

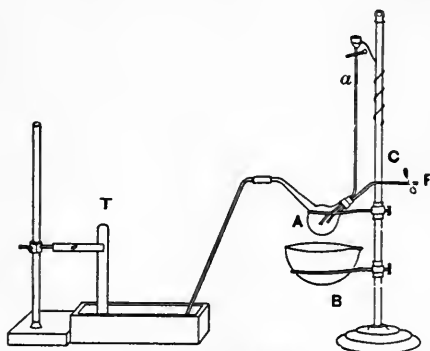


Fig. 22. Warington's Apparatus for Nitric Acid.

tion of all the measuring tubes are in the large jar filled with distilled water. The temperature of the surrounding water will soon be imparted to the contents of each tube and the volume of nitric oxid is read by bringing the level within and without the measuring-tube to the same point. The percentages are calculated for the given temperature and barometer pressure in the usual way; or to avoid computation, the volume can be compared directly with the volume furnished by the normal nitrate solution, which is a much simpler method.

350. Modification of Warington.—The method of procedure and description of apparatus used, as employed by Warington, are as follows:

The vessel in which the reaction takes place is a small tubulated receiver, A (Fig. 22), about four centimeters in diame-

ter, mounted and connected as shown in the illustration. The delivery tube dips into a jar of mercury in a trough containing the same liquid. The long supply funnel-tube *a* is of small bore, holding in all only one-half cubic centimeter. The connecting tube, F, carrying a clamp, is also of small diameter and serves to connect the apparatus with a supply of carbon dioxide.

In practice, the supply tube *a* is first filled with strong hydrochloric acid and carbon dioxide passed through the apparatus until the air is all expelled. This is indicated when a portion of the gas collected over the mercury, is entirely absorbed by caustic alkali.

At this point the current of carbon dioxide is stopped by the clamp C, and a bath of calcium chloride, B, heated to 140° is brought under the bulb A, until the latter is half immersed therein. The temperature of the bath is maintained by a lamp. By allowing a few drops of hydrochloric acid to enter the receiver, the carbon dioxide is almost wholly expelled. The end of the delivery tube is then connected with the tube, T, filled with mercury, and the apparatus is ready for use.

The nitrate, in which the nitric acid is to be determined, in a dry state, is dissolved in two cubic centimeters of the ferrous chloride solution (one gram of iron in 10 cubic centimeters), one cubic centimeter of strong hydrochloric acid is added, and the whole is then introduced into the receiver through the supply-tube, being followed by successive rinsings with hydrochloric acid, each rinsing not exceeding one-half cubic centimeter. The contents of the receiver are, in a few moments, boiled to dryness; a little carbon dioxide is admitted before dryness is reached, and again afterwards to drive over all remains of nitric oxide. In the recovered gas the carbon dioxide is first absorbed by caustic potash, and afterwards the nitric oxide by ferrous chloride. All measurements of the gas are made in Frankland's modification of Regnault's apparatus. The carbon dioxide should be as free as possible from oxygen. The carbon dioxide generator is formed of two vessels, the lower one consisting of a bottle with a tube in the side near the bottom; this bottle is supported in an inverted position and contains the marble from which the gas is generated.

The upper vessel consists of a similar bottle standing upright and containing the hydrochloric acid required to act on the marble. The two vessels are connected by a glass tube passing from the side tubule of the upper vessel to the inverted mouth of the lower vessel. The acid from the upper vessel thus enters below the marble. Carbon dioxid is generated and removed at pleasure by opening a stop-cock attached to the side tubule of the lower vessel thus allowing hydrochloric acid to descend and come in contact with the marble. A good Kipp's generator of any approved form may also be used instead of the simple apparatus above described.

The fragments of marble used are previously boiled in water in a strong flask. After boiling has proceeded for some time, a rubber stopper is fixed in the neck of the flask and the flame removed. Boiling will then continue for some time in a partial vacuum.

The hydrochloric acid is also well boiled and has dissolved in it a moderate quantity of cuprous chlorid. As soon as the acid has been placed in the upper reservoir, it is covered by a layer of oil. The apparatus being thus charged is at once set in active work by opening the stop-cock of the marble reservoir; the acid descends, enters the marble reservoir, and the carbon dioxid produced drives out the air. As the acid reservoir is kept on a higher level than the marble reservoir, the latter is always under internal pressure, and leakage of air from without, into the apparatus, can not occur.

The presence of the cuprous chlorid in the hydrochloric acid not only insures the removal of dissolved oxygen, but affords an indication to the eye of the maintenance of this condition. While the acid remains of an olive tint, oxygen is absent; but should the color change to a blue-green, more cuprous chlorid must be added. All the reagents employed should be previously boiled.

In order to secure absolute freedom from air, the following modifications on the above process have been adopted by Warington. The apparatus having been mounted as described, the funnel-tube attached to the bulb retort is filled with water, and the apparatus connected with the carbon dioxid generator. Car-

bon dioxid is then passed through the apparatus until a moderate stream of bubbles rise in the mercury trough. The stop-cock is left in this position, and the admission of gas is controlled by the pinch-cock. The bath of calcium chlorid is so adjusted as to cause the bulb retort to be almost entirely submerged, and the temperature of the bath is kept at 130° to 140°. Small quantities of water are next admitted into the bulb and expelled as steam in the current of carbon dioxid, the supply of this gas being shut off before the evaporation is entirely completed, so as to leave as little carbon dioxid as possible in the apparatus. Previous to very delicate experiments it is advisable to introduce through the funnel-tube a small quantity of potassium nitrate, ferrous chlorid, and hydrochloric acid, rinsing the tube with the latter reagent. Any trace of oxygen remaining in the apparatus is then consumed by the nitric oxid formed; and after boiling to dryness and driving out the nitric acid with carbon dioxid, the apparatus is in a perfect condition for a quantitative experiment.

351. Preparation of the Materials to be Analyzed.—According to Warington, soil extracts may be used without other preparation than concentration.

Vegetable juices which coagulate when heated require to be boiled and filtered or else evaporated to a thin sirup, treated, with alcohol, and filtered. A clear solution being thus obtained, it is concentrated over a water bath to a minimum volume in a beaker of small size. As soon as cool, it is mixed with one cubic centimeter of a cold saturated solution of ferrous chlorid and one cubic centimeter of hydrochloric acid, both reagents having been boiled and cooled immediately before use.

In mixing with the reagents, care must be taken that bubbles of air are not entangled, which is apt to occur with viscid extracts.

The quantity of ferrous chlorid mentioned is amply sufficient for most extracts, but it is well to use two cubic centimeters in the first experiment, the presence of a considerable excess of ferrous chlorid in the retort being thus insured. With bulky vegetable extracts more ferrous chlorid should be employed. To the sirup from 20 grams of mangel-wurzel sap, five cubic

centimeters of ferrous chlorid and two cubic centimeters of hydrochloric acid are usually added.

352. Measurement of the Gas.—The measurement of the gas was for some time conducted by the use of concentrated potash for absorbing the carbon dioxid, and ferrous chlorid for absorbing the nitric oxid. The use of the ferrous chlorid, however, was found to introduce a source of error. The treatment of the gas with oxygen and pyrogallol over potash has, therefore, been substituted by Warington for absorption by ferrous chlorid.

The chief source of error attending the oxygen process lies in the small quantity of carbon monoxid produced during the absorption with pyrogallol, but this error becomes negligible if the oxygen be only used in small excess. The amount of oxygen employed can be regulated by the use of Bischof's gas delivery tube. This may be made of a test-tube having a small perforation half an inch from the mouth. The tube is partly filled with oxygen over mercury, and its mouth is then closed by a finely perforated stopper made from a piece of wide tube and fitted tightly into the test-tube by means of a covering of rubber. When this tube is inclined, the side perforation being downwards, the oxygen is discharged in small bubbles from the perforated stopper, while mercury enters through the opening. Using this tube, the supply of oxygen is perfectly under control and can be stopped as soon as a fresh bubble ceases to produce a red tinge on entering. Warington concludes his description by stating that in the reaction proposed by Schloesing the analyst has a means of determining a very small quantity of nitric acid with considerable accuracy, even in the presence of organic matter; but to accomplish this, the various simplifications consisting in the omission of the stream of carbon dioxid, and the collection of the gas over caustic soda must be abandoned, and special precautions must be taken to exclude all traces of oxygen from the apparatus.

353. Schulze-Tiemann Method.—The modification of Schulze-Tiemann in the ferrous salt method consists chiefly in the omission of the use of carbon dioxid, and in the simplified form of apparatus, which permits rapid work and gives, also, accord-

ing to some authorities, very exact and reliable results.⁴² The extract, representing 500 grams of the fine soil, is reduced by evaporation to 100 cubic centimeters and placed in a glass flask, *A* (Fig. 23), of 500 cubic centimeters capacity. The flask is closed with a rubber stopper, carrying two bent glass tubes which pass through it. The tube *a b c* is drawn out into a point at *a* and reaches about two centimeters below the surface of the rubber stopper. The tube *e f g* passes just to the lower surface of the

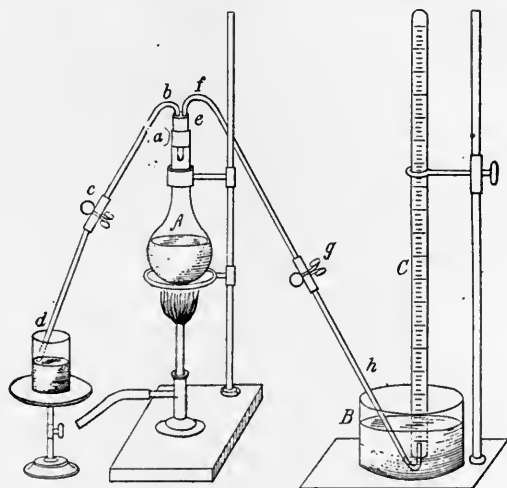


Fig. 23. Schulze-Tiemann's Nitric Acid Apparatus.

rubber stopper. The two tubes mentioned are connected, by means of rubber tubes and pinch-cocks, with the tubes *d* and *h*. The pinch-cocks at *c* and *g* must be capable of closing the tubes air-tight. The end of the tube *g h* passes into a crystallizing dish, *B*, and is bent upward to a point passing two to three centimeters into the measuring tube *C*. The point within the tube is covered with a piece of rubber tubing. The measuring tube *C* is divided into tenths of a cubic centimeter, and together with the crystallizing dish, *B*, is filled with a 10 per cent. solution of

⁴² *Zeitschrift für analytische Chemie*, 1870, 9 : 24, 401.

Die landwirtschaftlichen Versuchs-Stationen, 1867, 9 : 9.

Berichte der deutschen chemischen Gesellschaft, 1873, 6 : 1038.

boiled soda-lye, which is obtained by dissolving 12.9 parts of sodium hydroxid in 100 parts of water.

The liquid which is to be examined for nitric acid (the pinch-cocks being opened and the tube *g h* not dipping into the crystallizing dish), is boiled for one hour in order to drive the air out of the flask *A*. The end of the tube *e f g h* is then brought into the crystallizing dish containing the sodium hydroxid solution so that the steam escaping from the flask, *A*, escapes partly through the tube *b c d* and partly through the tube *f g h*, not allowing, however, the bubbles to enter the measuring tube *C*. To determine whether the air is all expelled, the pinch-cock at *g* is closed and the soda-lye will thereupon rise to *g* in case no air interferes. It is best to close the tube at *g* first with the thumb and finger, and then the rise of the soda-lye to that point can be determined by the impulse felt. The tube is then firmly closed by means of the pinch-cock *g*. The rest of the steam is allowed to escape through the tube *a b c d*, and the evaporation is continued until the contents of the flask are evaporated to about 10 cubic centimeters. The flask into which the tube *c d* dips is filled with freshly boiled water. The lamp is removed from the flask *A*, the pinch-cock is closed, whereupon the tube *c d* becomes filled with the freshly boiled water. The measuring tube, *C*, filled with freshly boiled soda-lye, is closed with the thumb and brought into the dish *B*, care being taken that no bubble of air enters. It is placed over the end of the tube *g h*.

The pressure of the external air will now flatten the rubber tubes at *c* and *g*. The flask at the end of *c d*, holding freshly boiled water, is then replaced with one filled with a nearly saturated solution of ferrous chlorid containing some hydrochloric acid. The flask containing the ferrous chlorid solution should be graduated so that the amount which is sucked into the flask *A* can be determined. The pinch-cock *c* is opened and from 15 to 20 cubic centimeters of the ferrous chlorid solution allowed to flow into *A*. The end of the tube *c d* is then placed in another flask containing strong hydrochloric acid, and the latter allowed to flow into the tube in small quantities at a time until all the ferrous chlorid is washed out of the tube *b c d* into *A*.

At the point *b* there is sometimes formed a little bubble of hydrochloric acid in the state of gas, which by heating the flask *A* completely disappears.

The flask *A* is next warmed gently until the rubber tubes at the pinch-cocks begin to assume their normal condition. The pinch-cock at *g* is now replaced by the thumb and finger, and as soon as the pressure within the flask *A* is somewhat stronger, caused by the nitric oxid gas evolved from the mixture, it is allowed to pass through the tube *efgh* and escape into the measuring cylinder *C*. By a manipulation of the finger and thumb at *g*, it is possible to prevent regurgitation of the sodium hydroxid into *A*, and at the same time to relieve the pressure of the nitric oxid in *A*, which would be difficult to do by means of the pinch-cock alone.

The boiling of the liquid is continued until there is no longer any increase of the volume of gas in the measuring cylinder *C*. After the end of the operation the tube *gh* is removed from the dish *B* and the measuring tube *C* is closed by means of the thumb while its end is still beneath the surface of the soda-lye, and it is shaken until all traces of any hydrochloric acid which may have escaped absorption are removed. It is then placed in a large glass cylinder filled with water at the temperature at which the volume of gas is to be read. After being kept at this constant temperature for about half an hour the volume of the nitric oxid can be read. For this purpose the measuring cylinder *C* is sunk into the water of the large cylinder until the level of the liquids within and without the tube is the same. The usual correction for pressure of the atmosphere, as determined by the barometer, and for the tension of the aqueous vapor at the temperature at which the reading is made, is applied. The correction is made by means of the following formula:

$$V' = \frac{V \times 273 \times (B - f)}{(273 + t) \times 760}$$

In this formula *V'* denotes the volume of the gas at the temperature of zero and at 760 millimeters barometric pressure; *V*, the volume of the gas as read at the barometric pressure observed,

B, and the temperature observed, t , while f denotes the tension of the aqueous vapor in millimeters of mercury pressure at the observed temperature, t . The tension of the aqueous vapor at temperatures from zero to 26° , expressed in millimeters of mercury, is given in the following table:

Temp. °	Tension in mm. mercury.	Temp. °	Tension in mm. mercury.	Temp. °	Tension in mm. mercury.
0	4.6	9	8.5	18	15.3
1	4.9	10	9.1	19	16.3
2	5.3	11	9.7	20	17.4
3	5.7	12	10.4	21	18.5
4	6.1	13	11.1	22	19.6
5	6.5	14	11.9	23	20.9
6	6.9	15	12.7	24	22.2
7	7.4	16	13.5	25	23.5
8	8.0	17	14.4	26	25.0

From the gas volume corrected by the above formula the nitric acid is calculated as follows:

One cubic centimeter of nitric oxid weighs at 0° and 760 millimeters barometric pressure 1.343 milligrams.

Since two molecules of NO (molecular weight 60) correspond to one molecule of N_2O_5 (108), we have the following equation: $60 : 108 = 1.343 : x$. Whence $x = 2.417$ milligrams, the weight of nitric acid (N_2O_5) corresponding to one cubic centimeter of nitric oxid.

354. Spiegel's Modification.—Spiegel noticed inaccuracies in the results of the ferrous chlorid method of estimating nitric acid when carbon dioxid is used, which sometimes amounted to three per cent. of the nitric acid present in the sample. The following suggestions are made by him for the improvement of the process:⁴³

As regards the use of carbon dioxid in the operation, the first difficulty consists in obtaining it entirely free from air. By the use of small pieces of marble, which, before being placed in the kipp apparatus are kept for a long while in boiling water, a product is obtained which, after 30 minutes of moderate evolution, leaves only a trace of unabsorbed gas in contact with potash-lye. The apparatus used is illustrated in Fig. 24.

⁴³ Berichte der deutschen chemischen Gesellschaft, 1890, 23 : 1361.

A is a round flask of about 150 cubic centimeters capacity, furnished with a well-fitting rubber stopper provided with two holes, one for the entrance of the funnel tube B and the other for the delivery tube C. The tube B ends about two centimeters above the bottom of A and carries a bulb-shaped funnel at its top capable of holding about 50 cubic centimeters. The gas tube D is ground into the bulb of B as shown in the figure.

After the flask has been filled with the solution to be ex-

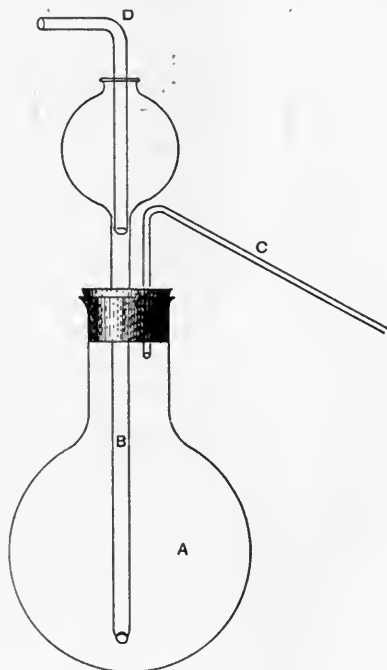


Fig. 24. Spiegel's Apparatus for Nitric Acid.

amined, carbon dioxide is conducted through D and the flask is heated to boiling until the gas which escapes through C no longer contains any air. The measuring tube is brought over the end of the delivery tube C, in the usual manner; but is not shown in the figure. In the funnel of B are placed 20 cubic centimeters of previously prepared and boiled ferrous chlorid solution and this liquid is allowed to flow partly into A by lift-

ing slightly the gas-tube D. About 40 cubic centimeters of concentrated, boiled hydrochloric acid are afterwards added to it in the same way. As soon as the liquid in the flask A is again boiling, the stream of carbon dioxide is shut off and allowed to flow again only towards the end of the operation, when the contents of the flask are reduced almost to dryness. As will be seen from the above directions, no unboiled liquids of any kind are to be used as reagents in the apparatus described. If the

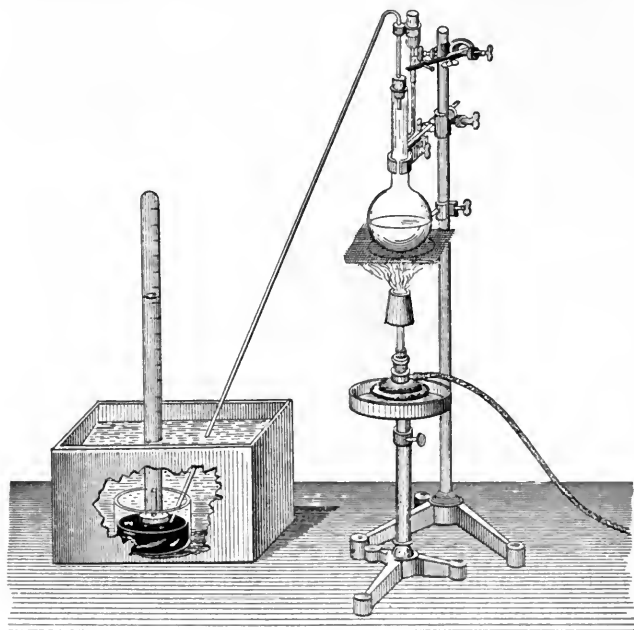


Fig. 25. De Konnick's Apparatus.

flask A were made much smaller the efficiency of this apparatus would be increased. It appears to have few, if any, advantages over Warington's process.

355. De Konnick's Modification of Schloesing's Method.—This modification consists in an arrangement of the gas delivery tube, whereby the regurgitation of the water in the measuring burette into the evolution flask is prevented by a device for sealing the

delivery tube with mercury.⁴⁴ The apparatus is arranged as shown in Fig. 25. The flask in which the decomposition takes place is provided with a long neck, into which a side tube is sealed and bent upwards, carrying a small funnel attached to it by rubber tubing. The piece of rubber tubing carries a pinch-cock, by means of which the solution containing the nitrate and hydrochloric acid can be introduced into the flask. The small gas delivery tube is arranged as shown in the figure, and carries at the end next the burette a device shown in Fig. 26. The cork represented in this device has radial notches cut in it, so as to permit of a free communication between the water in the burette and in the pneumatic trough. The open end of the burette, when the apparatus is mounted ready for use, rests on the notched sur-

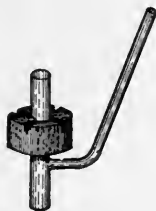


Fig. 26. End of Delivery Tube.

face of the cork, and the end of the delivery tube is placed in the crystallizing dish resting on the bottom of the pneumatic trough.

The end of the delivery tube, as indicated, has fused to it a vertical tube, open at both ends and from six to seven centimeters in length, and carrying the notched cork already described. The crystallizing dish in the bottom of the pneumatic trough is filled with mercury until the point of union of the delivery tube with the vertical end is sealed to the depth of a few millimeters. As the gas is evolved it bubbles up through the mercury into the measuring tube and the displaced water passes out through the notches in the cork. Should any back pressure supervene, the mercury at once rises in the delivery tube, which is of such a length as to prevent its entrance into the flask. The operation can then be carried on with absolute safety.

To make an estimation, there are placed in the flask about

⁴⁴ *Zeitschrift für analytische Chemie*, 1894, 33 : 200.

40 cubic centimeters of ferrous chlorid solution containing about 200 grams of iron to the liter, and also an equal volume of hydrochloric acid of 1.1 specific gravity. The side tube is also filled up to the funnel with the acid. The contents of the flask are boiled until all air is expelled, which can be determined by holding a test-tube filled with water over the end of the delivery tube. The solution containing the nitrate is next placed in the funnel, the pinch-cock opened and the liquid allowed to run into the flask by means of the partial vacuum produced by stopping the boiling and allowing the mercury to rise in the delivery tube. All the solution is washed into the flask by successive rinsings of the funnel with hydrochloric acid, being careful to allow no bubble of air to enter. The contents of the flask are again raised to the boiling-point and the nitric oxid evolved collected in the nitrometer. The solution examined should contain enough nitrate to afford from 60 to 80 cubic centimeters of gas. Without refilling the flask, from eight to nine determinations can be made by regenerating the ferrous chlorid by treatment with zinc chlorid. Care must be exercised not to add the zinc chlorid in excess, otherwise ammonia and not nitric oxid will be produced. The side tube and funnel must also be carefully freed from zinc chlorid by washing with hydrochloric acid.

356. Schmidt's Process.—In the case of a water, or the aqueous extract of a soil, according to the content of nitric acid, from 50 to 100 cubic centimeters are evaporated to 30 cubic centimeters, and the residue sucked into the generating flask of the apparatus, Fig. 27, and, with the rinsings with distilled water, evaporated again to from 20 to 30 cubic centimeters, and the flask then connected, as shown in the figure, to a schiff measuring apparatus B.⁴⁵ This apparatus is previously filled to *i* with mercury, and the bulb *g* connected with *k* by a rubber tube.

The apparatus is then filled with a 20 per cent. caustic soda solution previously boiled and still warm, until the bulb *g* is partially filled when raised a little above the cock *h*. Then *h* is closed and *g* held, by an appropriate support, on about the same level with *h*. The cock at *b* is then closed and *e* opened.

⁴⁵ Apotheker Zeitung, 1890, 5 : 287.

Meanwhile the ebullition in the flask is continued, and the air bubbles rising in the schiff apparatus are removed, from time to time, by carefully opening *h* and raising *g*. When bubbles no longer come over, the cock at *e* is closed and at *b* opened, and the steam issuing at *a* is conducted through a mixture of ferrous chlorid and strong hydrochloric acid to free it, as far as possible, from air. When the contents of the flask have been evaporated

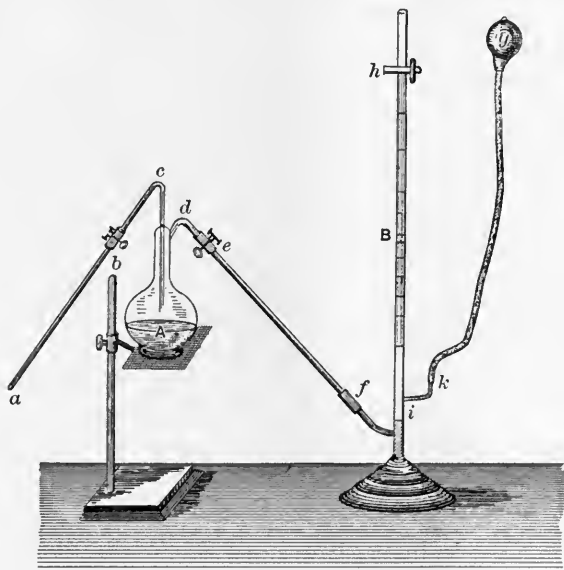


Fig. 27. Schmidt's Apparatus.

to about five cubic centimeters, *b* is closed and the lamp at once removed.

By carefully opening *b* about 10 cubic centimeters of a mixture of ferrous chlorid and hydrochloric acid are allowed to enter the flask, when *b* is closed and the flask slowly heated until the positive pressure is restored. The pinch-cock *e* is then opened and the contents of the flask evaporated nearly to dryness. The cock *e* is again closed and the flame removed. Another quantity (15 cubic centimeters) of ferrous chlorid and hydrochloric acid solution is sucked into the flask and the process of distillation repeated, whereby the whole of the nitric oxid is collected

in *h*. The nitric oxid evolved is measured in the usual way and calculated to nitric acid, one cubic centimeter of nitrogen dioxid being equal to 2.417 milligrams of nitric acid.

357. Merits of the Ferrous Chlorid Process.—The possibility of an accurate determination of nitrates, by decomposition with a ferrous salt in presence of an excess of hydrochloric acid, has been established by many years of experience and by the testimony of many analysts. The method is applicable especially where the quantity of nitrate is not too small and when organic matter is present. In the case of minute quantities of nitrate, however, the process is inapplicable and must give way to some of the colorimetric methods to be hereafter described.

In respect of the apparatus, modern practice has led to the preference of that form which does not require the use of carbon dioxid for displacing the air. Steam appears to be quite as effective as carbon dioxid and is much more easily employed. That form of apparatus should be used which is the simplest in construction and has the least cubical content.

The measurement of the evolved gas is most simply made by collecting over lye in an azotometer, reading the volume, noting the reading of the barometer and thermometer and then reducing to standard conditions of pressure and temperature by the customary calculations. Where a very strong lye is used the tension of the aqueous vapor may be neglected. While every analyst should have a thorough knowledge of the ferrous chlorid method and the principles on which it is based, it can not be compared in simplicity to the later methods with pure nitrates, which are based on the conversion of the nitric acid into ammonia by the action of nascent hydrogen. In accuracy, moreover, it does not appear to have any marked advantage over the reduction methods.

358. Mercury and Sulfuric Acid Method.—This simple and accurate method of determining nitric acid in the absence of organic matter is known as the Crum-Frankland process.⁴⁰

The method rests on the principle of converting nitric acid into

⁴⁰ Philosophical Magazine, 1847, [3], 30 : 426.

Journal of the Chemical Society, 1863, 21 : 101.

Sutton, Volumetric Analysis, 9th Edition, 1907 : 443.

nitric oxid by the action of mercury in the presence of sulfuric acid. The operation as at first described is conducted in a glass jar eight inches long by one and a half inches in diameter, filled with mercury and inverted in a trough containing the same liquid. The nitrate to be examined, in a solid form, is passed into the tube, together with three cubic centimeters of water and five of sulfuric acid. With occasional shaking, two hours are allowed for the disengagement of the gas, which is then measured.

359. Warington's Modification.—A graduated shaking-tube is employed, which allows the nitrate solution and oil of vitriol to be brought to a definite volume.⁴⁷ The nitrate solution, with rinsings, is always two cubic centimeters, and enough sulfuric acid is added to increase the volume to five cubic centimeters. The sulfuric acid should give no gas when shaken with distilled water. Any gas given off in the apparatus before shaking is not expelled but is included in the final result. The persistent froth sometimes noticed where some kinds of organic matter are present, is reduced by the addition of a few drops of hot water through the stop-cock of the apparatus. The nitric oxid is finally measured in Frankland's modification of Regnault's apparatus.

This method, accurate for pure nitrates, unfortunately fails in the presence of any considerable amount of organic matter.

According to Warington's observations, the presence of chlorids is no hindrance to the accurate determination of both nitric and nitrous acids by the mercury method. This simplifies the operation as carried on by Frankland, who directs that any chlorine present be removed before the determination of the nitric acid is commenced.

360. Noyes' Method.—In the analyses made by Noyes for the National Board of Health, the Crum-Frankland method was employed.⁴⁸ The apparatus used was essentially that which is now known as Lunge's nitrometer, and it will be described in the next paragraph. No correction is made by Noyes for the tension of aqueous vapor in the measurement of the nitric oxid because of the moderate dilution of the sulfuric acid by the liquid

⁴⁷ Journal of the Chemical Society, 1879, 35 : 376.

⁴⁸ Report of the National Board of Health, 1882 : 281.

holding the nitric compounds in solution. The chlorine is not removed from the dry residue of the evaporated water, as its presence in moderate quantity does not interfere with the accuracy of the process. In order to obtain the amount of nitrogen in the form of nitrates, the total volume of nitric oxid must be diminished by that due to nitrites present, which must be determined in a separate analysis. The method of manipulation is given in the following paragraph.

361. Lunge's Nitrometer.—The apparatus employed by Noyes, in a somewhat more elaborate form, is known as Lunge's nitrometer.⁴⁹ This apparatus is shown in Fig. 28. It consists of a

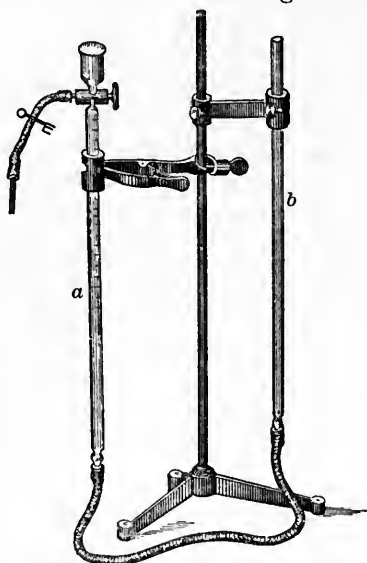


Fig. 28. Lunge's Nitrometer.

burette *a*, divided into one-fifth cubic centimeters. At its upper end it is expanded into a cup-shaped funnel attached by a three-way glass stop-cock. Below, the burette is joined to a plain tube *b*, of similar size, by means of rubber tubing. The apparatus is first filled with mercury through the tube *b*, the stop-cock being so adjusted as to allow the mercury to fill the cup at the top of *a*. The cock is then turned until the mercury in the cup flows out

⁴⁹ Berichte der deutschen chemischen Gesellschaft, 1878, 11 : 437.

through the side tube, carrying the rubber tube and clamp. The three-way cock is closed, and the solution containing the nitrate placed in the cup. By lowering the tube *b* and opening the cock the liquid is carefully passed into *a*, being careful to close the cock before all the liquid has passed out of the cup. By repeated rinsings with pure concentrated sulfuric acid, every particle of the nitric compound is finally introduced into *a*, together with a large excess of sulfuric acid. The total volume of the introduced liquid should not exceed 10 cubic centimeters. The mixture of the mercury, nitric compound, and sulfuric acid is effected by detaching *a* from its support, compressing the rubber connection between *a* and *b*, placing *a* nearly in a horizontal position, and quickly bringing it into a vertical position with vigorous shaking.

After about five minutes the reaction is complete, and the level of the liquids in the two tubes is so adjusted as to compensate for the difference in specific gravity between the acid mixture in *a* and the mercury in *b*; in other words, the mercury column in *b* should stand above the mercury column in *a* one-seventh of the length of the acid mixture in *a*. This secures atmospheric pressure on the nitric oxid which has been collected in *a*. The measured volume of nitric oxid should be reduced to 0° and 760 millimeters barometric pressure. Each cubic centimeter of nitric oxid thus obtained corresponds to 1.343 milligrams NO; 2.417 milligrams N₂O₅; 1.701 milligrams N₂O₃; 2.820 milligrams HNO₃; 4.521 milligrams KNO₃, and 3.805 milligrams NaNO₃.

362. Lunge's Improved Apparatus.—Lunge has improved his apparatus for generating and measuring gases and extended its applicability.⁵⁰ The part of it designed to measure the volume of a gas is the same in all cases. For generating the gas, the apparatus varies according to the character of the substance under examination.

The measuring apparatus is shown in Fig. 29. It is composed essentially of three tubes, conveniently mounted on a wooden holder with a box base for saving any spilled mercury. The support is not shown in the illustration.

The tubes A, B, C, are mutually connected by means of a

⁵⁰ Bulletin de la Société chimique de Paris, 1894, [3], 11 : 625.

three-way tube and rubber tubing, with very thick walls to safely hold the mercury without expansion. In the middle of the measuring tube A is a bulb of 70 cubic centimeters capacity. Above and below the bulb the tube is divided into tenths of a cubic centimeter, and its diameter is such, viz., 11.3 millimeters, that each cubic centimeter occupies a length of one centimeter. The upper

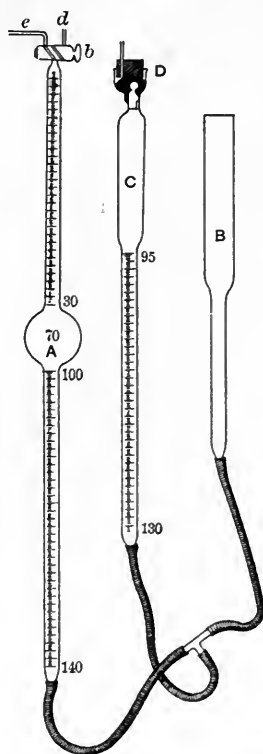


Fig. 29. Lunge's Improved Apparatus.

end of A is closed with a glass cock with two oblique perforations, by means of which communication can be established at will, either through *e* with the apparatus for generating the gas, or through *d*, with the absorption apparatus, or the opening be completely closed.

The volume of air under the observed conditions, which would

measure exactly 100 cubic centimeters at 0° and 760 millimeters pressure of mercury, is calculated by the formula

$$V = \frac{100 (273 + t) 760}{273 (b-f)} ;$$

where t equals observed temperature, b the barometric pressure less the correction noted below, and f the tension of the vapor of water under existing conditions. For example:

Temperature.....	18°
Barometric reading	755
Correction for b	2
Corrected barometer	753
Vapor of water tension	16

$$\text{Then } V = \frac{100 (273 + 18) 760}{273 (753 - 16)} = 109.9.$$

This indicates that 109.9 cubic centimeters of air would occupy a volume of 100 cubic centimeters when subjected to standard conditions.

The tubes A, B, and C, are filled with mercury of which about two and a half kilograms will be required. By means of the leveling tube B, the stopper in C being opened, the mercury in C is brought exactly to 109.9 cubic centimeters. The stopper in C is then closed, mercury poured into D, which is then closed with a rubber stopper, carrying a small glass tube, as indicated in the figure.

The leveling tube B serves to regulate the pressure on the gas in A, and this is secured by depressing or elevating it, as the case may require.

The tube for reducing the volume to standard conditions of temperature and pressure, viz., 0° and 760 millimeters of mercury, is shown in C. In its narrow part, which has the same internal diameter as A, it is graduated into tenths of a cubic centimeter. The upper end of C is furnished with a heavy glass neck D, surmounted by a glass cup. In the neck is placed a ground-glass stopper, carrying a groove below, which corresponds to a similar groove above in the side of the neck, whereby communication can be established at will between the interior of C and the exterior. The joint is also sealed by pouring mercury into D, as

is shown in the figure. When the stopper is well ground and greased the reduction tube may be raised or lowered as much as may be necessary without any danger of escape or entrance of gas. To determine the position of the reduction tube C the reading of the barometer and thermometer at room temperature is taken. From the reading of the barometer subtract one millimeter if the temperature be below 12° , two millimeters at a temperature from 12° to 19° , three from 20° to 25° , and four above 25° .

When a gas has been introduced into the measuring tube A it is brought to the volume which it would assume under standard conditions by adjusting the tube C, in such a way as to bring the mercury in C and A to the same height and the surface of the mercury in C is exactly at 100 cubic centimeters. The gas in A is then at the volume which it would occupy under standard conditions, and this volume can be directly read. This adjustment is secured by moving the tubes B and C up or down. If gases are to be measured wet, a drop of water should be put on the side of the upper part of C, and if dry, of sulfuric acid, before the adjustment for temperature and pressure.

363. Method of Manipulation.—By the action of mercury in the presence of sulfuric acid, the nitrogen in nitrates, nitrites, nitrosulfates, nitroses, nitrocellulose, nitroglycerol, and the greater number of explosives, may be obtained and measured as nitric oxid. The nitrogen compounds are decomposed in the apparatus shown in Fig. 30.

To make an analysis, the apparatus is filled with mercury, through F, until the two openings in the cock and *i* are entirely occupied with that liquid. The cock *h* is then closed, and the nitrogen compound, in solution, introduced through *g*, care being taken that no air enters *g* when F is depressed and *h* opened to admit the sample. The funnel *g* is washed several times with a few drops of sulfuric acid, which are successively introduced into G. The total liquid introduced should not exceed 10 or 15 cubic centimeters, of which the greater part should be sulfuric acid. The rubber tube connecting G and F is carefully closed with a clamp and G violently shaken for a few minutes until no further

evolution of nitric oxid takes place. In shaking, the apparatus should be so held as to prevent the escape of the mercury from the small tube *i* by keeping it closed with the finger or drawing over it a rubber cap.

After the evolution of the gas has ceased, the tube *e*, Fig. 29, is brought into contact with *i*, (Fig. 30) and the two are joined by a tight-fitting piece of rubber tubing in such a way as to exclude any particle of air. The tube *F*, Fig. 30, is lifted and *B* and *C*, Fig. 29, depressed. On carefully opening the cocks *h* and *b*, and bringing *i* and *e* into union, the gas is passed from *G* into *A*. When all the gas has entered *A* and the acid mixture from

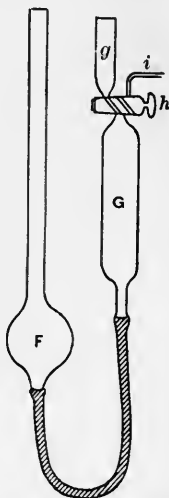


Fig. 30. Lunge's Analytic Apparatus.

G has reached *b*, the latter is closed, and also *h*. The apparatus *G* is disconnected and removed. The gas in *A* is then reduced to normal conditions by manipulating the reduction tube, *C*, in the manner already described.

The gas in *A* is measured dry by reason of having been generated in presence of rather strong sulfuric acid. Consequently, for this operation the adjustment of the volume of gas in *C* should be made in contact with a drop of strong sulfuric acid. In order to make the readings, a quantity of material must be

taken which will give not less than 30 and not more than 140 cubic centimeters of nitric oxid.

The quantities of the different compounds of nitric acid corresponding to the number of cubic centimeters of nitric oxid, measured under standard conditions, are shown in the following table:

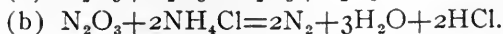
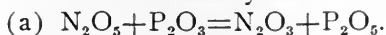
Cubic centimeters of NO.	Weight in milligrams.	Corresponding to		
		N ₂ O ₃ in milligrams.	HNO ₃ in milligrams.	NaNO ₃ in milligrams.
1.....	1.343	1.701	2.820	3.805
2.....	2.682	3.402	5.640	7.610
3.....	4.029	5.103	8.460	11.415
4.....	5.372	6.804	11.280	15.220
5.....	6.715	8.506	14.100	19.025
6.....	8.058	10.206	16.920	22.830
7.....	9.401	11.907	19.740	26.635
8.....	10.744	13.608	22.560	30.440
9.....	12.087	15.309	25.380	34.245

364. Utility of the Method.—Where it is desirable that the nitric oxid method be used, and at the same time heating be avoided, the decomposition of a nitrate by means of metallic mercury and sulfuric acid affords a convenient and accurate procedure. But, as a rule, there is no objection to the application of the lamp except in the case of explosives, and in such cases the mercury method appears to have no advantage over the ferrous chlorid process. Nevertheless, in the hands of a skilled worker, the results are reliable, and the process is a quicker one, on the whole, than by distillation with ferrous chlorid and hydrochloric acid.

365. Volumetric Method of Gantter.—The process proposed by Gantter for determining the nitrogen volumetrically in Chile saltpeter and other nitrates is based on the following principles:⁵¹

(1) If a nitrate be heated in contact with sulfuric and phosphorous acids, nitrous and phosphoric acids will be formed.

(2) If nitrous acid be boiled with ammonium chlorid, nitrogen will be quantitatively evolved from both compounds. These processes are illustrated by the following formulas:



⁵¹ *Zeitschrift für analytische Chemie*, 1895, **34**: 26.

It is seen from the above that the nitrate will give, by this treatment, double the volume of nitrogen which it contains. In practice, the two reactions may be secured in one operation by warming the nitrate solution slowly with sulfuric and phosphorous acids and ammonium chlorid. The nitric acid, as it becomes free, gives a part of its oxygen to the phosphorous compound, and the nitrous acid, in a nascent state, is at once reduced by the ammonium chlorid. There are two sources of error which must be guarded against in the work; a portion of the nitrogen may escape reduction to the elementary state, or some of the nitrate may fail to be decomposed. These errors are easily

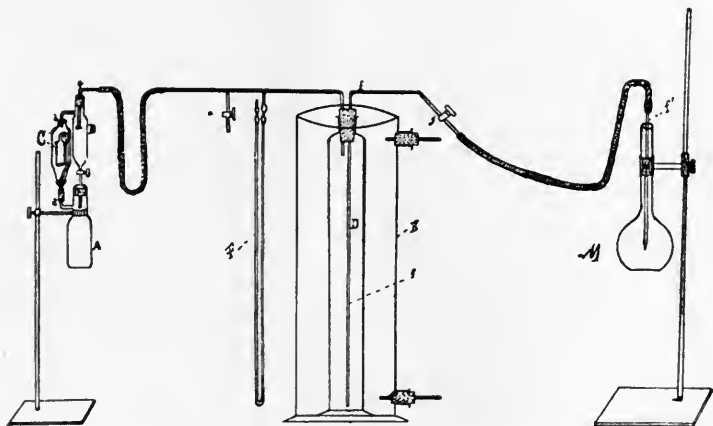


Fig. 31. Gantter's Nitrogen Apparatus.

avoided if the reaction be begun slowly, so that the evolution of gas may be gradual. The temperatures at first should, therefore, be kept as low as possible. The development of red fumes, showing the presence of undecomposed nitrogen oxids, shows that the results will be too low. It is necessary, also, to provide for the absorption of the hydrochloric acid which is formed. The reaction is very conveniently conducted in the apparatus shown in Fig. 31. The decomposition takes place in the flask A, and the mixed gases pass into the absorption bulb C. The delivery tube is very much expanded, as shown in the figure, so that no soda-lye can enter A during the cooling of the flask. The absorp-

tion bulb is connected with A and B by the tubes a and b, as shown. The tube d connects the apparatus with the gasvolumeter.⁵² The bulb B serves as a pipette for the introduction of the decomposing acid. The operation is conducted as follows: Three cubic centimeters of the nitrate solution, containing no more than 300 milligrams of the substance, are placed in the flask A, with half a gram each of crystallized ammonium chlorid and phosphorous acid. In the bulb B are placed seven cubic centimeters of sulfuric acid, to which has been added one-third its volume of water. Two cubic centimeters of acid are allowed to flow from B into A. The apparatus is brought to a constant temperature by being immersed in a large cylinder E, containing water at a temperature which can easily be controlled. When this constant temperature has been reached the apparatus is taken from the cooling cylinder, which contains also a smaller cylinder D, nearly filled with water and connected through f' with the measuring apparatus M. The barometer-tube F is half filled with colored water, so that the pressure may be equalized before and after the operation. The flask A is warmed very gently at first, and the nitrogen evolved is conducted into D, driving an equivalent volume of water into M. The evolution of the gas must be carefully controlled and the heat at once removed if it becomes too rapid. The appearance of a red color shows the evolution of oxids of nitrogen, rendering the analysis inexact. When the evolution of nitrogen has nearly ceased, the lamp is removed and some more sulfuric acid allowed to flow into A from B, after which A is again heated, this time to the boiling-point. All vapors of hydrochloric acid produced are absorbed by the soda-lye in C. The boiling is continued a few minutes, but not long enough to darken the liquid in A. After replacing the apparatus in the cylinder E, and bringing both temperature and pressure to the same point as before the beginning of the operation, the volume of nitrogen evolved is determined by measuring the water in M.

The apparatus is first set by using pure potassium or sodium nitrate. Since the temperature and pressure do not vary much

⁵² *Zeitschrift für analytische Chemie*, 1893, **32** : 553.

within an hour or two, the volume of water obtained with a sample of Chile saltpeter can be compared directly with that given off by the same weight of a pure potassium or sodium nitrate without correction.

Example.—Two hundred and fifty milligrams of potassium nitrate, containing 34.625 milligrams of nitrogen, displaced in a given case 60 cubic centimeters of water; therefore, one cubic centimeter of water equals 0.578 milligram of nitrogen. If 289 instead of 250 milligrams be taken, then the number of cubic centimeters of water displaced divided by five will give the per cent. of nitrogen.

366. Method of Difference.—In the analysis of Chile saltpeter by the direct method a variation of 0.25 per cent. in the content of nitrogen is allowed from the dealers' guaranty. This would allow a total variation in the content of sodium nitrate of 1.52 per cent. Dealers and shippers have always been accustomed to estimate the quantity of sodium nitrate in a sample by difference; *i. e.*, by estimating the constituents not sodium nitrate and subtracting the sum of the results from 100. Chile saltpeter usually contains sodium nitrate, water, insoluble ferruginous matters, sodium chlorid, sodium sulfate, magnesium chlorid, sodium iodate, calcium sulfate and sometimes small quantities of potassium nitrate.

When the total sodium nitrate is to be estimated by difference, the following procedure, suggested by Crispo, may be followed:⁵³

Water.—Dry 10 grams of the finely powdered sample to constant weight at 150°-160°.

Chlorin.—The residue, after drying, is dissolved and the volume made up to one-fourth liter with water and the chlorin determined in one-fifth thereof and calculated as sodium chlorid.

Insoluble.—Twenty grams are treated with water until all soluble matter has disappeared, filtered on a tared gooch, and the crucible dried to constant weight.

Sulfuric Acid.—The sulfuric acid is precipitated by barium chlorid in the slightly acid filtrate from the insoluble matter.

⁵³ L'Engrais, 1894, 9 : 877.

The acidity is produced by a few drops of nitric acid. The rest of the process is conducted in the usual way.

Magnesia.—This is precipitated by ammonium sodium phosphate, filtered, ignited, and weighed as pyrophosphate. The magnesia is then calculated as chlorid. Magnesia is rarely found in excess of one-fourth per cent. When this amount is not exceeded the estimation of it may be neglected without any great error. As has already been said, the chlorin is all calculated as sodium chlorid. If a part of it be combined with one-fourth per cent. of magnesia, it would represent 0.59 per cent. of magnesium chlorid instead of 0.73 per cent. sodium chlorid. In omitting the estimation of the magnesia, therefore, the importer is only damaged to the extent of 0.14 per cent. of sodium nitrate.

Sodium Iodate.—This body, present only in small quantities, may also be neglected. In case the content of this body should reach one-fourth per cent. the estimation of chlorin by titration, using potassium chromate as indicator, is impracticable. Such an instance, however, is rarely known.

Approximate Results.—When the determinations outlined above have been carefully made, it is claimed that the result obtained by subtraction from 100 will not vary more than from two-tenths to three-tenths per cent. from the true content of sodium nitrate. The method, however, cannot be considered strictly scientific and is much more tedious and chronophagous than the direct determination. In the direct determination, however, the analyst must assure himself that potassium is present in only appreciable quantities, otherwise the per cent. of sodium nitrate will be too low.

The presence of potassium nitrate is a detriment in this respect only; viz., that it contains a less percentage of nitrogen than the corresponding sodium salt. As a fertilizer, the value of Chile saltpeter may be increased by its content of potassium.

ESTIMATION OF NITRIC ACID BY OXIDATION OF A COLORED SOLUTION

367. **Principles of the Method.**—Solutions of organic coloring matter in certain conditions are decolorized by nitric acid. The process is one of oxidation and the disappearance of the natural

color marks the end of the reaction. Indigo is the only coloring matter that has been used to any extent in this process.

368. Method of Marx.—The indigo method as usually practiced is conducted according to the principle described by Marx.⁵⁴ There are required for the process the following reagents and apparatus:

a. A solution of pure potassium nitrate containing 1.8724 grams per liter. One cubic centimeter of the solution is equivalent to one milligram of nitric anhydrid (N_2O_5).

b. A solution of the best indigo carmine in water, which should be approximately standardized by solution in the manner described hereafter, and then diluted so that from six to eight cubic centimeters equal one milligram of nitric acid.

c. Chemically pure sulfuric acid of specific gravity 1.842, perfectly free from sulfurous and arsenious acids and nitrogen oxids.

d. Several thin flasks of about 200 cubic centimeters capacity.

e. A small cylindrical measure holding 50 cubic centimeters and divided into cubic centimeters.

f. A Mohr's burette divided into tenths of a cubic centimeter.

g. A 25 cubic centimeter pipette or another burette.

h. A five cubic centimeter pipette divided into cubic centimeters or half cubic centimeters.

i. A measuring flask of 250 cubic centimeters capacity.

Preliminary Trial.—Twenty-five cubic centimeters of the sample are transferred to a flask; the 50 cubic centimeter measure is filled with sulfuric acid and the burette with indigo solution. The sulfuric acid is added to the sample all at once, shaken for a moment, and the indigo run in as quickly as possible with shaking until a permanent greenish tint is produced. If the sample does not require more than 20 cubic centimeters of indigo solution of the above strength, it can be titrated directly, otherwise it must be diluted with a proper quantity of pure water, and subjected again to the preliminary trial.

The Actual Titration.—(1) Twenty-five cubic centimeters of the sample, properly diluted if necessary, are poured into a flask, and as much indigo as was used in the preliminary trial is added;

⁵⁴ *Zeitschrift für analytische Chemie*, 1868, 7 : 412.

a quantity of sulfuric acid, equal in volume to the liquid in the flask, is added all at once, the mixture shaken, and indigo solution run in quickly out of the burette until the liquid remains permanently of a greenish tint.

(2) The last experiment is repeated as often as may be necessary, adding to the water at first half a cubic centimeter less indigo than the total quantity used previously, afterwards proceeding as in (1) until the final test shows too little indigo used.

(3) From the rough titration of the indigo, calculate the amount of potassium nitrate solution corresponding with the indigo solution used in (2), multiply the result by 10, transfer this quantity of the standard nitrate solution to a 250 cubic centimeter flask, fill with pure water to the mark, and titrate 25 cubic centimeters of this fluid with indigo as in (2). If the quantity of indigo solution used is nearly the same as that required in (2), its exact value may be calculated, but if it is not, another nitrate solution may be made up in the 250 cubic centimeter flask, more closely resembling the sample in strength, and the titration with the indigo solution must be repeated.

(4) If the water contains any considerable amount of organic matter, it must first be destroyed by potassium permanganate. In this case, the estimation of the organic matter and nitric acid may be conveniently combined.

The use of permanganate in the above case is likely to introduce an error as has been shown by Warington. The method, therefore, can not be recommended in the presence of organic matter.

369. Method of Boussingault.—The process for the estimation of nitric acid by the decoloration of a solution of indigo is due originally to Boussingault.⁵⁵ In this method the extract, obtained by washing slowly 200 grams of soil until the filtrate amounts to 300 cubic centimeters, is evaporated until its volume is no greater than two or three cubic centimeters, and it is transferred to a test-tube, with washings, and again evaporated in the tube until the volume is not greater than that last mentioned. A few drops of solution of indigo are added, and then two cubic

⁵⁵ Encyclopédie chimique, 1888, 4 : 154.

centimeters of pure hydrochloric acid; the whole is then heated. As the color of the indigo disappears more is added. When the color ceases to fade, the liquid in the test-tube is concentrated by boiling. If concentration fail to destroy the blue or green color, another one-half cubic centimeter of hydrochloric acid is introduced. The reaction is completed when neither concentration nor fresh addition of hydrochloric acid destroys the excess of indigo present. The color produced by a small excess of indigo is a bright green; this tint is the final reaction sought. The small excess of indigo necessary to produce a green color is deducted in every experiment.

When more than mere traces of organic matter are present, Boussingault advises that the nitric acid be first separated by distillation and then reduced by the indigo solution. For this purpose the concentrated solution of the nitrate, two or three cubic centimeters, is placed in a small tubulated retort with two grams of manganese dioxid in fine powder. The retort is next half filled with fragments of broken glass, over which is poured one cubic centimeter of concentrated sulfuric acid. The retort is heated carefully by means of a small flame, which is kept in motion so as to successively come in contact with all parts of the bottom of the retort. The distillate is received in a graduated test-tube which is kept cool. The distillation is continued until the vapors of sulfuric acid begin to appear. The apparatus is allowed to cool, the stopper of the retort removed, two cubic centimeters of water introduced, and the distillation repeated until fumes of sulfuric acid are again seen. The distillation with water is made twice in order to remove every trace of nitric acid from the retort. The distillate is neutralized with a solution of potassium hydroxid and concentrated to two cubic centimeters, and the nitric acid estimated in the manner already described. The manganese dioxid used should be previously well washed and the sulfuric must be free of nitric acid.

Preparation of the Indigo Solution.—Fifty grams of indigo in fine powder are digested for 24 hours at 40° in a liter of distilled water. The water is poured off and replaced with a fresh sup-

ply. After the second decantation the residue is treated with 750 cubic centimeters of equal parts of water and pure concentrated hydrochloric acid and boiled for an hour. After cooling, the undissolved portion is collected on a filter and washed at first with hot, and afterwards with cold water, until the filtrate is no longer colored and is free of acid. The dried residue is treated with ether under a bell-jar, or in a continuous extraction apparatus until the ether is only of a faint blue tint. The 50 grams of indigo will yield about 25 grams of the purified article, which, however, will still leave a little ash on combustion.

Solution in Sulfuric Acid.—Five grams of the purified indigo are placed in a flask having a ground-glass stopper, treated with 25 grams of fuming sulfuric acid, and allowed to digest two or three days at a temperature of from 50° to 60°. From 70 to 200 drops of the solution thus made are placed in 100 cubic centimeters of water for use in the process.

Standardization of the Indigo Solution.—The solution as prepared above is standardized by a solution of one gram of pure potassium nitrate in 1000 cubic centimeters of distilled water. The oxidation of the indigo solution is accomplished as described above. Of this strength of standard nitrate solution two cubic centimeters are used, corresponding to two milligrams of potassium nitrate. The indigo solution for this strength potassium nitrate solution should have only 20 drops of the sulfuric acid solution of indigo to 100 cubic centimeters of water. If 20 grams of potassium nitrate are used for 1000 cubic centimeters of the standard solution, then 200 drops of the sulfindigotic acid should be used to 100 cubic centimeters of water.

370. Method of Warington.—The modification of the indigo method as used by Warington, applicable only in absence of organic matter, is the one chiefly employed in England.⁵⁶

Instead of the ordinary indigo of commerce, indigotin is used. The normal solution of the coloring matter is made of such a strength as to be equivalent to a solution of potassium nitrate containing 0.14 gram of nitrogen per liter. When large quantities of the coloring matter are to be used, it is advisable to pre-

⁵⁶ Journal of the Chemical Society, 1879, 35:578.

pare it about four times the strength given above and then dilute it as required. Four grams of sublimed indigotin will furnish more than two liters of the color solution.

The solution is prepared as follows :

Four grams of indigotin are digested for a few hours with five times that weight of Nordhausen sulfuric acid, diluted with water, filtered and made up to a volume of two liters. The strength of the indigotin solution is determined with a solution of potassium nitrate of the strength mentioned above. The process is performed as follows :

From 10 to 20 cubic centimeters of the standard nitrate solution are placed in a wide-mouthed flask of about 150 cubic centimeters capacity. A portion of the indigotin solution is added, such as will be deemed sufficient for the process, and the whole is well mixed. Strong sulfuric acid is measured from a burette into a test-tube, in volume equal to the united volumes of the nitrate solution and indigotin. The whole of the sulfuric acid is then poured, as quickly as possible, into the solution in the flask and rapidly mixed, and the flask transferred to a calcium chlorid bath, the temperature of which should be maintained at 140° . It is essential to the success of the operation that the sulfuric acid should be mixed with the greatest rapidity. It is poured in at once and the whole well shaken without waiting for the test-tube, containing the acid, to drain. The flask is covered with a watch-glass while it is held in the bath. As soon as the larger part of the indigotin is oxidized the flask in the bath is gently rotated. With very weak solutions of nitrate it may be necessary sometimes to keep the flask in the bath for five minutes. When the indigo color is quickly discharged, it shows the presence of nitric acid in considerable excess and a larger quantity of indigo must be used in the next experiment. The experiments are continued until just the quantity of indigotin necessary to consume the nitric acid is found, the amount of indigotin being in very slight excess, not exceeding one-tenth cubic centimeter of the indigotin solution used. The tint produced by the small excess of indigotin remaining is best seen by filling the flask with water. On substances of approximately known strength about four experiments are

usually necessary to determine the proper amount of indigotin, but with unknown substances a larger number may be necessary.

Usually in determinations of this kind it is directed to use double the volume of sulfuric acid mentioned above. In this case not only is the quantity of indigotin oxidized much greater than with a smaller portion of acid, but the prejudicial effect of organic matter is also greater when the smaller quantity of acid is employed.

An indigotin solution standardized as above is strictly to be used for a solution of nitrate of the strength employed during the standardization. The quantity of indigotin oxidized in proportion to the nitric acid present diminishes as the nitrate solution becomes more dilute. Instead of determining this during each series of experiments it may be estimated once for all and a table of corrections used.

The following table is based upon experimental determinations:

Strength of niter solution used.	Indigotin required, cc.	Difference between amounts of indigotin, cc.	Nitrogen corresponding to one cubic centimeter of indigotin, gram.	Difference between the nitrogen values, gram.	Difference in the nitrogen value for a difference of one cubic centimeter in the amount of indigotin, gram.
$\frac{8}{64}$ Normal....	10.00	0.000035000
$\frac{7}{64}$ "	8.71	1.29	0.000035161	0.000000161	0.000000125
$\frac{6}{64}$ "	7.43	1.28	0.000035330	0.000000169	0.000000132
$\frac{5}{64}$ "	6.14	1.29	0.000035627	0.000000298	0.000000231
$\frac{4}{64}$ "	4.86	1.28	0.000036008	0.000000381	0.000000298
$\frac{3}{64}$ "	3.57	1.29	0.000036763	0.000000756	0.000000586
$\frac{2}{64}$ "	2.29	1.28	0.000038209	0.000001445	0.000001129
$\frac{1}{64}$ "	1.00	1.29	0.000043750	0.000005541	0.000004295

The table is used as follows:

Suppose that 20 cubic centimeters of water under examination have required 5.36 cubic centimeters of indigotin solution for the oxidation of the nitric acid contained therein. By inspection of the table it is seen that this number is five-tenths cubic centimeter above the nearest quantity given, viz., 4.86 cubic centimeters. From the last column in the table it is found that the correction for five-tenths cubic centimeter of indigotin solution is 0.000000149 cubic centimeter, being half that for the one cubic centimeter given in the table. This is to be subtracted from the

unit value in nitrogen given in the first "gram" column of the table; viz., 0.000036008. It is thus seen that the 5.86 cubic centimeters of indigotin solution are equivalent to 0.000035859 gram of nitrogen per cubic centimeter. The water under examination, therefore, contains nine and six-tenths parts of nitrogen as nitric acid per million.

Attention must also be paid in standardizing indigotin solutions to the initial temperature. A rise in the initial temperature will be attended by a diminution in the quantity of indigotin oxidized. Experiments with a room temperature of 10° and a room temperature of 20°, being the initial temperatures of the experiments, showed that at the higher temperature the amount of indigotin consumed was about five per cent. less when the strong solutions of nitrate were employed. The indigotin solution, therefore, must be standardized at the same temperature at which the determinations are made.

If 20 cubic centimeters of the standard nitrate solution employed be used in setting the indigotin solution, this standard will enable the operator to determine nitric acid up to 17.5 parts of nitrogen per million in water or soil extracts.

The presence of an abundance of chlorids in the water under examination tends to diminish the content of nitric acid found, and also tends to introduce an error, which is sometimes of a plus and sometimes of a minus quantity, according to the strength of the nitric acid present. The reaction is shortened in weak solutions by the presence of chlorids, and the quantity of indigotin consumed is consequently increased. The error introduced by chlorids is usually of an insignificant nature.

On account of the interference of organic matters with the reaction of indigotin it is not of much use in the examination of nitrates washed out of soils, although in some cases the results may be quite accurate. This method must, therefore, be considered as applicable, in general, only to waters or soil extracts which contain little or no organic matter.

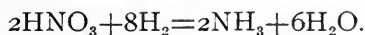
In analytical work pertaining particularly to agriculture, the use of the indigotin method for determining nitric acid has been largely employed, both in the analyses of soil extracts and drain-

age and irrigation waters. The method, however, can hardly survive as an important one in such work in competition with more modern, speedy and equally accurate processes of analysis.

DETERMINATION OF NITRIC NITROGEN BY REDUCTION TO AMMONIA

371. Classification of Methods.—When nitrogen is present in a highly oxidized state, *e. g.*, as nitric acid, it may be quickly and accurately estimated by reduction to ammonia. This action is effected, among other ways, by the reducing power of nascent hydrogen, and this substance may be secured in the active state by the action of an acid or alkali on a metal, or by means of an electric current. The processes depending on the use of a finely divided metal in the presence of an acid or alkali have come into general use within a few years, and are now employed generally instead of the more elaborate estimations depending on the combustion method by the use of copper oxid or in the colorimetric method with indigo.

The typical reaction which takes place in all cases is represented by the following equation:



The method will be considered under three heads; *viz.*, 1. Reduction in an alkaline solution; 2. Reduction in an acid solution; 3. Reduction by means of an electric current.

In the first class of processes the reduction and distillation may go on together. In the second class the reduction is accomplished first and the distillation effected afterwards, with the addition of an alkali. In the third class of operations the reduction is accomplished by means of an electric current and the ammonia subsequently obtained by distillation, or determined by nesslerizing. These processes may be applied to the nitrates or nitrites as such, or as occurring in rain and drainage waters and soil extracts. On account of the ease with which the analyses are accomplished, the short time required and the accuracy of the results, the reduction methods for nitrates have already commended themselves to analysts, and are quite likely to supersede all others for practical use where small yet weighable quantities of

nitrates are present. For the minute traces of nitrates found in rain and drainage waters, and in some soil extracts, the reduction method may also be applied, but in these cases the ammonia which is formed must be determined colorimetrically (nesslerizing) and not by distillation. The processes about to be described are especially applicable to the examination of fertilizers containing only small quantities of nitrates and of soils and waters rich in nitrates.

REDUCTION IN ALKALINE SOLUTIONS

372. Extraction of the Nitrates.—Place one kilogram of the dry soil or fertilizers poor in nitrates, calculated to water-free substance, on a percolator of glass or tin. Moisten the soil thoroughly with pure distilled water, and allow to stand for half an hour. Add fresh portions of pure distilled water until the filtrate secured amounts to one liter. If the first filtrate be cloudy before use it may be refiltered.

373. Qualitative Test for Nitrates.—Evaporate five cubic centimeters of the extract as obtained above in a porcelain crucible, having first dissolved a small quantity of pure brucin sulfate therein. When dry, add to the residue a drop of concentrated sulfuric acid free of nitrates. If the nitrate calculated as potassium nitrate does not exceed the two-thousandth part of a milligram, only a pink color will be developed; with the three-thousandth part of a milligram, a pink color with reddish lines; with the four-thousandth part of a milligram, a reddish color; with the five-thousandth part of a milligram, a distinct red color.

374. Sodium-Mercury Amalgam Method.—The reduction is effected by means of hydrogen evolved by the action of a preparation of sodium amalgam. Place 100 cubic centimeters of mercury in a flask of half a liter capacity; warm until paraffin will remain melted over the surface; drop successively in the paraffin-covered mercury pieces of metallic sodium of the size of a pea until 6.75 grams have united with the mercury. The amalgam thus prepared contains 0.5 per cent. of metallic sodium and may be preserved indefinitely under the covering of paraffin.

Estimation of the Nitrates.—Evaporate 100 cubic centimeters

of the soil extract to dryness on a steam-bath. Dissolve the soluble portions of the residue in 100 cubic centimeters of ammonia-free distilled water, filtering out any insoluble residue. Place the solution in a flask, add 10 cubic centimeters of sodium amalgam, stopper the flask with a valve which will permit the escape of hydrogen, and allow to stand in a cool room for 24 hours. Add 50 cubic centimeters of milk of lime and titrate the ammonia produced by distillation with standard acid and estimate as nitrogen pentoxid. Where the amount of ammonia is small, nesslerizing may be substituted for titration.

375. Method of the Experiment Station at Möckern.—The principle of this reaction is based on the reducing action exercised by nascent hydrogen on a nitrate, the hydrogen being generated by the action of soda-lye on a mixture of zinc dust and finely divided iron.⁵⁷

Ten grams of nitrate are dissolved in 500 cubic centimeters of water. Of this solution 25 cubic centimeters, corresponding to one-half gram, are placed in a distillation flask of about 400 cubic centimeters capacity, 120 cubic centimeters of water added, and about five grams of well washed and dried zinc dust and an equal weight of reduced iron. To the solution are added 80 cubic centimeters of soda-lye of 32° B. The flask is connected with the condensing apparatus and the distillation carried on synchronously with the reduction, the ammonia being collected in 20 cubic centimeters of titrated sulfuric acid. The distillation is continued from one to two hours, or until 100 cubic centimeters have been distilled, and the remaining sulfuric acid is titrated in the usual way. Soil extracts and sewage waters should be concentrated until they have approximately the proportion of nitrates given above.

376. The Halle Zinc-Iron Method.—For determining the nitrogen in Chile saltpeter the foregoing method is conducted at the Halle Station as follows:⁵⁸ Ten grams of the nitrate are dissolved in one liter and 50 cubic centimeters of the solution cor-

⁵⁷ Böttcher, *Die landwirtschaftlichen Versuchs-Stationen*, 1892, 41 : 165.

⁵⁸ Bieler und Schneidewind, *Die agricultur-chemische Versuchsstation, Halle a/S.*, 1892 : 50.

responding to half a gram of the sample, used for each determination. The apparatus employed is shown in Fig. 32. A mixture of five grams of zinc dust and an equal weight of iron filings is employed as the source of hydrogen. The reduction takes place in an alkaline medium secured by adding to the other materials mentioned 80 cubic centimeters of soda-lye of 1.30 specific gravity. The respective quantities of iron and zinc may be measured instead of weighed, as exact proportions are not required. After the addition of all the materials the flask is allowed to stand for an hour at room temperature. The distillation is then commenced and continued until at least 100 cubic centimeters of distillate have been collected. The receiving flasks are ordinary erlenmeyers, each of which contains 20

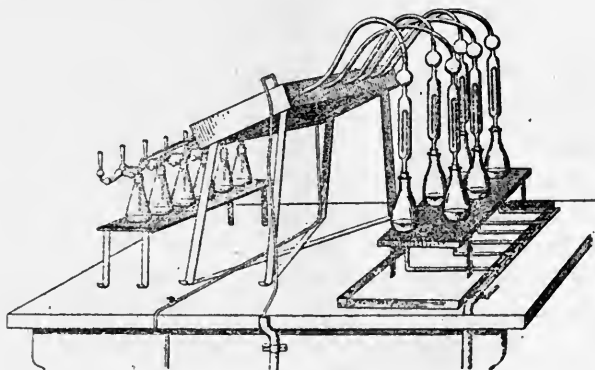


Fig. 32. Halle Nitric Acid Apparatus.

cubic centimeters of set sulfuric acid, as in the usual kjeldahl process. The receiving flasks are sealed with a few drops of water by the bulb tubes shown in the figure. After the end of the operation the water in each one of the bulb tubes is washed back into its proper flask with freshly boiled water. During the vigorous evolution of hydrogen at the beginning of the operation, some kind of safety arrangement is necessary to prevent the particles of soda-lye being carried over by the bubbles of that gas. The siphon bulb shown in the figure is found effective for this purpose. In this operation better results are obtained by condensing the escaping steam, and for this reason the block tin tubes are

conducted through a tank supplied with a current of cold water. The ends of the tubes should not dip below the surface of the liquid in the receivers. When the condensed liquid collects in considerable quantities in the safety tube the lamp should be extinguished under the flask, which permits the return of the liquid to the flask by means of the siphon. This should be done two or three times during the progress of the distillation to prevent a too high concentration of the soda-lye, thus endangering the flask. The excess of the acid in the receiver is determined by titration, as in the regular kjeldahl method. Blank determinations are made, from time to time, and corrections made in harmony therewith.

377. Investigations of Beck.—A late contribution to the analysis of Chile saltpeter is that of Beck.⁵⁹

Beck examined the direct method of Ulsch, subsequently described, and the indirect method which is so commonly employed by dealers, depending on the determination of the other principal ingredients and subtracting this from 100 to get the per cent. of nitrate of soda in the mixture. This last method is particularly unsatisfactory, since it gives 1.5 per cent. of sodium nitrate too much. The quantity of perchlorate which is present is also important and for technical purposes, such as the nitration of cellulose, etc., it is recommended not to use any sample which yields more than one per cent. of a sodium salt due to perchlorate.

Beck expresses the hope that the producers of Chile saltpeter in the future will cease to urge the use of the indirect method and will refrain from attacking the validity of the direct methods, and calls attention to the fact that the increasing possibility of producing nitric acid and nitrates directly from the atmosphere may supersede the necessity of using the natural salt.

The factors for calculating the percentage of nitric acid when it is reduced to ammonia may be based upon the number of cubic centimeters of half-normal sulfuric acid required for 10 cubic centimeters of a solution containing 33 grams of sodium nitrate in one liter. The factors are as follows:

⁵⁹ *Zeitschrift für analytische Chemie*, 1906, **45** : 669.

For N :	2.125 (log = 0.32783)
“ N ₂ O ₅ :	8.188 (log = 0.91318)
“ NaNO ₃ :	12.893 (log = 1.11318)

378. Method of Devarda.—The inconvenience due to slow action and other causes, arising from the use of pure metals in the reduction of nitrates to ammonia, has been overcome, to some extent, by Devarda, by use of an alloy, in a state of fine powder, consisting of aluminum, copper, and zinc.⁶⁰ The alloy consists of 45 per cent. of aluminum, 50 per cent. of copper, and five per cent. of zinc. In dissolving, the copper is left in a finely divided state, which is a great help in distillation in preventing bumping.

The analytical process is carried out as follows: The solution containing the nitrate, in quantity equivalent to about one-half gram of potassium nitrate, is placed in a flask having a capacity of about one liter, and diluted with 60 cubic centimeters of water and five cubic centimeters of alcohol, after which 40 cubic centimeters of caustic potash solution, of specific gravity 1.3 are added. From two to two and one-half grams of the alloy described above are introduced, and the flask attached to a condenser with a receiver containing standard acid. The connection between the flask and the condenser is made by means of a tube having on the limb next the flask a bulb filled with glass beads to prevent the contents of the flask splashing over into the receiver, and on the other limb another bulb to prevent the acid in the receiver finding its way into the distillation flask, should regurgitation occur. When the flask has been thus connected with the condenser it is gently heated for half an hour, at the end of which time the evolution of hydrogen will have slackened or ceased, and the distillation is then begun, at first cautiously, until the zinc of the alloy has completely dissolved, and then more vigorously, the time necessary being about 20 minutes from the time when the contents of the flask begin to boil. The distillate is caught in standard acid and the ammonia determined by titration of the residual acid in the ordinary way. It is to be noted that the strength of the alkali used is of importance, as, if it be too strong, the action on the alloy is unduly vigorous at the beginning of the

⁶⁰ Chemiker-Zeitung, 1892, 16 : 1952.

operation, and if too weak, the contents of the flask have to be heated overmuch, the result in both cases being the formation of a fine spray of caustic solution, which is very difficult to stop, even with complicated washing attachments to the distilling flask. The test analyses on pure nitrates are satisfactory. This method has been used with satisfaction in the laboratory of the Bureau of Chemistry, but does not appear to have any special advantage over the process of Ulsch, to be described further on.

379. **Variation of Stoklasa.**—Stoklasa has subjected the method of Devarda to a comparative test with the following methods:⁶¹

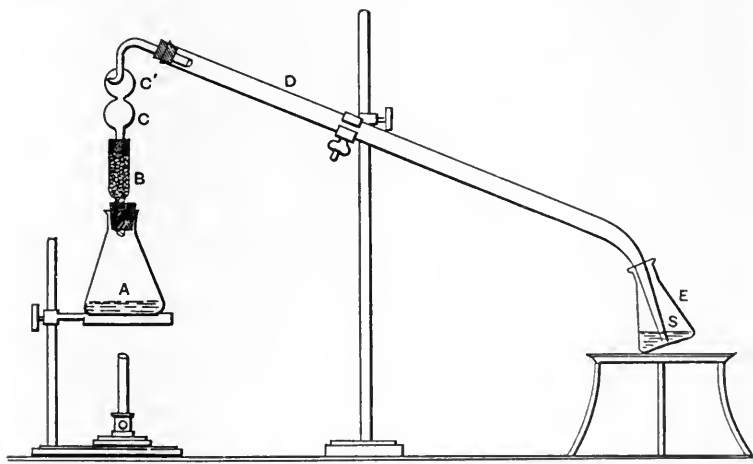


Fig. 33. Stoklasa's Nitric Acid Apparatus.

1. Wagner's schloesing-grandean method.
2. Lunge's nitrometer method.
3. Stutzer's method.

The reduction takes place in a copper erlenmeyer A, Fig. 33, in which, in addition to the solution containing the nitrate, are placed 200 cubic centimeters of water, 40 cubic centimeters of potassium hydroxid solution of 33° B., five cubic centimeters of alcohol, and finally two and one-half grams of the finely powdered devarda alloy. The distillate passes through a tube B filled with glass pearls and into the condenser D through the bulbs CC'.

⁶¹ Zeitschrift für angewandte Chemie, 1893, 6 : 161.

After the flask is connected with the distilling apparatus, it is gently warmed and the reduction is ended in about 20 minutes. The ammonia which is formed is distilled into E, containing the standard acid S, requiring about 20 minutes more. The comparative results given, show that the devarda method is equally accurate as any of the other methods mentioned, giving practically theoretical results.

In so far, however, as speed of an analysis is concerned, the first place is awarded to the lunge nitrometer method, with which a complete analysis can be made in from 30 to 40 minutes. In the second rank, so far as speed is concerned, the devarda method is recommended. All the methods give accurate results.

380. Method of Sievert.—Two grams of potassium or sodium nitrate are dissolved, and the solution made up to 1000 cubic centimeters.⁶² Fifty cubic centimeters of the solution are placed in a 600 cubic centimeter flask and diluted with 50 cubic centimeters of water, and from 18 to 20 grams of caustic alkali added. After the alkali is dissolved, 75 cubic centimeters of 96 per cent. alcohol are added and a few pieces of bone-black to prevent foaming. From 10 to 15 grams of zinc or iron dust are added to the flask which is closed and connected with a U-tube holding about 200 cubic centimeters, which contains about 10 cubic centimeters of normal sulfuric acid. This U-tube is kept cool by being immersed in water. The whole mixture is allowed to stand for three or four hours and the alcohol is distilled slowly, the ammonia formed by the reduction of the nitrates being carried over with it. The distillation lasts for about two hours. The contents of the U-tube are carefully rinsed into a dish and the excess of sulfuric acid titrated with one-fourth normal soda-lye.

For soil extracts and substances containing unknown quantities of nitric acid, a preliminary test will indicate approximately the amount thereof, and this will be an indication for the quantity to be used in the analysis.

The method of Stutzer differs from the foregoing in the employment of aluminum dust instead of iron or zinc.⁶³ The reducing

⁶² Liebig's *Annalen der Chemie*, 1862, 125 : 293.

⁶³ *Zeitschrift für angewandte Chemie*, 1890, 3 : 695.

power of aluminum, however, varies greatly according to the method in which the metal has been prepared. Pure aluminum prepared by the electric method, reduces the nitric acid much less vigorously than the metal prepared by the older methods of fusion with sodium. For this reason the method of Stutzer is not to be preferred to that of Sievert.

REDUCTION IN AN ACID SOLUTION

381. **Variation of the Sodium-Amalgam Process.**—This method is described by Monnier and Auriol.⁶⁴

The principle of the operation depends on the reduction of

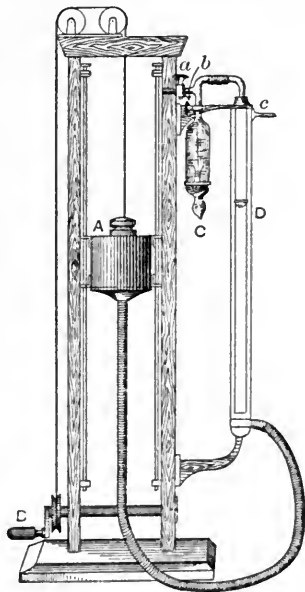


Fig. 34. Apparatus of Monnier and Auriol.

the dissolved nitrate by titrated sodium amalgam in presence of an acid, and the estimation of the quantity of nitric acid present from the deficit in the volume of hydrogen. The apparatus employed is conveniently mounted as shown in Fig. 34. The brass vessel A is movable by means of the cord on the pulley B, in such

⁶⁴ Archives des Sciences physiques et naturelles, Genève, 1894, [3], 31 : 352.

a way as to be fixed at any required altitude. It is filled with water and connected by a rubber tube to the cooling tube D. Within the cooling tube there is a graduated cylinder open at its lower end. Its upper end is connected directly with the apparatus C. The cooling tube D has a small side tube *c* near its upper end, by means of which the air can enter or escape when the position of A is changed. The apparatus C, in which the reaction takes place, is a glass cylinder. Its upper end is continuous with the T-tube provided with the stop-cocks *a* and *b*. One arm of the T permits connection with the graduated measuring tube by means of a rubber union. The lower end of C is closed with a large hollow ground-glass stopper, carrying a small receptacle within, so that it forms two separate water-tight compartments, open at the top.

The sodium amalgam is prepared as follows:

In a clay crucible are heated 400 grams of mercury, and, little by little, with constant stirring, four grams of dry sodium are added. When cold, the amalgam is placed in a burette, having a ground-glass stopper, and covered with petroleum. The strength of the amalgam is established in the following manner. A small glass thimble, ground even at the top, is filled with the amalgam and struck off even with a ground-glass straight edge. In this way the same quantity of amalgam is taken for each test. This measured portion of the amalgam is placed in the inner vessel of the glass stopper to C. Ten cubic centimeters of water, containing 60 centigrams of tartaric acid, are placed on the outer ring of the glass stopper, which is then inserted, well oiled, in C, closing it air- and water-tight. The tartaric acid solution also carries a piece of litmus paper, so that its constant acidity may be insured. The vessel A is fixed in a position which brings the water in the graduated burette and tube D exactly to the 0 mark. The cock *a* is closed, *b* opened, and C is inverted until all the amalgam is poured into the solution of tartaric acid. The evolved hydrogen mixed with the air contained in the apparatus, is passed into the graduated burette. After 15 minutes, the reaction is ended. The water level within and without the graduated tube is restored

and the volume of gas evolved noted and reduced by the usual tables to 0° and 760 millimeters pressure of the barometer.

An amalgam prepared as above gives about three cubic centimeters of hydrogen for each gram. The thimble holds from 12 to 15 grams.

The estimation of nitric acid is made in a solution containing about one-tenth per cent. of nitrate. Ten cubic centimeters are used, to which six-tenths gram of tartaric acid is added, and placed in the outer part of the glass stopper. The rest of the process is conducted exactly as described above. The deficit in hydrogen is calculated to nitrogen pentoxid.

The reduction by sodium amalgam is not so convenient a form of estimating nitric acid as many of the other forms of using nascent hydrogen. As practiced by calculating from the deficit of hydrogen, however, it has some advantages by reason of the fact that no heating is required. The presence of organic neutral bodies, or even those of an acid nature, like humus, does not, therefore, interfere with the work. Likewise, mineral bodies in solution, which are not reduced by nascent hydrogen, do not interfere with the accuracy of the reaction.

382. Method of Schmitt.—In the method of Schmitt 40 cubic centimeters of glacial acetic acid are placed in a flask of 600 cubic centimeters content, and 15 grams of a mixture of zinc and iron dust added.⁶⁵ To this quantity of the solution containing the nitrate, representing about half a gram of the pure nitrate, is added with constant shaking, in portions which do not evolve hydrogen too rapidly. After about 15 minutes when the evolution of hydrogen has somewhat diminished, an additional 15 grams of the metal dust are added. If the contents of the flask become thick they are diluted with water. The reduction is complete in from 30 to 40 minutes. The contents of the flask are saturated with enough soda-lye not only to neutralize the excess of acetic acid, but to keep the zinc hydroxid also in solution. For this purpose about 200 cubic centimeters of soda-lye of 1.25 specific gravity are necessary. The ammonia is obtained by distillation into standard acid in the usual way.

⁶⁵ Chemiker-Zeitung, 1890, 14 : 1410.

The flask is covered during the reduction to prevent loss by spraying. It must be noted that it is essential that the iron be finely divided; it is mixed with the powdered zinc in equal parts.

The total nitrogen can be determined in guanos and nitrate mixtures by the following simple alteration in procedure: One gram of the substance is dissolved in water, five cubic centimeters of glacial acetic acid, and from two to three grams of the mixed metallic powder added, and the whole gently heated for 10 or 15 minutes. After the contents of the flask have cooled, 25 cubic centimeters of sulfuric acid are cautiously added in small portions, undue frothing being restrained by the addition of a fragment of paraffin wax. The acetic acid is driven off by heating, and the remaining contents of the flask boiled until the organic matter is completely decomposed as in the kjeldahl process. About two hours boiling is required. Neutralization and distillation are accomplished as in the ordinary manner. The method is also applicable to the determination of nitrates in drinking water, provided nitrites and ammonia be absent.

383. Method of Ulsch.—In practice the method of Ulsch has come into general use.⁶⁶

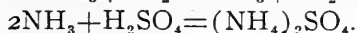
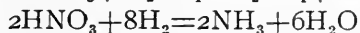
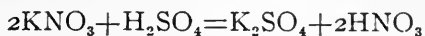
For the determination of nitrogen in nitrates by this method half a gram of saltpeter or four-tenths gram of sodium nitrate is dissolved in 25 cubic centimeters of water, in a flask with a content of about 600 cubic centimeters. Five grams of iron reduced by hydrogen, and 10 cubic centimeters of sulfuric acid diluted with two volumes of water are then added to the flask. To avoid mechanical losses during the evolution of hydrogen, a pear-shaped glass stopper is hung in the neck of the flask. After the first violent evolution of hydrogen has passed, the flask is slowly heated until, in about four minutes, it is brought to a gentle boil. The boiling is continued for about six minutes when the reduction is complete. About 50 cubic centimeters of water are added, an excess of soda-lye and a few particles of zinc; then the ammonia is distilled and collected in standard acid in the usual way.

The method of Ulsch can also be applied, according to Fricke,

⁶⁶ *Chemisches Central-Blatt*, 1890, 2 : 926.

to the analysis of nitrates contained in drinking and drainage waters, and it is regarded by him as one of the best methods to be employed in such investigations.⁶⁷

The method of Ulsch has given entirely satisfactory results, and is generally used in preference to other methods in cases where a considerable quantity of nitrates is present. It is based on the following reactions:



384. Ulsch Method Applicable to Mixed Fertilizers.—The method of Ulsch, which is found to give good results with pure nitrates or with nitrates in the absence of other forms of nitrogen, may also be adapted to mixed fertilizers containing nitrogen in more than one form. Street has developed such a method and shown, by analytical data, that it is applicable in a great number of cases.⁶⁸ The variation is based on the substitution of magnesia for soda in the distillation and is carried on as follows:

Place one gram of the sample in a half-liter flat-bottomed flask. Add about 30 cubic centimeters of water, one gram of reduced iron, and 10 cubic centimeters of sulfuric acid diluted with an equal volume of water, shake well, and allow to stand for a short time. This will remove the danger of an explosion caused by the otherwise violent action which takes place. Close the neck of the flask with a rubber stopper through which passes a glass dropping-bulb filled with water. The flask having been stoppered, place it on a slab to which a moderate heat is applied. Allow the solution to come slowly to a boil and then boil for five minutes and cool. Add about 100 cubic centimeters of water, a little paraffin, and about five grams of magnesium oxid. Boil for 40 minutes, after which time all the ammonia will be distilled, and collect the ammonia in set acid.

The magnesia causes a slight frothing, which can easily be controlled by adding a little paraffin and by bringing to a boil very gradually. Fully 40 minutes are necessary to distil all the

⁶⁷ *Zeitschrift für angewandte Chemie*, 1891, 4 : 241.

⁶⁸ *Division of Chemistry, Bulletin* 35, 1892 : 88.

ammonia. Tests were made after boiling for 30 minutes and traces of ammonia were still found; after 40 minutes these traces entirely disappeared.

The method is a quick one. One man can easily do six determinations at a time, and these six determinations can be made in but a little over an hour. Magnesia gives results closely agreeing with theory and causes a very slight frothing, which can be easily controlled. One gram of reduced iron is sufficient in all ordinary complete fertilizers.

Magnesia is preferred to caustic soda in the distillation because it produces less frothing and by reason of the danger of some of the soda-lye being carried over mechanically and thus tending to produce an error of a plus nature. In the use of magnesia, assurance must be had that it is strongly in excess. Being less active in its effects, a longer time for the distillation must be taken than when soda-lye is used. The modified ulsch method just described is recommended provisionally, and with the expectation that each analyst will ascertain its true merits before allowing it to displace longer approved processes.

385. Krüger's Method for Nitric Acid.—About 0.3 gram of the nitrate dissolved in water is mixed with 20 cubic centimeters of a hydrochloric acid solution of stannous chlorid holding 150 grams of tin per liter.⁶⁹ One and a half grams of spongy tin prepared by the action of zinc on stannous chlorid are added. The flask containing the mixture is heated until the tin is dissolved, by which time the nitric acid is completely reduced. The subsequent distillation and titration are accomplished as usual. In the case of nitro and nitroso compounds, after the solution of the tin, 20 cubic centimeters of sulfuric acid are added and heated until sulfuric vapors escape. After cooling, the amido-substances formed are oxidized by potassium bichromate before the distillation takes place.

Krüger also estimates the nitrogen in benzol, pyridin, and chinolin derivatives by dissolving them in sulfuric acid, using from 0.2 to 0.8 of a gram of the alkaloidal bodies, and, after cooling the solution, oxidizing by adding finely powdered potas-

⁶⁹ *Berichte der deutschen chemischen Gesellschaft*, 1894, **27** : 609, 1636.

sium bichromate. About half a gram more of the potassium bichromate should be used than is necessary for the oxidation of the substances in solution. The entire oxidation does not consume more than from 15 to 30 minutes.

REDUCTION OF THE ELECTRIC CURRENT

386. Method of Williams-Warington.—This process is applicable to solutions or extracts of fertilizers, soils, etc., and rain or drainage waters containing only a small amount of nitrates. From the losses which naturally occur during the evaporation of water, even with all the precautions usually observed, Warington was led to try some method for the determination of nitrates and nitrites in waters without previous concentration.⁷⁰ The reduction of these bodies by the copper-zinc couple formed the basis of these experiments, and they resulted in the following method of manipulation, which is based on a process devised by Williams.⁷¹

The method consists in boiling rapidly one liter of the solution of a fertilizer or rain water in a retort, with a little magnesia previously raised to a low red heat and then washed, until 250 cubic centimeters have distilled. The residue is made up to 800 cubic centimeters, transferred to a wide-mouthed, stoppered bottle supplied with strips of copper and zinc forming electric couples, and set aside, at a temperature of from 21° to 24°, for three days. A measured portion of the solution is distilled and the ammonia determined in the distillate by nesslerizing.

This plan has two advantages: First, the ammonia, as well as the nitrogen as nitrates and nitrites, can be determined in the course of the same operation and in the same sample of the solution. For this purpose it is only necessary to fit the retort to an efficient condenser to remove all ammonia from the apparatus by boiling distilled water in the retort before introducing the solution. The distillate of 250 cubic centimeters obtained as described above, is well mixed and the ammonia determined in from 25 to 100 cubic centimeters thereof, diluted to 150 cubic centimeters with ammonia-free water. The nitrogen, as nitrates

⁷⁰ *Journal of the Chemical Society*, 1889, **55** : 538.

⁷¹ *Journal of the Chemical Society*, 1881, **39** : 100.

and nitrites, is determined directly and alone. The error of the determination is as small as nesslerizing admits of, since it is possible, if necessary, to distil until the full amount of ammonia is obtained.

The determination of nitric nitrogen, in a given sample, by the above method gave a mean quantity of product of 0.162 part per million, while the determination, in the same sample, by the modified schloesing method, gave 0.125 part per million. This result confirms the supposition that in the complete evaporation necessary to the manipulation of the schloesing method there is a loss of nitrogen.

387. Nitrogen in Rain Water.—The amount of nitrogen as nitrates and nitrites in the rain water at Rothamstead, for the 12 months ending April 1, 1888, was found, by the schloesing method, to be 0.614 pound per acre, the total rainfall being 21.96 inches. For the year ending April 1, 1889, by the copper-zinc method, it amounted to 0.917 pound per acre, the total rainfall being 29.27 inches. The amounts found in other localities are quite different from the above, as, for instance, the mean of seven stations in Germany for 13 years, beginning in 1864, shows 10.18 pounds of nitrogen per acre. The average amount for 10 years at the observatory of Mont Sauris, near Paris, shows 12.36 pounds of nitrogen per acre. The average for three years at Lincoln, as determined by Professor G. Gray, shows 1.6 pounds of nitrogen per acre per annum. At Tokio, in Japan, Kellner found, for one year, 1.02 pounds per acre.

388. Determination of the Ammonia.—The method used at Rothamstead is to make one determination of ammonia in the whole of the distillate obtained, the strength of which is regulated by varying the amount introduced into the retort, so that it shall be equal to about two cubic centimeters of the standard ammonia solution. A 150 cubic centimeter cylinder is first filled with the rain water, and 50 cubic centimeters of nessler reagent added. The depth of tint indicates what quantity of rain water will be required for distillation. This having been determined, the appropriate volume of the rain water, provided it does not exceed 600 cubic centimeters, is placed in the retort described.

above, and the distillation continued until the 150 cubic centimeter cylinder is filled. The titration is made in the usual way.

389. Preparation of the Copper-Zinc Couple.—For 800 cubic centimeters of boiled rain water, prepared as described, six strips of zinc foil, four inches long by one and a quarter inches wide, are bent at right angles along their center to obtain stiffness. The zinc strip is cleansed and coated with copper by washing in a series of five beakers containing, respectively, dilute solution of sodium hydroxid, very dilute sulfuric acid, a three per cent. solution of copper sulfate, ordinary distilled water, and distilled water free from ammonia. Through these five beakers the zinc foil is successively passed. It is rinsed both after the alkali and the acid, but after the copper has been deposited, the strips are simply drained and carefully placed in the distilled water, it being difficult to rinse without removing the copper. The couples should be entirely submerged when placed in the rain water. The strips should remain in the copper sulfate solution long enough to be well covered with copper.

390. Substitution of an Aluminum-Mercury Couple for Copper-Zinc.—Ormandy and Cohen have proposed to use an aluminum-mercury couple for the copper-zinc in the process described above.⁷²

This couple acts more quickly than the copper-zinc, and the results are equally accurate. Nitrites are reduced in about one hour by this apparatus, while the zinc-copper couple of Gladstone and Tribe requires about six times as long. Aluminum foil, free of grease, should be used. The foil should be heated over a bunsen just before amalgamation. The clean, very thin foil is coated with mercury by shaking with a concentrated solution of mercuric chlorid. It should be prepared immediately before use.

The amalgamated foil is introduced into the sample of solution to be analyzed, and left until all the aluminum is converted into oxid. The presence of the oxid favors the prevention of bumping during the subsequent distillation. The distilled ammonia, collected in dilute acid, is determined by nesslerizing, the free

⁷² Journal of the Chemical Society, 1890, 57 : 811.

ammonia in the sample having been previously determined. The increase in ammonia is due to nitrates or nitrites reduced by the couple.

IODOMETRIC ESTIMATION OF NITRIC ACID IN NITRATES

391. Method of De Koninck and Nihoul.—This process is applicable only in the absence of organic bodies and other reducing agents.

The principle on which it rests, as applied by McGowan, is as follows⁷³

When a fairly concentrated solution of a nitrate is warmed with an excess of pure, strong hydrochloric acid, the nitrate is completely decomposed, and the production of nitrosyl chlorid and chlorin is quantitative. The reaction, as shown by Tilden, is represented by the following equation:⁷⁴



One molecule of nitric acid thus yields two atoms of chlorin and one molecule of nitrosyl chlorid capable of setting free three atoms of iodin. The iodin can be estimated in the usual manner by titration with sodium thiosulfate. The nitrosyl chlorid is decomposed by the potassium iodid, nitric oxid escaping.

The apparatus employed is shown in Fig. 35.

A is a small, round-bottomed flask, into the neck of which a glass stopper *x* is accurately ground. The capacity of the bulb is about 46 cubic centimeters, and the length of the neck, from *x* to *y*, 90 millimeters. The first condenser is a simple tube, slightly enlarged at the foot into two small bulbs.⁷⁵ The length from *a* to *b* is 300 millimeters, from *b* to *c* 180 millimeters, and from *e* to *f* 30 millimeters. The capacity of the bulb B is 25 cubic centimeters, and the total capacity of the two bulbs and tube, up to the top of C, 41 cubic centimeters. This condenser is immersed up to the level of *c*, in a beaker of water. D is a geissler bulb apparatus, E is a calcium tube, filled with broken glass, which acts as a tower and *g* is a small funnel, attached by rubber and clip

⁷³ Journal of the Chemical Society, 1891, 59 : 530.

⁷⁴ Journal of the Chemical Society, 1874, 27 : 630; 1875, 28 : 514.

⁷⁵ Sutton, Volumetric Analysis, 9th Edition, 1907 : 77.

to the branch T-tube *h*. Between the T-tube *i* and the wash-bottle for the carbon dioxid is placed a short piece of glass tubing, *s*, containing a strip of filter paper, slightly moistened with iodid of starch solution. This tube *s* is really hardly necessary, as no chlorin escapes backwards if a moderate current of carbon dioxid is kept passing, but it serves as a check. A glance at the joints *o*, *p*, and *q*, which are of narrow india-rubber tubing, is sufficient to show that, by using this arrangement, practically no rubber is exposed to the action of the chlorin. The tiny piece

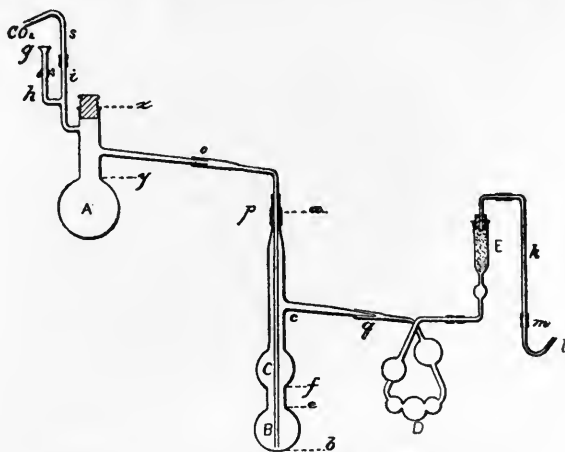


Figure 35. McGowan's Apparatus for the Iodometric Estimation of Nitric Acid.

of rubber tubing at the joint *o* may be done away with, the narrower tube there being accurately ground into the wider one; this makes the condensing apparatus practically perfect.

The actual operation is performed in the following manner:

The evolution flask is washed and thoroughly dried, and the nitrate (say, about 0.25 gram of potassium nitrate) is introduced from the weighing tube. Two cubic centimeters of water are added, and the bulb is gently warmed, so as to bring the nitrate into solution, after which the stopper of the flask is firmly inserted. About 15 cubic centimeters of a solution of potassium iodid (one in four) are run into the first condensing tube, any iodid adhering to the upper portion of the tube being washed down with a little water, and five cubic centimeters of the same solution, mixed

with from eight to 10 cubic centimeters of water, are sucked into the geissler bulbs while the glass in the tower E is also thoroughly moistened with the iodid. The geissler bulbs should be so arranged that gas bubbles through only the last of them, the liquid in the others remaining quiescent.

All the joints having been made tight the carbon dioxide is turned on briskly and passed through the apparatus until a small tubeful collected at *l*, over caustic potash solution, shows that no appreciable amount of air is left in it. The small outlet tube *l* is replaced by a tube, filled with broken glass which has been moistened with the above-mentioned iodid solution, and closed by a cork through which an outlet tube passes, the object of this trap tube being to prevent any air getting back into the apparatus. The brisk current of carbon dioxide is continued for a minute or two longer, so as to practically expel all the air from this last tube. The stream of gas is now stopped for an instant, and about 15 cubic centimeters of pure concentrated hydrochloric acid, free from chlorine, run into A through the funnel *g* (into the tube of which it is well to have run a few drops of water before beginning to expel the air from the apparatus), and A is shaken so as to mix its contents thoroughly. A slow current of carbon dioxide is again turned on (one to two bubbles through the wash-bottle per second), and A is gently warmed over a burner. It is a distinct advantage that the reaction does not begin until the mixed solutions are warmed, when the liquid becomes orange-colored, the color again disappearing after the nitrosyl chloride and chlorine have been expelled. The warming is very gentle at first in order to make sure of the conversion of all the nitric acid, and also because the first escaping vapors are relatively very rich in chlorine; afterwards the liquid in A is briskly boiled. A very little practice enables the operator to judge as to the proper rate of warming. When the volume of liquid in A has been reduced to about seven cubic centimeters (by which time it is again colorless), the stream of carbon dioxide is slightly quickened and the apparatus allowed to cool a little. The burner is now set aside for a few minutes, and two cubic centimeters more of hydrochloric acid, previously warmed in a test-tube, run in gently

through *g*; there is no fear either of the iodid solution running back, or of any bubbles of air escaping through *y* if this is done carefully. This is a precautionary measure, in case a trace of the liberated chlorin might have lodged in the comparatively cool liquid in the tube *h*. The carbon dioxid is once more turned on slowly and the liquid in *A* is boiled again until it is reduced to about five cubic centimeters. It is now only necessary to allow the apparatus to cool, passing carbon dioxid all the time, after which the contents of the condensers are transferred to a flask and titrated with thiosulfate. At the end of a properly conducted experiment, the glass in the upper part of tower *E* should be quite colorless and there should be only a mere trace of iodine showing in the lower part of the tower, while the liquid in the last bulb of the Geissler apparatus ought to be pale yellow. During the operation, the stopper of *A* and the various joints can be tested from time to time by means of a piece of iodid of starch paper, and before disjoining it is well to test the escaping gas (say at *m*) in the same way, to make sure that all nitric oxid has been thoroughly expelled.

The method is capable of giving accurate results, but it is not preferable to the reduction or colorimetric processes.

392. Method of Gooch and Gruener.—The principle on which this method rests depends on the decomposition of a nitrate in presence of a hot saturated solution of manganous chlorid and hydrochloric acid in an atmosphere of carbon dioxid.⁷⁶ The products of decomposition are passed into a solution of potassium iodid and the liberated iodine is titrated with standard sodium thiosulfate. The products of the reaction are chlorin, nitric oxid, and possibly nitrosyl chlorid, and under proper precautions the iodine set free is quantitatively proportional to the weight of nitrate decomposed. The manganous mixture is acted on slowly at ordinary temperatures, but on heating, the nitrate is decomposed with the formation of a higher manganese chlorid and nitric oxid. When the heat is continued a sufficient length of time the chlorin from the higher chlorids is evolved and only manganous chlorid remains. During the heating the color of

⁷⁶ American Journal of Science, 1892, [3], 44 : 117.

the solution passes from green to black and at the end the green color is restored. The apparatus employed is shown in Fig. 36.

A plain pipette bent as is shown in the figure serves as the generating flask and for the attachment on the one hand to the carbon dioxid apparatus and on the other to the system of absorption bulbs for holding the potassium iodid. The latter should be glass, sealed to the evolution bulb of the pipette to prevent the action of the evolved gases on organic materials. The point of the potassium iodid apparatus is drawn out so as to be pushed well into the second receiver, being held in place by a

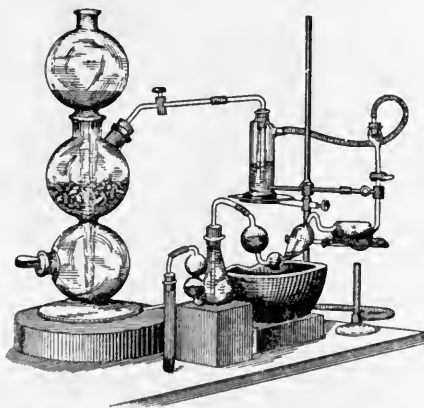


Figure 36. Apparatus of Gooch and Gruener.

piece of rubber tubing. The third receiver acts simply as a trap to exclude the air from the absorption apparatus. The first receiver contains in solution three grams, the second one, and the third a fraction of a gram of potassium iodid for each one tenth of a gram of nitrate used. During the reaction the first receiver is kept cool by immersion in water. Before connecting the apparatus with the carbon dioxid generator the solution of manganous chlorid and afterwards the nitrate solution are drawn into the bulb of the pipette by gentle suction. After connecting the apparatus the current of carbon dioxid is started and kept up until all the air is expelled. Heat is then applied to the bulb of the pipette and the distillation continued until all the liquid has passed over. At the end of the reaction the contents

of the receivers are united by disconnecting the apparatus from the carbon dioxid generator and passing water through the pipette. The introduction of the manganous chlorid into the mixture does not interfere with the titration of the iodine. This is accomplished in the usual way with sodium thiosulfate using starch as an indicator. The quantity of material used contains about the amount of nitric acid that is found in two-tenths of a gram of potassium nitrate. This method, so similar to the preceding, is somewhat less complex, and, to that extent, preferable to it.

ESTIMATION OF NITRIC ACID BY COLORIMETRIC COMPARISON

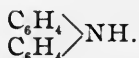
393. **Delicacy of the Method.**—The remarkable delicacy of those methods of chemical analysis which depend on the production of a pronounced color, which can be compared with that produced by a known quantity of a given substance, has been long illustrated by the nesslerizing process for the estimation of ammonia. By such methods minute amounts of substances can be quantitatively determined with great accuracy, when they would escape all effort for their estimation by gravimetric methods. Processes based on this principle are, therefore, peculiarly applicable to the detection and estimation of oxidized nitrogen in waters, fertilizer and soil extracts, whether they be present as nitric, nitrous, or ammoniacal compounds. The very delicacy of the process is the chief objection to its use since, except in the most experienced hands, and without the observance of all of the conditions of manipulation, errors may vitiate the results.

In the following paragraphs will be given with sufficient detail for the needs of the analyst, the principles and practice of the colorimetric comparison methods which have been approved as best by the experience of analysts. These methods are applicable especially to cases in which only minute quantities of the substances looked for are present, and where celerity of determination is especially desirable. They are, therefore, of especial value in the analysis of rain, drainage, and irrigation waters, and of soil and fertilizer extracts poor in oxidized nitrogen.

394. **Hooker's Method.**—The quantitative action in this method depends upon the deep green coloration given by nitric acid, when dissolved in sulfuric acid and carbazol.⁷⁷ Other oxidizing bodies, such as iron, chlorin, bromin, chromic acid, etc., give the same reaction, but not in such a prominent manner. Such bodies, with the exception of chlorin and iron, are not often found in the solutions with which the agricultural chemist is occupied. In the application of the process, iron, if present, in quantities greater than one-tenth part per one hundred thousand, must be removed. Chlorids, also, even when present in very small quantities, interfere with the delicacy of the reaction and must be removed. Easily destructible organic matter tends to lower the result, but not materially, unless present in large excess. Calcium carbonate and sulfate, soda, and other alkalis, in the quantities in which they are usually present in such solutions, do not affect the result.

The following reagents are required:

1. Concentrated sulfuric acid.
2. An acetic acid solution of carbazol; diphenylimid,



3. A sulfuric acid solution of carbazol.
4. Standard solutions of potassium nitrate.
5. A solution of aluminum sulfate.
6. A solution of silver sulfate.

1. The sulfuric acid used for all purposes in the process should be entirely free from nitrogen oxids. It may be readily tested by dissolving in it a small quantity of carbazol. If the solution be at first golden-yellow or brown, the acid is sufficiently pure; if it be green or greenish, another and better sample must be found. It is essential also that the specific gravity of the acid be fully 1.84, and it is well to ascertain that this is really the case.

2. The acetic acid solution is prepared by dissolving six-tenths gram of carbazol in about 90 cubic centimeters of strongest acetic acid, by the aid of gentle heat. It is allowed to cool, and is then made up to 100 cubic centimeters by the further addition

⁷⁷ American Chemical Journal, 1889, 11 : 249.

of acetic acid. The exact strength of this solution, is of no material importance to the success of the process, and the above proportions have been selected principally because they are convenient. The solution will remain unchanged for several months. The use of this solution merely facilitates the preparation of that next described, which will not keep, and has, consequently, to be freshly prepared for each series of determinations.

3. The sulfuric acid solution of carbazol is easily made in a few seconds, but it is advisable to allow it to stand from one and one-half to two hours before using. It is prepared by rapidly adding 15 cubic centimeters of sulfuric acid to one cubic centimeter of the above described acetic acid solution. This quantity usually suffices for from two to three nitrate estimations. When freshly prepared it is golden-yellow or brown; it changes gradually, however, and in the course of one and one-half or two hours it becomes olive-green. This change is probably due to traces of oxidizing agents, which occur in the sulfuric and acetic acids, and which, although not present in sufficient quantity to act immediately, gradually bring about the reaction described. The greenish color does not interfere with the process, as might at first be supposed; on the contrary, the solution is not sensitive to small quantities of nitric acid until it has undergone the change to olive-green, and it is for this reason that it should be prepared about two hours before required for use. This solution may be thoroughly depended on for six hours after preparation. The intensities of color produced by the more concentrated solutions of nitrates after this time gradually approach each other and become ultimately the same.

4. The standard solutions of potassium nitrate are very readily prepared. The solutions which are to be compared directly with the waters examined, may be prepared as required, but if many determinations are to be made with a variety of samples, it will be found best to prepare a complete series, differing from each other by 0.02 part nitrogen in 100,000. This series may include solutions containing quantities of nitrogen in 100,000 parts, represented by all the odd numbers from 0.03 up to 0.39. It will be found convenient to prepare them in quantities of 100 cubic

centimeters at a time, from a stock solution of potassium nitrate which contains 0.00001 gram nitrogen, or 0.000045 nitric acid in one cubic centimeter. Each cubic centimeter of this solution, when diluted to 100 cubic centimeters, represents 0.01 nitrogen in 100,000, and consequently if it is desired to make a solution containing 0.35 part nitrogen in 100,000, 35 cubic centimeters are made up to 100 cubic centimeters, and so on. The solution of potassium nitrate (b) is best prepared from a stronger one (a) containing 0.0001 gram nitrogen to the cubic centimeter, or 0.7214 gram potassium nitrate to the liter; 100 cubic centimeters of (a) made up to one liter give the solution (b). It is obvious that the series of solutions above described could be made directly from (a), but by first making (b) greater accuracy is secured.

5. For purposes which will be presently described, a solution of aluminum sulfate is required, containing five grams to the liter. The salt used must be free from chlorin and iron; and the solution should give no reaction when tested with carbazol.

6. The solution of silver sulfate is required for the removal of chlorin from the water or soil extract to be examined. It is prepared by dissolving 4.3943 grams of the salt in pure distilled water and making up to one liter. The sulfate is preferably obtained by dissolving metallic silver in pure sulfuric acid. The solution should be tested with carbazol in the same way as will be presently described for water; if perfectly pure, no reaction will be obtained. As silver sulfate is often prepared by precipitation from the nitrate, it is very apt to contain nitric acid, and consequently, if the source of the salt be unknown, this test should on no account be omitted. The analytical process is carried on as follows:

Two cubic centimeters of the solution containing the minute quantity of nitric acid are carefully delivered by means of a pipette into the bottom of a test-tube; four cubic centimeters of sulfuric acid are added, and the solution thoroughly mixed by the help of a glass rod. The test-tube is then immersed in cold water, and when well cooled one cubic centimeter of the sulfuric acid solution of carbazol is added, and the whole again mixed as before. The intensity of the color is observed, and a little

experience enables a fairly good opinion to be formed of the quantity of nitric acid present. Suppose that the sample be roughly estimated to contain about 0.15 part nitrogen per 100,000; in such a case solutions of potassium nitrate containing 0.11, 0.15, 0.19 part nitrogen are selected from the series. Two cubic centimeters are taken from each and treated, side by side, with a fresh quantity of the sample, precisely as described for the preliminary experiment, the various operations being performed as nearly simultaneously as possible with each of the samples, and under precisely similar conditions. Two or three minutes after the carbazol has been added, the intensity of the color of each is observed. If that given by the sample is matched by any of the standard solutions, the estimation is at an end. Similarly, if it falls between two of these, the mean may be taken as representing the nitrogen present in cases in which great accuracy is not required. If this be done, the maximum error will be 0.02 part nitrogen, or 0.09 part nitric acid per 100,000. If greater exactness be required, or it be found that the color given by the sample is either darker or lighter than that given by all the standard solutions, a new trial must be made. In such a case the sample must be again tested simultaneously with the solutions with which it is to be compared. This is rendered necessary principally for the reason that the shade of the solutions to which the carbazol has been added is apt to change on standing. Hence it is desirable that the sample, and the standard potassium nitrate with which it is to be compared, should have the carbazol added at as nearly the same time as possible. When finally the color falls between that given by any two consecutive members of the standard potassium nitrate series, the estimation may be considered at an end, and the mean of these solutions taken as representing the nitrogen present.

The greatest neatness should be observed in all steps of the analysis. The quantity of nitric acid to be estimated is so small that if the greatest care be not exercised throughout, sources of error may be readily introduced. The test-tube should be rinsed out with nitrate-free water before being used, and dried. The tint is determined by looking through the tube and not through

the length of the column of liquid. A comparison camera such as is described in Volume I, page 591, may be used to advantage.

Influence of Nitrites.—If the quantity of nitrous acid in the water is known a correction can be applied for nitrates by deducting one-fifth of the number found for nitrites when estimated as nitrates.

Influence of Iron.—Although ferrous salts give no reaction with carbazol, nitrates are apt to be overestimated in their presence. On the other hand, ferric compounds, like other oxidizing agents, may give a characteristic green color with carbazol. In all cases when iron is present in any considerable quantity it is best to remove it by rendering the sample slightly alkaline, evaporating to dryness, and redissolving the soluble residuc until the solution reaches the original volume.

Influence of Chlorids.—The presence of chlorids furnishes by far the most serious source of error in the process by intensifying the action of the nitric acid. If, however, nitrates be absent, chlorids give no reaction with carbazol. The chlorids are removed by the standard silver sulfate solution, the quantity of chlorids present having been first determined by a standard silver nitrate solution. For this purpose an ordinary sugar flask can be employed, marked at 100 and 110 cubic centimeters. This flask is filled to the 100 cubic centimeter mark with the sample to be examined; the necessary quantity of silver sulfate is added and then two cubic centimeters of the solution of aluminum sulfate, previously described, and the contents of the flask brought up to 110 cubic centimeters by the addition of pure distilled water. The whole is shaken up and filtered, the first portion of the filtrate being rejected. The aluminum sulfate, by reacting with the carbonates usually present in the water and producing the precipitation of alumina, facilitates the removal of the precipitated silver chlorid.

The above described method, on account of its delicacy, is not well suited to aqueous solutions of soils and fertilizers except where the quantity of nitric nitrogen present is extremely minute.

Spiegel also first suggested the use of diphenylamin for de-

testing the presence of nitrates,⁷⁸ a method afterwards worked out by Hooker.⁷⁹

395. Phenylsulfuric Acid Method.—Rideal also proposes a variation of the method described by Hooker, which consists in the substitution of phenylsulfuric acid for carbazol.⁸⁰

The solutions required are:

(a) A standard solution of potassium nitrate containing 0.7215 gram of the pure crystallized salt in a liter of water.

(b) Phenylsulfuric acid (acid phenyl sulfate), prepared by dissolving 15 grams of pure crystallized phenol in 92.5 cubic centimeters of pure, redistilled sulfuric acid free from nitrates and diluted with seven and one-half cubic centimeters of water.

The process is conducted as follows:

A known volume of the sample, from 25 to 100 cubic centimeters, according to its richness in nitrates, is evaporated to dryness in a porcelain dish, one cubic centimeter of phenylsulfuric acid, one cubic centimeter of pure water and three drops of strong sulfuric acid added, and the mixture gently warmed. A yellow color shows the presence of nitrates. Dilute to about 25 cubic centimeters with water and add ammonia in slight excess. Pour into a narrow nessler tube, adding the washings, and make up to 100 cubic centimeters. Imitate the color of the solution with the standard potassium nitrate treated with the same reagents.

The phenylsulfuric acid should be prepared some time before use, as the fresh solution imparts a greenish tint to the yellow of the ammonium picrate formed.

396. Method of Gill.—The phenyl sulfate process, as described by Leffman, is conducted as follows:⁸¹

Solutions Required.—*Acid phenyl sulfate (Phenoldisulfonic Acid)*: Thirty-seven grams of strong sulfuric acid are added to three grams of pure phenol and heated for six hours in, not upon the water bath, and preserved in a tightly stoppered bottle.

⁷⁸ *Zeitschrift für Hygiene*, 1887, 2 : 163.

⁷⁹ *Journal of the Franklin Institute*, 1889, 127 : 61.

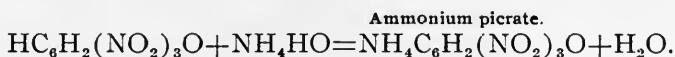
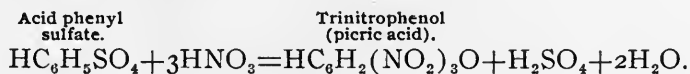
⁸⁰ *Chemical News*, 1889, 60 : 261.

⁸¹ *Examination of Water for Sanitary and Technical Purposes*, 5th Edition, 1903 : 50.

Standard potassium nitrate: 0.722 gram of potassium nitrate, previously heated to a temperature just sufficient to fuse it, is dissolved in water, and the solution made up to 1000 cubic centimeters. One cubic centimeter of this solution contains 0.0001 gram of nitrogen.

Analytical Process.—A measured volume of the sample is evaporated just to dryness in a platinum or porcelain basin. One cubic centimeter of the phenoldisulfonic acid is added and thoroughly mixed with the residue by means of a glass rod. One cubic centimeter of water and three drops of strong sulfuric acid are added, and the dish gently warmed. The liquid is then diluted with about 25 cubic centimeters of water, ammonium hydroxid added in excess, and the solution made up to 50 cubic centimeters.

The reactions are:



The ammonium picrate imparts to the solution a yellow color, the intensity of which is proportional to the amount present.

One cubic centimeter of the standard solution of potassium nitrate is similarly evaporated in a platinum dish, treated as above, and made up to 50 cubic centimeters. The color produced is compared to that given by the water, and one or the other of the solutions diluted until the tints of the two agree. The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrate present, as the following example shows:

One cubic centimeter of standard nitrate is treated as above and made up to 100 cubic centimeters, representing 0.0001 gram nitrogen.

Suppose 100 cubic centimeters of the sample similarly treated are found to require dilution to 150 cubic centimeters before the tint will match that of the standard; then

$$100 : 150 :: 0.001 : 0.0015$$

i. e., the sample contains one and one-half milligrams of nitrogen as nitrate per liter.

The ammonium picrate solution keeps very well, especially in the dark. A good plan, therefore, is to make up a standard solution equivalent to 10 milligrams of nitrogen as nitrate per liter, to which the color obtained from the sample may be directly compared.

The results obtained by this method are quite accurate. Care should be taken that the same quantity of phenoldisulfonic acid be used for the sample and for the comparison liquid, otherwise different tints instead of depths of tints are produced.

With subsoil, fertilizer and other solutions probably containing much nitrate, 10 cubic centimeters of the sample are sufficient for the test, but with river and spring waters, 25 to 100 cubic centimeters may be used. When the organic matter is sufficient to color the residue, it will be well to purify the sample by addition of aluminum hydroxid and subsequent filtration, before evaporating. This method may also be used to determine small quantities of nitrates when the amount is too small for estimation by the ferrous chlorid or reduction processes.

Mason calls attention to the fact that chlorids interfere with the delicacy of the process, giving readings decidedly lower than the truth.⁸² The method is so easy and convenient, however, that Mason was led to add salt to the comparison standards rather than to abandon the process. In the conduct of this method the chlorin in the water to be examined is first to be determined and the standard solution is treated with sodium chlorid in sufficient quantity to afford the same quantity of chlorin as in the sample. The results are found to be very satisfactory. If the chlorin be less than 10 parts per million it does not interfere with the determination. The solutions are prepared as follows:

Phenol-sulfonic acid—

Sulfuric acid, pure and concentrated.....370 grams

Pure phenol 30 grams

These reagents are placed in a flask and kept surrounded by

⁸² Examination of Water, 3rd Edition, 1906 : 50.

boiling water for 6 hours. Disulfonic instead of monosulfonic acid is thus produced by the prolonged high temperature, and this reacts readily upon the nitrate.

Standard potassium nitrate—prepared as described above.

397. Variation of Johnson.—The ammonium picrate method has given very satisfactory results as practiced by Johnson, who varies the process as described below.⁸³

The standard solution of potassium nitrate is prepared by dissolving 0.7215 gram of the pure salt in a liter of distilled water, and diluting 100 cubic centimeters of this solution to one liter with distilled water. Ten cubic centimeters of this dilute solution contain nitrogen equivalent to one part as nitrates in 100,000.

The Solution of Acid Phenyl Sulfate.—This is prepared by pouring two parts, by measure, of pure crystallized phenol liquefied by hot water into five parts, by measure, of pure concentrated sulfuric acid and digesting in the water-bath for eight hours. After cooling, add one and one-half volumes of distilled water and one-half volume of strong hydrochloric acid to each volume of the above mixture.

The analytical processes are carried on as follows: Ten cubic centimeters of the sample or extract under examination and 10 cubic centimeters of the standard potassium nitrate are placed in small beakers and put near the edge of a hot plate. When nearly evaporated they are put on the top of the water-bath and left there until completely dry. The residue, in each case, is treated with one cubic centimeter of the acid phenyl sulfate and the beakers placed on the top of the water-bath. In an extract very poor in nitric acid a red color ought not to appear for about 10 minutes.

After standing about 15 minutes, the beakers are removed, and the contents of each washed successively into 100 cubic centimeter flasks; about 20 cubic centimeters of 0.96 per cent. ammonia are then added, the 100 cubic centimeters made up by the addition of water, the yellow liquid transferred to the nessler glass and the tints appropriately compared.

⁸³ *Chemical News*, 1890, 61 : 15.

398. **Estimation of Nitric in Presence of Nitrous Acid.**—The detection of nitrous in presence of nitric acid can be accomplished by the method proposed by Griess, as described further on, through the development of azocolors with metaphenylenediamin and other bodies, which are not produced under similar conditions by nitric acid. The detection and estimation of nitric in the presence of nitrous acid, however, is not so easy. Lunge and Lwoff propose brucin for this purpose, which, contrary to most authorities, does not give the red-yellow color with nitrous acid.⁸⁴ The reagent is prepared by dissolving 0.2 gram of brucin in 100 cubic centimeters of pure and concentrated sulfuric acid. It is almost impossible to prepare a sulfuric acid which does not give a trace of color with brucin; but with the purest acids this trace may be neglected.

A solution of nitrate is also prepared containing 0.01 milligram of nitrogen as nitric acid in one cubic centimeter. It is made by dissolving 0.0721 gram of pure potassium nitrate in 100 cubic centimeters of distilled water, and diluting 10 cubic centimeters thereof with pure concentrated sulfuric acid to 100 cubic centimeters. Both solutions are conveniently preserved in burettes with glass stop-cocks. The liquid to be tested for nitric acid is mixed with sulfuric acid in such a way that the mixture will have a specific gravity of 1.7. If the liquid to be tested is water, this concentration is reached by adding three times its volume of the strong acid. For the comparison of colors, cylinders of colorless glass are employed, marked at 50 cubic centimeters. They are about 24 centimeters high and extend about 10 centimeters above the mark. There is placed in the cylinder one cubic centimeter of the solution of nitrate in sulfuric acid, and the same quantity of the brucin mixture, and it is filled to the mark with pure sulfuric acid. The contents of the cylinder are poured into a flask and warmed at from 70°-80°, until the final yellow tint is secured, and then poured into the cylinder again. The liquid to be tested is treated in exactly the same way. The tints are then equalized by pouring out a part of the contents of the deeper colored cylinder, taking account of the volume, and filling up with pure concentrated sulfuric acid.

⁸⁴ *Zeitschrift für angewandte chemie*, 1894, 7 : 347.

In this manner the content of nitric acid in the liquid under examination can be compared directly with the solution of potassium nitrate of known strength. The coloration is distinctly produced with 0.01 milligram in 50 cubic centimeters of liquid, at least three-fourths of which must be sulfuric acid.

399. Piccini Process.—The method proposed by Piccini may also be used.⁸⁵

About five cubic centimeters of the nitrite solution are placed in a small beaker, some pure urea dissolved therein and a few drops of sulfuric acid, and then held in boiling water for three minutes. The nitrous acid is thus completely destroyed. Ammonium chlorid may be substituted for urea. The reaction is represented by the equation, $\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$. The nitric acid present is then determined by diphenylamin or other suitable reagents. Diphenylamin reacts both with nitrous and nitric acids, producing a blue or violet tint. Warrington calls attention to a slight difference, however, in its deportment with these two acids. When the solution of the reagent is not too strong a drop of it produces but little turbidity when added to water or to a solution containing nitric acid. When, however, nitrous acid is present, a cream-colored turbidity is produced. The violet color also appears at once on adding sulfuric acid when a nitrite is present, while in the case of nitrates, more sulfuric acid is required, except when the solution is very strong. In this connection, it must not be forgotten that in heating nitrites with urea or ammonium chlorid in the presence of a slight excess of sulfuric acid, a trace of nitric acid may be formed.

400. Colors Produced by Diphenylamin.—In some descriptions of the color reactions produced by diphenylamin in the presence of nitrates and nitrites and sulfuric acid, the distinctive color produced is described as blue. This color is actually produced in certain conditions, which are not always easy to secure. Attention is called to this variation in tint in Volume I, page 532. With nitrites, the blue color is rather easily produced with varying proportions of nitrous acid, but such is not the case with nitrates

⁸⁵ Journal of the Chemical Society, 1891, 59 : 489.

Gazzetta chimica italiana, 1879, 9 : 395.

and chlorates. The prevailing colors developed with nitrates are reddish yellow, green and dirty violet, and with chlorates, red-brown, green and gray. The reactions, therefore, as usually produced are not always reliable, and Alvarez has proposed modifications of the process as follows:⁸⁶

The reagent is prepared by dissolving 0.1 gram of diphenylamin and the same quantity of re-sublimated resorcin and adding five or six drops of the solution to a fragment of the salt to be tested (nitrites, nitrates or chlorates of the alkalies), placed in a flat-bottomed porcelain capsule.

The following phenomena are observed: With nitrates a very permanent yellowish green tint is obtained, and after spreading out over the surface of the dish the edges of the spot become blue. By the addition of alcohol an orange color is obtained. With nitrites a deep blue violet color is produced and by moving the liquid so as to wet the whole interior of the dish, the edges become red. On adding alcohol a red color is formed. With chlorates the results are not satisfactory.

ESTIMATION OF NITROUS ACID BY COLORIMETRIC COMPARISON

401. Application of the Method.—The most minute traces of nitrous acid may be detected by colorimetric methods, and the determination of the quantity present may be approximated with great exactness by comparison with a solution of a nitrite of known strength. Especially in following the progress of nitrification is this method, in some of its forms, of essential importance. In delicacy and celerity it has the same advantages as the colorimetric methods for the determination of nitric acid, and the same skill must be exhibited and the same precautions observed as in the case of nitric acid in order to avoid errors.

402. Metaphenylenediamin Method.—This process depends upon the development of a yellow color in water containing nitrous acid on the addition of a reagent containing metaphenylenediamin; ($m-C_6H_4(NH_2)_2$). This variety of the phenylenediamins is readily obtained from common dinitrobenzene. It melts

⁸⁶ *Chemical News*, 1905, **91** : 155.

at 63° and boils at 287°. In order to preserve the reagent in shape for use it should be prepared in the following manner:

Dissolve two grams of the chlorid in 10 cubic centimeters of ammonia, and place the solution in a glass-stoppered flask. To this solution are added five grams of powdered animal-black, and the whole vigorously shaken. After allowing to settle, the shaking is repeated at intervals of an hour, three or four times, and the flask then allowed to remain at rest for 24 hours.

The supernatant liquid is generally sufficiently decolorized by this treatment. If not, the shaking and subsidence must be repeated until a completely colorless liquid is obtained. The solution can be kept indefinitely in contact with the animal-black. Aqueous and alcoholic solutions of the salt can not be kept.

The test is made by mixing five drops of the reagent with five cubic centimeters of sulfuric acid. The mixture must be colorless. To the mixture add 100 cubic centimeters of the water or solution to be tested, and heat on the water bath for five minutes. A yellow coloration indicates the presence of nitrous acid.

The metaphenylenediamin test is fairly satisfactory in perfectly colorless waters and aqueous extracts. Many waters and soil and fertilizer extracts, however, have a yellowish tint, and this interferes in a marked way with a proper judgment of the yellow triaminazobenzol developed in the application of the above test.

The decoloration of such waters by means of sodium carbonate or aluminum hydroxid is a matter of some difficulty, and not wholly without action on the nitrites which may be present. The method, therefore, is inferior to the one next described.

403. Sulfanilic Acid and Naphthylamin Test for Nitrous Acid.

--A very delicate test for the presence of nitrous acid, first described by Griess, is the coloration produced thereby in an acid solution of sulfanilic acid and naphthylamin.⁸⁷

⁸⁷ *Berichte der deutschen chemischen Gesellschaft*, 1879, **12** : 426.
Zeitschrift für analytische Chemie, 1879, **18** : 597.
Zeitschrift für angewandte Chemie, 1889, **2** : 666.
Bulletin de la société chimique de Paris, 1889, [3], **2** : 347.
This work, **1** : 533.

Sulfuric or acetic acid may be used as the acidifying agent, preferably the latter. The solutions are prepared as follows:

(1) Dissolve one-half gram of sulfanilic acid in 150 cubic centimeters of dilute acetic acid.

(2) Boil 0.1 gram of naphthylamin with 20 cubic centimeters of water, decant the colorless solution from the residue and acidify it with 150 cubic centimeters of dilute acetic acid.

The two solutions may at once be mixed and preserved in a well-stoppered flask. The action of light on the mixture is not hurtful, but air should be carefully excluded because of the traces of nitrous acid which it may contain. Whenever the mixed solutions show a red tint it is an indication that they have absorbed some nitrous acid. The red color may be discharged and the solution again fitted for use by the introduction of a little zinc dust, and shaking.

The water, or aqueous solution of a soil or fertilizer, to be tested for nitrites, is treated in portions of about 20 cubic centimeters with a few cubic centimeters of the mixed reagent and warmed to 70°-80°. If nitrous acid, in the proportion of one part to one million be present, the red color will appear in a few minutes. If the content of nitrous acid be greater, *e. g.*, one part in one thousand, only a yellow color will be produced, unless a greater quantity of the reagent be used.

Leffmann recommends the following method of conducting the determinations:⁸⁸

Solutions required: *1-4-amidobenzenesulfonic acid solution (sulfanilic acid)*.—Dissolve 0.5 gram in 150 cubic centimeters of diluted acetic acid, sp. gr. 1.04.

α -amidonaphthalene acetate solution.—Boil 0.1 gram of solid α -amidonaphthalene (α -naphthylamin) in 20 cubic centimeters of water, filter the solution through a plug of washed absorbent cotton, and mix the filtrate with 180 cubic centimeters of diluted acetic acid. All water used must be free from nitrites, and all vessels must be rinsed out with such water before tests are applied, since appreciable quantities of nitrites may be taken up from the air.

⁸⁸ Examination of Water for Sanitary and Technical Purposes, 5th edition, 1903: 54.

Standard Sodium Nitrite.—0.275 gram pure silver nitrite is dissolved in pure water, and a dilute solution of pure sodium chlorid added until the precipitate ceases to form. It is then diluted with pure water to 250 cubic centimeters and allowed to stand until clear. For use, 10 cubic centimeters of this solution are diluted to 100. It is to be kept in the dark.

One cubic centimeter of the dilute solution is equivalent to 0.00001 gram of nitrogen.

The silver nitrite is prepared in the following manner: A hot concentrated solution of silver nitrate is added to a concentrated solution of the purest sodium or potassium nitrite available, filtered while hot and allowed to cool. The silver nitrite will separate in fine needle-like crystals, which are freed from the mother-liquor by filtration with the aid of a filter pump. The crystals are dissolved in the smallest possible quantity of hot water, allowed to cool and crystallize, and again separated by means of the pump. They are then thoroughly dried in the water bath, and preserved in a tightly-stoppered bottle away from the light. Their purity may be tested by heating a weighed quantity to redness in a tared, porcelain crucible and noting the weight of the metallic silver. One hundred and fifty-four parts of silver nitrite leave a residue of 108 parts of silver.

Analytical Process.—Twenty-five cubic centimeters of the water, soil or fertilizer solution are placed in a color-comparison cylinder, the measuring vessel and cylinder having previously been rinsed with the water to be tested. By means of a pipette two cubic centimeters each of the test solutions are dropped in. It is convenient to have three pipettes for this test, and to use them for no other purpose. In any case the pipette must be rinsed out thoroughly with nitrite-free water each time before using, as nitrites, in quantity sufficient to give a distinct reaction, may be taken up from the air.

One cubic centimeter of the standard nitrite solution is placed in another clean cylinder, made up with nitrite-free water to 25 cubic centimeters and treated with the reagents, as above.

In the presence of nitrites a pink color is produced, which, in dilute solutions, may require half an hour for complete develop-

ment. At the end of this time the two solutions are compared, the colors equalized by diluting the darker, and the calculation made as explained under the estimation of nitrates.

The reactions consist in the conversion of the sulfanilic acid into diazobenzenesulfonic anhydrid, by the nitrite present; this compound is then in turn converted by the amidonaphthalene into azo- α -amidonaphthalene-1-4-benzenesulfonic acid. The last named body gives the color to the liquid.

The method pursued by Tanner, in the preparation of the reagents, is as follows:

Sulfanilic acid is prepared by mixing 30 grams of anilin slowly, with 60 grams of fuming sulfuric acid, in a porcelain dish. The brown, sirupy liquid formed is carefully heated until quite dark in color, and until the evolution of sulfurous fumes is noticed. After cooling, the thick, semi-fluid mass is poured into half a liter of cold water and allowed to stand for some hours. The liquid portion is decanted from the nearly black undissolved crystalline mass. To the residue half a liter of hot water is added and allowed to stand until cold, and the liquid again decanted. The undissolved portion is treated with one liter of hot water and filtered. The filtrate is treated with animal charcoal to decolorize it, and allowed to stand for 24 hours and again filtered, the filtrate diluted to 1500 cubic centimeters and used as required. This solution tends to turn pink on keeping, and thus its color interferes with the delicacy of the test, and a small amount of animal-char is kept in a small bottle containing the portion for immediate use, and this bottle is filled, from time to time, from the larger one.

The solution of naphthylamin hydrochlorate is made with one gram of the salt dissolved in 100 cubic centimeters of water. The solution is to be occasionally filtered, and not more than 100 cubic centimeters should be prepared at a time.

The analytical operations are carried on as follows:

A standard solution of pure potassium nitrite, made from the silver salt in distilled water perfectly free from nitrites, is placed in a color-glass, similar to those used in the nessler reaction,

together with a second glass containing the water to be tested. These glasses should be marked to hold 100 cubic centimeters at the same depth. To each of the tubes a few drops of pure hydrochloric acid are added and two cubic centimeters of the sulfanilic solution. Afterwards, to each tube are added two cubic centimeters of the solution of naphthylamin hydrochlorate, and it is allowed to stand for 20 minutes, at the end of which time the color is fully developed. Each tube is covered by a piece of glass in order to prevent access of air. It is unnecessary to add that the standard solutions of nitrite of different strength should be employed until the one is found which resembles, as nearly as possible, the color developed in the sample of water or extract under examination. The application of this test in ascertaining the progress of nitrification is described in Volume I, page 532.

404. Method of Mason.—Mason prefers the old method of using as reagents azobenzolnaphthlamin sulfonic acid.⁸⁹ He prepares his reagents as follows:

Sulfanilic acid.—Dissolve one gram of the salt in 100 cubic centimeters of hot water. The solution keeps well.

Naphthylamin hydrochlorid.—Boil one-half gram of the salt with 100 cubic centimeters of water for ten minutes, keeping the volume constant. Place in a glass stoppered bottle. The solution tends to grow slightly pink on standing, but not sufficiently so as to interfere with its use.

Standard solution of sodium nitrite.—Pure sodium nitrite may be used but the silver nitrite as prepared above is preferred.

Determination.—To determine nitrites place 100 cubic centimeters of the water to be examined (decolorized with aluminum hydrate if necessary) in a nessler tube. Acidify with one drop of concentrated HCl. The addition of too much acid might cause the nitrates to respond to the reaction. Add two cubic centimeters of the sulfanilic acid solution of hydrochlorid of naphthylamin, mix, cover with a watch glass, and set aside for 30 minutes. Prepare at the same time other nessler tubes containing known amounts of the standard solution of sodium nitrite and diluted to the 100 cubic centimeter mark with

⁸⁹ Examination of water, 3rd edition, 1906 : 42.

nitrite-free distilled water, adding the reagents as above. At the end of the time stated (30 minutes) examine the depth of the pink color formed, and by comparing the unknown with the known an accurate determination of the amount of nitrogen present as nitrites may be made.

If much gas be burning in the room, nitrites will be in the atmosphere. Hence, cover the tubes or remove them from the room during the half-hour interval before reading.

It may be worth while to call attention to the fact that the error due to the presence of burning lamps is often much greater than is suspected. In Mason's water laboratory the pure distilled water is prepared by the use of a large copper retort heated by a very broad bunsen burner. Only one other lighted burner is constantly in the room, and that a small one.

405. Lunge and Lwoff's Process for Nitrous Acid.—The reaction of nitrous acid with *a*-naphthylamin, first described by Griess, may be made reliable, quantitatively, by proceeding as below:⁹⁰

Boil 0.100 gram of pure white *a*-naphthylamin for 15 minutes with 100 cubic centimeters of water, add five cubic centimeters of glacial acetic acid, or its equivalent of dilute acid, and afterwards one gram of sulfanilic acid dissolved in 100 cubic centimeters of hot water. The mixture is kept in a well closed flask. A slight red tint in the mixture is of no significance, inasmuch as this completely disappears when one part of it is mixed with 50 parts of the liquid to be examined. If the coloration be very strong it can be removed by adding a little zinc dust. One cubic centimeter of this reagent will give a distinct coloration with 0.001 milligram of nitrous nitrogen in 100 cubic centimeters of water.

The analysis is conducted in cylinders of white glass marked at 50 cubic centimeters. One cubic centimeter of the above reagent is placed in each of two cylinders with 40 cubic centimeters of water and five grams of solid sodium acetate. In one of the cylinders is placed one cubic centimeter of a normal solution of a nitrite prepared by dissolving 0.0493 gram of pure sodium nitrite corresponding to 10 milligrams of nitrogen in 100 cubic centimeters of water, and adding 10 cubic centimeters of

⁹⁰ Zeitschrift für angewandte Chemie, 1894, 7 : 349.

this solution to 90 cubic centimeters of pure sulfuric acid. This secures a normal solution of nitrosylsulfuric acid, of which each cubic centimeter corresponds to 0.01 milligram of nitrogen.

In the other cylinder is placed one cubic centimeter of the solution to be examined, and the contents of both cylinders are well mixed so that the nitrous acid in a nascent state may act on the reagent. The colors are compared after any convenient period, but, as a rule, after five minutes.

The chief improvement made by Lunge and Lwoff on the method of Griess is in keeping the reagent in a mixed state ready for use, by means of which any nitrous impurities in the components thereof are surely indicated. Its advantage over the method of Ilosvay consists in using the comparative normal nitrite solution as nitrosylsulfuric acid, in which state it is much more stable.⁹¹

406. Estimation of Nitrous Acid with Starch as Indicator.—The method of procedure, depending on the blue color produced in a solution of starch in presence of a nitrite and zinc iodid when treated with sulfuric acid, is not of wide application on account of the interference produced by organic matter. The soil or fertilizer extract or water is treated in a test-tube, with a few drops of starch solution and some zinc iodid, to which is added some sulfuric acid. The decomposition of the nitrite is attended with the setting free of an equivalent amount of iodine which gives a blue coloration to the starch solution. The depth of the tint is imitated by treating a standard solution of nitrite in a similar way until the proper quantity is found, which gives at once the proportion of nitrite in the sample examined. This process, however, is scarcely more than a qualitative one.

407. Estimation of Nitrites by the Method of Chabrier.—In order to make the estimation of the evolved nitrous acid more definite by the iodine method, Chabrier has elaborated a plan for titrating it with a reducing agent.⁹²

The substance chosen for this purpose is sodium hyposulfite. In point of fact, it is not the nitrous acid which is attacked by

⁹¹ Bulletin de la Société chimique de Paris, 1894, [3], 11 : 218.

⁹² Encyclopédie chimique, 1888, 4 : 262.

the hyposulfite, but the equivalent amount of free iodine representing it. In the case of a soil or fertilizer where the quantity of nitrites is usually very small, it is well to use as much as one kilogram for making the extract. The extraction should be made rapidly, with water free of nitrites, in order to avoid any reducing action on the nitrates which may be present. In the case of water,

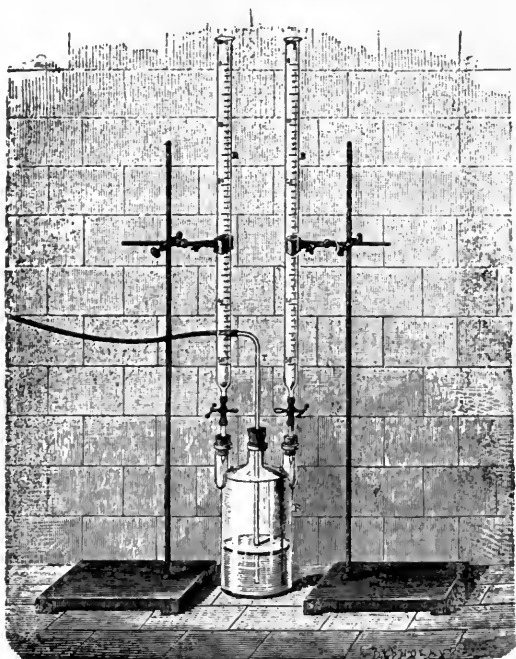


Figure 37. Apparatus of Chabrier.

from five to 10 liters should be evaporated to a small volume. The concentration should take place in a large flask, rather than in an open dish, in order to avoid any possibility of the absorption of nitrites produced by combustion in the flame of the burner. When the volume has been reduced to about 100 cubic centimeters, it is transferred to a small flask and the concentration continued until only 10 or 15 cubic centimeters are left. The residue is filtered into a woulff bottle, shown in Fig. 37, of about 100 cubic centimeters capacity.

One of the side tubules carries a burette, containing five per cent. sulfuric acid, the other one is filled with a hyposulfite solution of known strength. The middle tubule serves to introduce a glass tube through which carbon dioxide or illuminating gas passes for the purpose of driving out the air from the solution and the flask. If carbon dioxide be used it should be generated by the action of sulfuric acid on marble. The cork holding this is furnished with a slot or valve to permit the exit of the air and the excess of the gas.

Before inserting the middle stopper, a few cubic centimeters of potassium iodide solution and a few drops of thin starch paste are added, the potassium salt being always used in excess of the nitrite supposed to be present.

After the air has all been expelled from the flask, the analytical process is commenced, the carbon dioxide current being slowly continued. At first, a few drops of the dilute sulfuric acid are allowed to flow into the flask. As soon as the liquid is colored blue, a sufficient quantity of the thiosulfate solution is added to discharge the color. The successive addition of acid and thiosulfate is continued until another portion of the acid fails to develop the blue color, thus indicating that all the nitrite has been decomposed. From the volume of thiosulfate used, the quantity of nitrite is calculated.

The Thiosulfate Solution.—The thiosulfate solution is conveniently prepared, when a large number of analyses is to be made, by dissolving 25 grams of pure crystallized sodium thiosulfate in 100 cubic centimeters of water and diluting any convenient part thereof to 100 or 1000 cubic centimeters, according to the supposed strength of nitrite solution under examination.

For fixing the strength of the solution dissolve 3.348 grams of pure iodine in a solution of potassium iodide and make the volume up to one liter. Each cubic centimeter of this solution corresponds to one milligram of nitrous acid. A given volume of the iodine solution is titrated against the thiosulfate, but it is best not to add the starch paste until the greater part of the iodine has been removed. The starch paste is then added and the titration continued until the blue color has been discharged. Ten

cubic centimeters of the iodine solution is a convenient quantity for the titration and the thiosulfate should be diluted by adding to 10 cubic centimeters of the solution mentioned above, 990 cubic centimeters of water. Each liter of this dilute solution contains two and a half grams of the sodium thiosulfate.

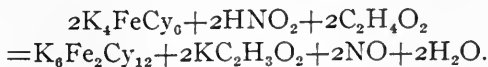
Example.—Suppose that it has required 21.3 cubic centimeters of thiosulfate to absorb 10 cubic centimeters of the iodine solution; further, that 10 liters of water have been evaporated and titrated as described above, and that the volume of thiosulfate employed is 13.8 cubic centimeters. From this is derived the following formula: $\frac{13.8 \times 10}{21.3} = 6.48$ milligrams of nitrous acid; or 0.648 milligram per liter.

408. Estimation of Nitrous Acid by Coloration of Solution of Ferrous Salt.—This method, due to Piccini, is based on the production of the well-known brown color formed by the action of nitric oxid on a ferrous salt.⁹³ The nitrite is decomposed by heating with acetic acid while nitrates thus treated do not develop the reaction. The tint produced is imitated, as above, by testing against a standard solution of nitrite. Ferrous chlorid is to be preferred to other ferrous salts for the above purpose. The process should be carried on in solutions free of air.

VOLUMETRIC METHOD FOR NITROUS ACID

409. Estimation of Nitrous Acid by Decomposition with Potassium Ferrocyanid.—The method of Schaeffer was first described in 1851, but little attention has been paid to it since. The method was brought into notice again by Deventer:⁹⁴

The reaction depends upon the decomposition of nitrous acid by potassium ferrocyanid in the presence of acetic acid with the formation of potassium ferricyanid and acetate, and nitric oxid. The reaction is expressed by the following equation:



A eudiometer with a glass stop-cock is arranged as shown in

⁹³ Pélégot, *Traité de Chimie analytique appliquée à l'Agriculture*, 1883 : 261.

⁹⁴ *Berichte der deutschen chemischen Gesellschaft*, 1893, 26 : 589.

Fig. 38. The lower part of the eudiometer is closed with a rubber stopper carrying a glass tube which ends in the pan *f* as shown at *e*. The eudiometer is filled to the stop-cock with a solution of potassium ferrocyanid of about 14 per cent. strength. The dish *f* is also filled up to the height indicated in the figure with the same solution. The solution of nitrite is used in such

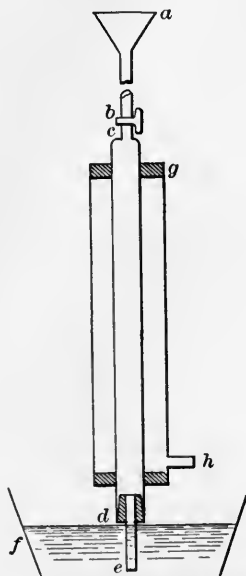


Figure 38. Schaeffer's Nitrous Acid Method.

quantities that the nitric oxid evolved will occupy a space of about 20 cubic centimeters. The whole eudiometer should contain about 57 cubic centimeters. The nitrite solution is added to the eudiometer by means of a funnel *a*. The vessel containing it is washed out with a little water and with acetic acid and finally with a few cubic centimeters of strong potassium ferrocyanid solution. The last fluid flows through the solution of nitrite and acetic acid and thus mixes it with the solution already in the eudiometer. The liquids reacting on each other float together on the strong ferrocyanid solution and each one of them is at once pressed downward by the gases which are evolved. When the evolution of gas becomes slower the apparatus should be shaken

for about 20 minutes, moving it back and forth without taking the bottom of it out of the dish. When there is no longer any evolution of gas, water is added through *a* slowly, until the heavy potassium ferrocyanid solution is almost completely driven out of the eudiometer. The opening of the tube at *e* is then closed with the thumb, the apparatus is taken out of the dish, shaken for some time in a vertical direction and again placed in the dish. Water of any required temperature is now allowed to flow through the jacket *gh*, until the temperature is constant, when the volume of nitric oxid is read. The whole experiment can be performed in less than an hour. Operating in this way, at the end there is in the eudiometer a liquid which is not very different from water and one whose coefficient of solubility for nitric oxid is practically the same as that of water. The gas volume read is to be corrected for temperature, pressure, tension of the aqueous vapor, height of the water column in the eudiometer, and, after the end of the calculation, five per cent. of the volume of water remaining in the eudiometer is to be added to the volume of gas obtained. This is to compensate for the volume of the gas absorbed by the water. The method gives good quantitative results.

410. General Observations.—The determination of nitrous acid in itself is of little interest in fertilizer examinations. It exists in fertilizers only in negligible quantities. Its determination is of greater importance in sanitary water analysis than in fertilizer control. It is of some importance, however, in connection with the occurrence of nitric acid, and this fact warrants the space which has been given to its discussion.

411. Method of Collecting Samples of Rain Water for Analysis.—In pot and field experiments with fertilizers the study of the drainage waters is of supreme importance. For this reason the methods for determining nitrous and nitric acids have been given in detail. The collection of the drainage waters is an important factor of this study. Warrington collects rain water in a large leaden gauge having an area of 0.001 of an acre.⁹⁵ Of the daily collection of rain, dew and snow water, an aliquot

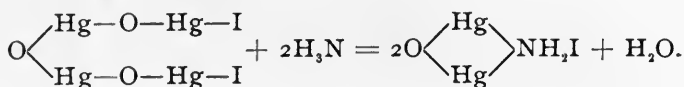
⁹⁵ Journal of the Chemical Society, 1889, 55 :537.

part, amounting to a gallon for each inch of precipitation, is placed in a carboy; at the end of each month the contents of the carboy are mixed, and a sample removed for analysis. In the carboy, receiving the rain for nitric acid estimation, a little mercuric chlorid is placed each month with the view of preventing any change of ammonia into nitric acid. It may be doubted, however, if this precaution is necessary, as the rain water thus collected always contains a very appreciable amount of lead; and experiments have shown that on the whole rain water more frequently gains than loses ammonia by keeping.

Preparation of the Sample.—The method first employed by Warrington was to concentrate 10 pounds of the rain water in a retort, a little magnesia being used to decompose any ammonium nitrite or nitrate present. Concentration by evaporation in the open air, and especially over gas, results in a distinct addition to the nitrites present. When concentrated to a small bulk, the water is filtered and evaporated to dryness in a very small beaker. The nitrogen, as nitrates and nitrites, is then determined by the methods already described.

DETERMINATION OF FREE AND ALBUMINOID AMMONIA IN RAIN AND DRAINAGE WATERS AND SOIL AND FERTILIZER EXTRACTS

412. Nessler Process.—The quantities of free ammonia in rain and most drainage waters are minute, but may reach considerable magnitude in some sewages. By reason of these minute proportions, gravi- and volumetric methods are not suitable for its quantitative determination. Recourse is, therefore, had to the delicate colorimetric reaction first proposed by Nessler. This reaction is based on the yellowish brown coloration produced by ammonia in a solution of mercuric iodid in potassium iodid. The coloration is due to the formation of oxydi-mercuric ammonium iodid, $\text{NH}_2\text{Hg}_2\text{OI}$, and the reaction takes place between the molecule of free ammonia and the mercuric iodid dissolved in the alkaline potassium iodid as represented by the following equation:



Nessler Reagent.—Dissolve 35 grams of potassium iodid in 100 cubic centimeters of water. Add gradually to this solution, a solution of 17 grams of mercuric chlorid in 300 cubic centimeters of water until a permanent precipitate of mercuric iodid is formed. Add enough of a 20 per cent. solution of sodium hydroxid to make 1000 cubic centimeters.

The mixed solutions, at room temperature, are treated with additional mercuric chlorid until the precipitate formed, after thorough stirring, remains undissolved. This precipitate is allowed to subside, and when the supernatant liquid is perfectly clear, it is decanted or filtered through asbestos and kept in a well-stoppered bottle in a dark place. The part in use should be transferred to a smaller bottle as required. The solution should be made for a few days before using, since its delicacy is increased by keeping. The nessler reagent should show a faint yellow tint. If colorless it is not delicate, and shows the addition of an insufficient quantity of mercuric chlorid. When properly prepared, two cubic centimeters of the reagent poured into 50 cubic centimeters of water containing 0.05 milligram of ammonia will at once develop a yellowish brown tint.

Preparation of Ammonia-Free Water.—To pure distilled water add pure, recently-ignited sodium carbonate, from one to two grams per liter, and distil. When one-fourth of the whole has passed over, the distillate may be regarded as free from ammonia, and 50 cubic centimeters of the following distillate should give no reaction with the nessler reagent. The distillation is continued until the residual volume in the retort is about one-fourth of the original, and the distillate free of ammonia is carefully preserved in close glass-stoppered bottles previously washed with ammonia-free water. Pure water, free of ammonia, may also be obtained by distilling with sulfuric acid.

Comparative Solution of Ammonium Chlorid Containing 0.00001 Gram Ammonia in One Cubic Centimeter.—Dissolve 3.15 grams H_4NCl in ammonia-free water and make the volume up to one liter. Dilute 10 cubic centimeters of the above solution to 1000 with water, free from ammonia.

Solution Containing 0.00001 Gram Nitrogen in One Cubic

Centimeter.—Dissolve 3.82 grams H_4NCl in water, free from ammonia and dilute to 1000 cubic centimeters. Dilute 10 cubic centimeters of the above solution to 1000.

The Distillation.—Any kind of suitable retort or flask con-

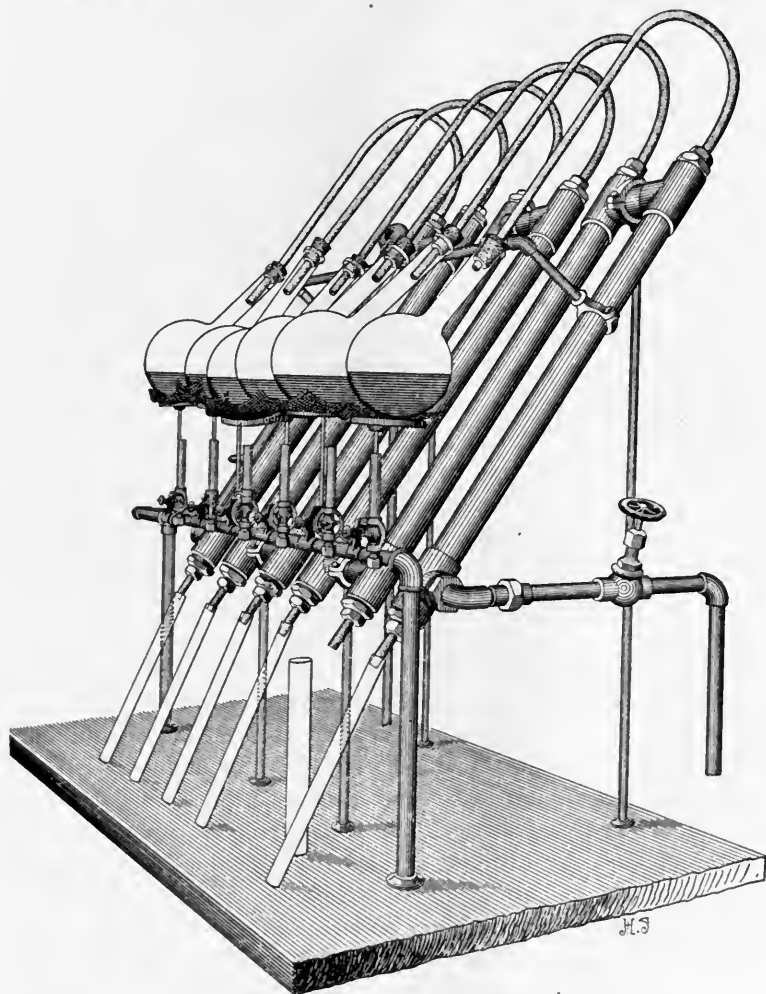


Fig. 39. Water Distilling Apparatus, Bureau of Chemistry.

nected with a good condenser may be used. The capacity of the retort should be from 700 to 1000 cubic centimeters. The

retorts and condensers used by the water laboratory of the Bureau of Chemistry are shown in Fig. 39. The retorts having been previously rinsed with distilled water, receive 500 cubic centimeters of the liquid to be tested for ammonia, together with a few pieces of recently ignited pumice stone, to prevent bumping, and five cubic centimeters of the 20 per cent. sodium carbonate solution to render the contents alkaline. The water is raised to the boiling-point and with gentle ebullition 50 cubic centimeters of distillate collected. The distillate is conveniently collected in a color-comparison cylinder of thin white glass and flat bottom, about two and a half centimeters in diameter, and marked at 50 and 100 cubic centimeters. Two cubic centimeters of the nessler reagent are added, and if ammonia be present a yellowish-brown color will be developed, the intensity of which is matched by taking portions of the ammonium chlorid solution, diluting to 50 cubic centimeters with pure water and treating with the same quantity of the nessler reagent. The process is repeated until a distillate is obtained which gives no reaction for ammonia. The sum of the quantities obtained in the several distillates gives the total amount of ammonia in the 500 cubic centimeters of the water. In most cases practically all the ammonia is obtained in three or four portions of the distillate.

Albuminoid Ammonia.—The residue from the process just described is employed for the purpose of determining the albuminoid ammonia. Two hundred grams of potassium hydroxid and eight grams of potassium permanganate are dissolved in 1000 parts of distilled water. Fifty cubic centimeters of the solution are placed in a porcelain dish with 100 cubic centimeters of distilled water and evaporated to 50 cubic centimeters. This liquid is placed in the retort and the distillation resumed and continued until an ammonia-free distillate is obtained. The total albuminoid ammonia is determined by taking the sum of the quantities in the several distillates.

Mason varies the nesslerizing process from the above in the following detail:⁹⁶

⁹⁶ Examination of Water, 3rd Edition, 1906 : 56.

Preparation of the Nessler Solution.—Sixteen grams of mercuric chlorid are dissolved in about one-half liter of pure water and 35 grams of potassium iodid in about 200 cubic centimeters of pure water and the first solution is poured slowly into the second until a slight excess is indicated by the appearance of a color or a precipitate. To the mixture are added 160 grams of solid potassium hydrate, and when this is dissolved, the volume is made up to one liter. A strong solution of mercuric chlorid is added little by little until the red mercuric iodid which is formed is not redissolved. The precipitate should not be removed by filtration but allowed to subside, and the completed reagent shows a pale straw color. The reaction which takes place in the presence of ammonia is represented as follows:



Pure Water.—Mason prepares pure water in a five gallon copper retort using good spring water which is treated with a few crystals of potassium permanganate and subjected to distillation until 50 cubic centimeters when nesslerized give no brown color in 10 minutes. The distillation should not be pushed too far otherwise ammonia may be generated from any organic matter which may be present in the water.

413. Nessler Reagent of Ilosvay.—To secure greater delicacy in nesslerizing, Ilosvay uses a reagent prepared as follows:⁹⁷

Dissolve two grams of potassium iodid in five cubic centimeters of water, heat the solution gently, and add three grams of mercuric iodid. After the solution is cooled, add another portion of three grams of the mercury salt, and then 20 cubic centimeters of water, and wait until the precipitation is complete. After filtering, there are added to the filtrate from 20 to 30 cubic centimeters of a 20 per cent. solution of potassium hydroxid. Only the limpid supernatant liquid is used in the analytical work. With this reagent, Ilosvay has been able to detect 0.02 milligram of ammonia in 110 cubic centimeters of water.

⁹⁷ Bulletin de la Société chimique de Paris, 1894, [3], 11 : 216.

PART THIRD

POTASH IN FERTILIZING MATERIALS AND FERTILIZERS

414. Introduction.—The potash present in unfertilized soils has been derived from the decay of rocks containing potash minerals. Among these potash producers feldspars are perhaps the most important. For a discussion of the nature of their decomposition and the causes producing it, the first part of Volume I may be consulted. Potash is quite as extensively distributed as phosphoric acid, and no true soils are without it in some proportion. Its presence is necessary to plant growth and it forms, in combination with organic and mineral acids, an essential part of the vegetable organism, existing in exceptionally rich quantities in the seeds. It is possible that potash salts, such as the chlorid, sulfate, and phosphate, may be assimilated as such, but, as with other compounds, we must not deny to the plant the remarkable faculty of being able to decompose its most stable salts and to form from the fragments thus produced entirely new compounds. This is certainly true of the potash compounds existing in plants in combination with organic acids. The potash which is assimilated by plants exists in the soil chiefly in a mineral state, and that added as fertilizer is chiefly in the same condition. That part of the potash in a soil arising directly from the decomposition of vegetable matters may exist partly in organic combination, but this portion, in comparison with the total quantity absorbed by the plant, is insignificant.

It is then safe to assume that at least a considerable part of the potash absorbed by the plant is changed from its original form of combination by the vegetable biochemical forces, and is finally incorporated in the plant tissues in forms determined by the processes of vegetable metabolism.

The analyst is not often called upon to investigate the forms

in which the potash exists in plants, when engaged in investigation of fertilizers. It is chiefly found in combination with organic and phosphoric acids, and on ignition will appear as phosphate or carbonate in the ash.

POTASH IN MINERAL DEPOSITS

415. Occurrence and History.—The generally accepted theories of the manner in which potash has been collected into deposits suited to use as a fertilizer are described below.

The most extensive potash deposits known are those in the neighborhood of Stassfurt, in Germany. The following description probably represents the method of formation of these deposits:⁹⁸

The Stassfurt salt and potash deposits had their origin, thousands of years ago, in a sea or ocean, the waters of which gradually receded, leaving near the coast, lakes which still retained communication with the great ocean by means of small channels. In that part of Europe the climate was then tropical, and the waters of these lakes rapidly evaporated, but were constantly replenished through these small channels connecting them with the main body. Decade after decade this continued, until by evaporation and crystallization the various salts present in the sea water were deposited in solid form. The less soluble material, such as sulfate of lime or "anhydrite," solidified first and formed the lowest stratum. Then came common rock salt, with a slowly thickening layer which ultimately reached 3000 feet, and is estimated to have been 13,000 years in formation. This rock salt deposit is interspersed with lamellar deposits of "anhydrite," which gradually diminish towards the top and are finally replaced by the mineral "polyhalit," which is composed of sulfate of lime, sulfate of potash, and sulfate of magnesia. The situation in which this polyhalit predominates is called the "polyhalit region," and after it comes the "kieserit region," in which, between the rock salt strata, kieserit (sulfate of magnesia) is embedded. Above the kieserit lies the "potash region," consisting mainly of deposits of carnallit, a mineral compound

⁹⁸ Potash, Published by the German Kali Syndicate, 1906.

of chlorids of potash and magnesia. The carnallit deposit is from 50 to 130 feet thick and yields the most important of the crude potash salts and that from which are manufactured most of the concentrated articles, including muriate of potash.

Overlying this region is a layer of impervious clay which acts as a water-tight roof to protect and preserve the very soluble potash and magnesia salts, which, had it not been for the protection of this overlying stratum, would have been long ages ago washed away and lost by the action of the water percolating from above. Above this clay roof is a stratum of varying thickness of anhydrite, and still above this is a second salt deposit, probably formed under more recent climatic and atmospheric influences or possibly by chemical changes resulting in dissolving and subsequent precipitation of the compounds. This salt deposit contains 98 per cent. (often more) of pure salt, a degree of purity rarely elsewhere found. Finally, above this are strata of gypsum, tenacious clay, sand and limestone, which crop out at the surface.

The perpendicular distance from the lowest to the upper surface of the Stassfurt salt deposits is about 5000 feet (a little less than a mile), while the horizontal extent of the bed is from the Harz Mountains to the Elbe River in one direction, and from the city of Magdeburg to the town of Bernburg in the other.

According to Fuchs and de Launay the saline formation near Stassfurt is situated at the bottom of a vast triassic deposit surrounding Magdeburg.⁹⁹ The quantity of sea water which was evaporated to produce saline deposits of more than 500 meters in thickness must have been enormous and the rate of evaporation great. It appears that a temperature of 100° would have been quite necessary, acting for a long time, to produce this result.

These authors, therefore, admit that all the theories so far advanced to explain the magnitude of these deposits are attended with certain difficulties. What, for instance, could have caused a temperature of 100°? The most reasonable source of this high temperature must be sought for in the violent chemical action produced by the double decompositions of such vast quantities

⁹⁹ *Traité des Gîtes minéraux*, 1893, 1 : 429.

of salts of different kinds. There may also have been at the bottom of this basin some subterranean heat such as is found in certain localities where boric acid is deposited.

Whatever be the explanation of the source of the heat, it will be admitted that at the end of the permian period there was thrown up to the northeast of the present saline deposits a ridge extending from Helgoland to Westphalia. This dam established throughout the whole of North Germany saline lagoons in which evaporation was at once established, and these lagoons were constantly fed from the sea.

There was then deposited by evaporation, first of all, a layer of gypsum and afterwards rock salt, covering with few exceptions the whole of the area of North Germany.

But around Stassfurt there occurred at this time geologic displacements, the saline basin was permanently closed and then by continued evaporation the more deliquescent salts, such as polyhalit, kieserit, and carnallit, were deposited.

These theories account with sufficient ease for the deposition of the saline masses, but do not explain why in those days the sea water was so rich in potash and why potash is not found in other localities where vast quantities of gypsum and common salt have been deposited. It may be that the rocks composing the shores of these lagoons were exceptionally rich in potash and that this salt was, therefore, in a certain degree, a local contribution to the products of concentration.

416. Sources of Supply.—The Stassfurt deposits, which have for many years been almost the sole source of potash in fertilizers, were first known as mines of rock salt. In 1839, having previously been acquired by the Prussian treasury, they were abandoned by reason of the more economical working of rock salt quarries in other localities. It was determined thereafter to explore the extent of these mines by boring, and a well was sunk to the depth of 246 meters, when the upper layer of the salt deposit was reached. The boring was continued into the salt to a total depth of 581 meters without reaching the bottom. The results of these experiments were totally unexpected. Instead of getting a brine saturated with common salt, one was obtained con-

taining large quantities of potassium and magnesium chlorids.¹ Shafts were sunk in other places, and with such favorable results that in 1862 potash salts became a regular article of commerce from that locality. At first these salts were regarded as troublesome impurities in the brine from which common salt was to be made, but at this time the common salt has come to be regarded as the disturbing factor. At the present time the entire product is controlled by a syndicate of nine large firms located at Stassfurt and vicinity. Outside of the syndicate properties a shaft has been sunk at Sonderhausen and also at Anderbeck (Halberstadt), which, however, have produced only carnallit.

It is thus seen that the potash deposits extend over a wide area in Germany, and there is little fear of the deposits becoming exhausted in many centuries. In this country no potash deposits of any commercial importance have been discovered; but the geological conditions requisite to these formations have not been wanting, and their future discovery is not improbable.

417. Deposits of Potash Salts in Alsace.—Up to the present time it has been supposed that the deposits of potash salts in Germany were confined to Saxony and to the Duchy of Anhalt.² The investigations of recent years have shown also that there are deposits in Mecklenburg, in the Duchy of Brunswick and in the provinces of Hanover and Oldenburg. It has also been reported recently that extensive deposits have been found in Alsace between the towns of Soultz and Regisheim, on the north, and Niedermonchviller on the south. These deposits were found at the depths of 500 and 700 meters, consisting of a layer of potash salts of superior quality one meter in thickness, and of an inferior quality of five meters in thickness. The crude salts were found to contain from 20 to 40 per cent. of potassium chlorid. The total quantity of potash salts produced in Germany in 1906 is estimated at 5,500,000 tons and of a value of \$20,500,000.

418. Mining the Salts.—The potash-bearing strata, from 1200 to 2500 feet below the earth's surface, are reached by ordinary

¹ Maercker, *Die Kalidüngung*, 2nd Edition, 1893 : 1.

² *The American Fertilizer*, 1908, 28 : 15.

mine shafts. In sinking these shafts great care is taken to preserve unbroken the cap materials impervious to water, and thus to prevent the highly soluble potash-bearing salts from being rapidly leached or washed away. This inflow of water is made impossible by sinking iron tubes or lining the shafts with concrete. Water is the great danger in potash mining, and has destroyed valuable mines. Generally, potash mines have a reserve or emergency shaft, some distance from the working shaft, protected by strong safety-pillars. Another mining difficulty is the "pillaring" or supporting the mine-roof as its mineral supports are cut away. Formerly pillars of salt were left for this purpose, but they disintegrated so rapidly as to be dangerous, and the safer system was adopted of completely filling up the excavations with the waste salts and rock salt. Within the mines, potash salts are broken down by blasting as in ordinary mining. In many of the works electricity is used for motor power and in lighting. The mines are necessarily kept perfectly dry, and visitors are free from the inconvenience and discomfort usual to underground workings. The carnallit blastings tear off large blocks, which are broken up by the miners and transported in small cars to the shafts, thence to be hoisted to the surface and delivered to the chemical works for grinding and further treatment.

419. Methods of Conducting the Mining Operations.—These are shown in the accompanying illustrations. Fig. 40 shows the general appearance of the interior of a mine, especially the manner in which the strata after deposition have been twisted and displaced by seismic disturbances. In Fig. 41 is illustrated the manner of drilling preparatory to a blast, and also the débris of the blasting and other mining operations. The tunnels are so driven as to support the superincumbent mass. A noon-day luncheon party is shown in Fig. 42. The illustrations are from photographs furnished by the German Kali Syndicate.

420. Manufacturing the Concentrated Salts.—As has been intimated, at the mine mouths are extensive and completely equipped chemical works which refine the crude salts and separate their constituents into products best suited to the various chemical in-



Fig. 40. Scene Showing Mining Operation.



Fig. 41. Drilling in Potash Mine Preparatory to Blasting.



Fig. 42. Scene During Lunch Hour in a Potash Mine.

dustries.³ A most important feature of the refining is the reduction in weight by rejecting useless constituents of the salts, thus securing the valuable potash in a small bulk—an essential consideration for the man who pays the freight or handles the products. Yet to refine closely is an expensive process, and much study and great care are necessary to balance properly the amount of concentration against the diverse uses and the cost of shipping and handling the various materials. In estimating the quantity of potash in the different products, chemists are accustomed to make use of the term “actual potash,” that is, potassium oxid (K_2O). The object of this is to establish a basis of comparison of all potash salts; therefore, when “potash” is named in potash products, it is understood that the word refers to the amount of actual potash present, and not the quantity of sulfate or chlorid of potash, as the case may be. As a matter of fact, potash is not sold commonly in the form of “actual potash” (K_2O), but as sulfate of potash, muriate (chlorid) of potash, sulfate of potash-magnesia, etc. Sulfate of potash is simply actual potash combined with sulfuric acid; and muriate of potash, actual potash combined with muriatic (hydrochloric) acid.

In manufacturing muriate of potash from the crude minerals found in the Stassfurt mines, all lime, soda, magnesia and other salts are removed. Crude carnallit, as it comes from the mines, contains on an average 15 per cent. muriate of potash; the manufacturing process consists in separating this 15 per cent. from the 85 per cent. of other crude ores, and makes use of the chemical knowledge that these other salts are either more soluble or less soluble in water and other solutions than pure muriate of potash. The coarsely ground carnallit is “charged” into a large dissolving vat containing a boiling, saturated solution of magnesium chlorid (a by-product of the process, as shown below). The mixture is agitated thoroughly by means of a “blow-up,” or live steam jet, and is boiled until it shows a degree of concentration equal to 32° Beaumé. The contents are drawn off into settling tanks, from which the clear solution is run into crystallizing vats and left three or four days to cool and crystallize,

³ German Kali Works, The Stassfurt Industry, 1902 : 29.

the deposit containing about 60 per cent. pure muriate of potash. The liquors drawn from the crystallizing vats are boiled down (now almost exclusively in a vacuum apparatus, but formerly in open pans), during which process some chlorid of sodium and sulfate of magnesium are separated. This second solution is settled and run into crystallizing vats where practically all the potash separates as crystals of pure artificial mineral carnallit ($\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$), which is treated precisely as was the crude carnallit and gives a nearly pure muriate of potassium in one crystallization.

The crystallized muriate of potash thus produced is contaminated by chlorids of sodium and magnesium, through adhering solutions, and these impurities are removed by a series of washings with water. The liquor from these washings of the crystals is saved and used on fresh batches of the mineral ore. The crystals of muriate of potash are dried and are from 70 to 99 per cent. pure (KCl). The last "mother liquors," or solutions from the crystallizing vats (from which all the potash has been separated), are used for the manufacture of bromin and chlorid of magnesium.

The muriate of potash (chlorid of potassium) manufactured at Stassfurt is of various grades and contains actual potash in the following proportions:

Pure Muriate of Potash.		Actual Potash.
70 to 75 per cent.	contains	46.7 per cent.
80 to 85 per cent.	contains	52.7 per cent.
90 to 95 per cent.	contains	57.9 per cent.
98 per cent.	contains	62.0 per cent.

When sold for fertilizing purposes it is on the basis of 80 per cent. pure muriate of potash, corresponding to 50.5 per cent. actual potash. The price is based on this average and is increased or decreased according to the percentage above or below it of pure muriate contained, as shown by chemical analysis. Muriate of potash serves as a basis for the manufacture of many other potash salts, such as nitrates, chlorates, etc.

There are many by-products in the manufacture of muriate of potash, notably magnesium chlorid and sulfate of soda, which latter, owing to its purity and freedom from acid salts, is largely

used in the manufacture of the cheaper grades of glass. From the residuum of the first solution of carnallit, treated with cold water, kieserit (sulfate of magnesia) settles out in fine crystalline particles, and is moulded into blocks. Large quantities of bromin and iron bromid are obtained at the end of the process. Some of the Stassfurt factories also prepare calcined magnesia, hydrate of magnesia, calcium chlorid, carbonate of potash, carbonate of potash-magnesia, etc.

In order to obtain the complete extraction of potash, the processes of manufacture are complex, and solutions and salts require repeated handling. It naturally follows that the separation of commercially pure salts from solutions of other salts is an expensive process, and that it is only by the most painstaking care and full utilization of every possible by-product that potash salts can be produced and sold at the present low prices.

Sulfate of potash is manufactured in less quantities than muriate, owing to the smaller demand for it in the market; but its consumption is rapidly increasing. There are several processes of manufacture. The one in general use is to concentrate a solution of kainit to a certain specific gravity, and then allow it to cool slowly in large crystallizing vats. The resulting crystals are washed and dried, and form the commercial salt sulfate of potash-magnesia, containing generally 40 per cent. of sulfate of potash, but when calcined, 48 per cent. In the manufacture of sulfate of potash a solution of sulfate of potash-magnesia and a given quantity of muriate of potash are boiled together, whereupon the less soluble sulfate of potash separates and falls as a precipitate, after which the solution is boiled down to a certain specific gravity, and cooled slowly in crystallizing vats, where the residual potash separates as crystals of sulfate of potash. As it is sold, it varies from 90 to 96 per cent. pure, equivalent to 46 to 52 per cent. actual potash.

The following tables give the average analyses of the more important Stassfurt potash salts. The figures show the pounds of various substances in 100 pounds of the different salts.

The numerous by-products obtained in refining the crude potash salts are utilized in many ways and for various purposes. Some

of them contain from 20 to 30 per cent. actual potash, but in most cases in such combination as not to pay for the necessarily expensive extraction. Because of this comparatively large content of potash, however, they are dried, calcined, pulverized, and mixed with crude salts, or other poorer forms of potash, to increase the potash content of these salts and give them added value for agricultural purposes.

Besides the agricultural use of potash salts, large quantities are consumed by the chemical industry in Germany, the United States and other countries, in the manufacture of caustic potash, carbonate, nitrate, chlorate, chromate, bichromate, alum, cyanid, bromid, permanganate and yellow prussiate of potash and of other compounds.

COMPOSITION OF CRUDE SALTS (NATURAL PRODUCTS).

	Kainit. Per cent.	Carnallit. Per cent.	Sylvinit. Per cent.
Actual Potash (K_2O).....	12.8	9.8	17.4
Minimum Guarantee (K_2O)	12.4	9.0	12.4
Sulfate of Potash (K_2SO_4).....	21.3	1.5
Muriate of Potash (KCl).....	2.0	15.5	26.3
Sulfate of Magnesia ($MgSO_4$).....	14.5	12.1	2.4
Chlorid of Magnesia ($MgCl_2$)	12.4	21.5	2.6
Chlorid of Sodium (NaCl).....	34.6	22.4	56.7
Sulfate of Lime ($CaSO_4$)	1.7	1.9	2.8
Insoluble Substances.....	0.8	0.5	3.2
Water	12.7	26.1	4.5

SULFATES (NEARLY FREE OF CHLORIDS).

	Sulfate of Potash.		Sulfate of Potash Magnesia.
	90 per cent.	96 per cent.	
Actual Potash (K_2O).....	49.9	52.7	27.2
Minimum Guarantee (K_2O)	48.6	51.8	25.9
Sulfate of Potash (K_2SO_4)	90.6	97.2	50.4
Muriate of Potash (KCl)	1.6	0.3
Sulfate of Magnesia ($MgSO_4$).....	2.7	0.7	34.0
Chlorid of Magnesia ($MgCl_2$).....	1.0	0.4
Chlorid of Sodium (NaCl).....	1.2	0.2	2.5
Sulfate of Lime ($CaSO_4$).....	0.4	0.3	0.9
Insoluble Substances.....	0.3	0.2	0.6
Water.....	2.2	0.7	11.6

COMPOSITION OF SALTS CONTAINING CHLORIDS.

	Muriate of Potash.			Potash Manure Salts.	
	90/95 per cent.	80/85 per cent.	70/75 per cent.	Minimum 20 per cent.	Minimum 30 per cent.
Actual Potash	57.9	52.7	46.7	21.0	30.6
Minimum Guarantee	56.8	50.5	44.1	20.0	30.0
Sulfate of Potash	1.7	2.0	1.2
Muriate of Potash ..	91.7	83.5	72.5	31.6	47.6
Sulfate of Magnesia	0.2	0.4	0.8	10.6	9.4
Chlorid of Magnesia	0.2	0.3	0.6	5.3	4.8
Chlorid of Sodium..	7.1	14.5	21.2	40.2	26.2
Sulfate of Lime	0.2	2.1	2.2
Insoluble Substances	0.2	0.2	0.5	4.0	3.5
Water.....	0.6	1.1	2.5	4.2	5.1

421. **Detailed Description of the Principal Salts Used in the Manufacture of Fertilizers.**—Some of the salts of potash such as kainit, are used as fertilizers just as they are taken from the mine. Others, such as carnallit and sylvinit, may be used directly as fertilizer, but more commonly are subjected to a process of manufacture or concentration whereby other compounds are produced. A description of the more important salts follows.

422. **Kainit.**—The most important of the natural salts of potash for fertilizing purposes is the mixture known as kainit. It is composed in a pure state of a molecule each of potassium, sulfate, magnesium sulfate, magnesium chlorid, and water. Chemically it is represented by the symbols:

$K_2SO_4.MgSO_4.MgCl_2.H_2O$. Its theoretical percentage of potash (K_2O), oxygen=16, is 23.2.

Pure kainit, however, is never found in commerce. It is mixed naturally as it comes from the mines with common salt, potassium chlorid, gypsum, and other bodies. The content of potash in the commercial salt is, therefore, only a little more than half that of the pure mineral. In general it may be taken at 12.5 per cent., of which more than one per cent. is derived from the potassium chlorid present. The following analysis given by Maercker may be regarded as typical:⁴

⁴ Die Kalidüngung, 2nd Edition, 1893 : 5.

	Per cent.
Potassium sulfate.....	21.3
Magnesium sulfate	14.5
Magnesium chlorid.....	12.4
Potassium chlorid	2.0
Sodium chlorid.....	34.6
Calcium sulfate (gypsum)	1.7
Water	12.7
Alumina.....	0.8

Kainit occurs as a crystalline, partly colorless, partly yellow-red mass. When ground, in which state it is sent into commerce, it forms a fine, gray-colored mass containing many small yellow and red fragments. It is not hygroscopic, and if it becomes moist it is due to the excess of common salt which it contains.

According to Maercker, kainit was formerly regarded as a potassium magnesium sulfate. But this conception does not even apply to the pure salt, much less to that which comes from the mines. If, therefore, the agronomist desires a fertilizer free from chlorin he would be deceived in choosing kainit, which may sometimes contain nearly 50 per cent. of its weight of chlorids.

Where a fertilizer free of chlorin is desired, as, for instance, in the culture of tobacco, kainit cannot be considered. In many other cases, however, the chlorin content of this body, instead of being a detriment, may prove positively advantageous, the chlorids, on account of their easy diffusibility through the soil, serving to distribute the other ingredients.

Kainit is regarded in some localities as a check against the ravages of insects and as a preventative of cotton blight.

By reason of the presence of common salt and magnesium chlorid, the ground kainit delivered to commerce tends to harden into compact masses. To prevent this, in Germany it is recommended to mix it with about two and a half per cent. of finely ground, dry peat.

Such a mixture is recommended in all cases where the freshly ground kainit is not to be immediately applied to the soil.

The greater part of the crude kainit mined is sold directly as a fertilizer, but a part is used also in the manufacture of high grade sulfate.

In some of the recently opened mines a mixture of sylvin, kieserit and rock salt is formed, known as Hartsalz. This mixture contains almost the same percentage of potash as kainit.⁵

423. Carnallit.—This mineral is a mixture of even molecules of potassium and magnesium chlorids crystallized with six molecules of water. It is represented by the symbols $KCl.MgCl_2.6H_2O$. As it comes from the mines it contains small quantities of potassium and magnesium sulfates and small quantities of other accidental impurities. Existing, as it does, in immense quantities in strata averaging more than 85 feet in thickness, it has been extensively used for the manufacture of the commercial potassium chlorid (muriate of potash). As mined its color varies through white, red, yellow and gray. In the strong light of the electric lamp the brilliancy of carnallit crystals and their varied colorings produce a strikingly beautiful effect in the galleries of the mines. For many purposes in agriculture, for instance, fertilizing tobacco fields, it is not suited, and it is less widely used as a fertilizer in general than its alteration product, kainit. Its direct use as a fertilizer, however, is rapidly increasing since later experience has shown that chlorin compounds are capable of a far wider application in agriculture without danger of injury than was formerly supposed. As it comes from the mines, the Stassfurt carnallit has the following composition:⁶

	Per cent.
Potassium chlorid.....	15.5
Magnesium chlorid.....	21.5
Magnesium sulfate.....	12.1
Sodium chlorid.....	22.4
Calcium sulfate.....	1.0
Water.....	26.1
Undetermined.....	0.5

Pure carnallit would have the following composition:

	Per cent.
Chlorin.....	38.3
Potassium.....	14.0
Magnesium.....	8.7
Water.....	39.0

⁵ German Kali Works, The Stassfurt Industry, 1902 : 12.

⁶ Maercker, Die Kalidüngung, 2nd Edition, 1893 : 7.

Equivalent to

	Per cent.
Potassium chlorid.....	26.8
Magnesium chlorid	34.2
Water	39.0

The commercial article as taken from the mines, as is seen above, has less potash (K_2O) than kainit, the mean content being about nine per cent. Those proposing to use this body for fertilizing purposes should bear in mind that it contains less potash and more chlorin than kainit.

Carnallit occurs in characteristic brown-red masses. On account of its highly hygroscopic nature it should be kept as much as possible out of contact with moist air and should not be ground until immediately before using.

By reason of the greater bulk in proportion to its content of potash and its hygroscopic nature and consequent increased difficulty in handling, the cost per unit of potash in carnallit is greater than in kainit.

In some localities small quantities of ammonium chlorid have been found with carnallit, but not to exceed one-tenth per cent. It has, therefore, no practical significance to the farmer, but may be of interest to the analyst.

424. Polyhalit.—Polyhalit is a mineral occurring in the Stassfurt deposits consisting of a mixture of potassium, magnesium, and calcium sulfates, with a small proportion of crystal water. This mineral, on account of its being practically free of chlorin, is one especially desirable for use in those cases, as in the culture of tobacco, where chlorids are injurious. Unfortunately, it does not occur in sufficient quantities to warrant the expectation of its ever being found in masses large enough to become a general article of commerce. It is found only in pockets or seams among the other Stassfurt deposits, and there is no assurance given on finding one of these deposits of polyhalit that it will extend to any great distance. The composition of the mineral is shown by the following formula: $K_2SO_4.MgSO_4.(CaSO_4)_2.H_2O$. Its percentage composition is shown by the following numbers:

	Per cent.
Potassium sulfate	28.90
Magnesium sulfate	19.93
Calcium sulfate	45.18
Water	5.99

The percentage of potash corresponding to the above formula is 15.62. It, therefore, contains a considerable excess of potash over kainit, and on account of its freedom from chlorids is preferred for many purposes.

425. Krugit.—This mineral occurs associated with polyhalit and differs from it only in containing four molecules of calcium sulfate instead of two. Its formula is: $K_2SO_4 \cdot MgSO_4 \cdot (CaSO_4)_4 \cdot H_2O$. As it comes from the mines it is frequently mixed with a little common salt. Its mean percentage composition as it comes from the mines is given in the following numbers:

	Per cent.
Potassium sulfate	18.60
Magnesium sulfate	14.70
Calcium sulfate	61.00
Sodium chlorid.....	1.50
Water	4.20

The percentage of potash corresponding to the above formula is 10.05. It is, therefore, less valuable than kainit in so far as its content of potash is concerned. This salt also exists in limited quantities and is not likely to become an important article of commerce.

426. Sylvin.—One of the alteration products of carnallit is a practically pure potassium chlorid, which as it occurs in the Stassfurt mines is known as sylvin. The alteration of the carnallit arises from its solution in water, from which, on subsequent evaporation, the potassium chlorid is deposited alone. This mineral is found in only limited quantities in the Stassfurt deposits, and it therefore does not have any great commercial importance.

427. Sylvinit.—This mineral has been mined in recent years in considerable quantities. It is, in fact, only common salt carrying large quantities of potassium chlorid together with certain other accidental impurities. It was probably formed by the drying up of a saline mass in such a way as not to permit the complete separation of its mineral constituents. The average com-

position of sylvinite as it comes from the mines is given in the following table:

	Per cent.
Potassium chlorid	30.55
Sodium chlorid.....	46.05
Potassium sulfate.....	6.95
Magnesium sulfate	4.80
Magnesium chlorid.....	2.54
Calcium sulfate	1.80
Water and insoluble.....	7.29

This salt is richer in chlorin than any other of the Stassfurt potash minerals, containing altogether 79.14 per cent. of chlorids. Its potash content amounts to 23.04 per cent., but in proportion to the potash which it contains, it is relatively poorer in chlorin than kainite and carnallite. On account of its high content of potash the cost of a unit thereof as contained in sylvinite is less than in kainite and carnallite.

428. Kieserite.—The mineral kieserite is essentially magnesium sulfate and it does not necessarily contain any potash salts. Under the name of kieserite, however, or bergkieserite, there is mined a mixture of carnallite and kieserite, which is a commercial source of potash. The mixture contains the following average content of the bodies named:

	Per cent.
Potassium chlorid	11.80
Magnesium sulfate	21.50
Magnesium chlorid.....	17.20
Sodium chlorid.....	26.70
Calcium sulfate	0.80
Water	20.70
Insoluble	1.30

This mixture contains only about seven per cent. of potash and would not prove profitable when used at a distance from the mines on account of the cost of freight. It has proved valuable, however, for a top dressing for meadow lands in the vicinity of Stassfurt.

429. Schönite.—Among the Stassfurt deposits there occurs in small quantities a mineral, schönite, which is composed of the sulfates of potassium and magnesium. The quantity of the mineral

occurring naturally is very small, and, therefore, it has no commercial importance. When, however, kainit is washed with water the common salt and magnesium chlorid which it contains being more soluble, are the first leached out, and the residue has approximately the composition of the pure mineral. This mixture, as prepared in the way mentioned above, has the following average composition:

	Per cent.
Potassium sulfate.....	50.40
Magnesium sulfate	34.00
Sodium chlorid.....	2.50
Water	11.60

The percentage of potash corresponding to the above composition is 27.2. This substance being so rich in potash, and practically free of chlorids, is well suited to transportation to great distances and for general use in the field. Since, however, a considerable expense attends the manufacture of the artificial schönit, the advantages above named give it very little, if any, advantage in competition with the other potash salts, as they come from the mines. It has, however, an especial value for the fertilization of tobacco and vines.

430. Potassium Sulfate.—Several grades of potassium sulfate are found in the market for fertilizing purposes, some of them quite pure, containing over 97 per cent. of the pure sulfate. The following data show the composition of a high grade and low grade potassium sulfate of commerce:

	High grade. Per cent.	Low grade. Per cent.
Potassium sulfate.....	97.20	90.60
Potassium chlorid	0.30	1.60
Magnesium sulfate.....	0.70	2.70
Magnesium chlorid.....	0.40	1.00
Sodium chlorid.....	0.20	1.20
Insoluble	0.20	0.30
Water.....	0.70	2.20

Naturally, high grade sulfates of this kind can only be prepared in chemical factories built especially for the work. The result is that the potash per unit is raised greatly in price. When, however, the fertilizers are to be transported to a great distance,

the saving in freight often more than compensates for the higher price of the potash. It therefore happens that there are many places in this country where the actual price of potash per pound is less in high grade sulfates than in kainit or carnallit. When, in addition to this, the especial fitness of the high grade sulfates for certain kinds of fertilization, especially tobacco growing, is considered, it is seen that at this distance from the mines these high grade salts are of no inconsiderable importance. The percentage of potash in the high grade sulfates often exceeds 50.

431. Potassium-Magnesium Carbonate.—This salt has lately been manufactured and used to a considerable extent, especially for tobacco fertilizing. As furnished to the trade it has the following average composition:

	Per cent.
Potassium carbonate	35 to 40
Magnesium carbonate... ..	33 to 36
Water of crystallization	25
Potassium chlorid, potassium sulfate, and insoluble..	2 to 3

The content of potash, as is seen from the above formula, amounts to from 20 to 25 per cent. The compound is completely dry, is not hygroscopic, and is, therefore, always ready for distribution. It is especially to be recommended for all those intensive cultures where it is feared that chlorids and sulfates will prove injurious, especially in the cultivation of tobacco.

432. Potash in Factory Residues.—The residues from the potash factories in Stassfurt and vicinity contain considerable quantities of potash and attempts have been made to recover this waste and put it into form for fertilizing uses. The waste waters of the factories are sometimes collected and evaporated, and the residue incinerated. The content of potash in these residues is extremely variable, usually quite low, and they, therefore, can not be recommended for fertilizing purposes; especially if they are to be transported to any distance.

433. Production of Crude Salts.—The following table gives the production of crude salts, in the Stassfurt region from 1888 to the close of 1901:

(METRIC TONS OF 2204 POUNDS.)

Year	Carnallit	Rock kieserit	Sylvinit	Kainit and hartsalz	Total
1888	849,603	10,754	2,220	375,574	1,238,151
1889	798,721	9,354	28,329	362,611	1,199,015
1890	838,526	6,951	31,917	401,871	1,279,265
1891	818,862	5,816	32,661	512,794	1,369,833
1892	736,751	5,783	32,669	585,775	1,360,978
1893	794,660	4,807	49,140	689,994	1,538,601
1894	851,339	3,865	63,495	729,301	1,648,000
1895	782,944	3,012	76,097	669,532	1,531,585
1896	856,223	2,841	90,390	833,025	1,782,479
1897	851,272	2,619	84,105	1,012,186	1,950,182
1898	990,998	2,444	94,270	1,120,616	2,208,328
1899	1,317,948	2,066	100,653	1,063,195	2,483,862
1900	1,697,803	2,047	147,791	1,189,394	3,037,035
1901	1,860,189	2,335	190,034	1,432,136	3,484,694

Carnallit leads in the total quantity mined, followed closely by kainit and hartsalz. The relative quantity of carnallit, however, is decreasing, while that of kainit and sylvinit is increasing.

These salts were either sold directly from the mines for agricultural purposes, or manufactured into more concentrated potash products for use in agriculture, or in the arts and other manufactures. The greater part of the crude salts manufactured into concentrated products was converted into muriate of potash.

434. Production of Concentrated Potash Salts.—The following table gives full detailed data as to the various concentrated salts produced from 1884 to the close of 1901 :

(METRIC TONS OF 2204 POUNDS.)

Year	Muriate of potash, 80 per cent.	Sulfate of potash, 90 per cent.	Sulfate of potash-magnesia		Potash manure salt	Kieserit in blocks	Kieserit ground and calcined
			Crystallized, 40 per cent.	Calcined, 48 per cent.			
1884	106,330	3,000	400	8,000	9,500	17,800
1885	104,500	4,000	450	9,000	8,400	18,500
1886	110,200	3,639	472	10,111	8,161	19,500
1887	130,000	10,528	500	6,285	8,163	24,018
1888	132,000	10,916	522	11,350	13,918	28,325
1889	131,593	7,321	671	9,215	17,285	31,824
1890	134,760	13,839	907	10,830	17,620	32,005
1891	143,488	18,981	1,053	11,400	16,045	28,559
1892	121,028	15,466	708	11,842	16,895	23,855	11
1893	132,529	16,361	739	12,643	17,344	24,386	105
1894	147,936	15,243	1,780	12,718	19,728	26,440	216
1895	145,027	13,403	898	8,249	19,724	25,115	142
1896	155,805	13,889	1,051	4,622	19,253	24,987	211
1897	158,863	15,403	922	7,415	23,042	25,669	214
1898	174,380	17,781	914	10,535	24,284	19,934	728
1899	180,672	24,656	579	8,459	70,916	28,216	260
1900	206,471	31,255	932	12,150	129,863	28,508	358
1901	211,421	28,196	936	11,750	147,170	26,727	361

435. Consumption of Potash for Agricultural Purposes in Different Countries.—The following tables show the consumption of potash for agricultural purposes in the principal countries of the world for six years, and the relative quantity used per acre of land under cultivation:

(a) TOTAL CONSUMPTION IN TONS CALCULATED IN PURE POTASH (K_2O).

Country	1895	1896	1897	1898	1899	1900
Germany.....	60,182	75,585	89,683	96,414	107,688	117,712
United States...	33,907	38,018	46,628	51,663	50,855	66,595
France.....	5,033	5,892	7,266	6,532	8,772	8,229
Sweden.....	5,061	5,719	6,869	7,637	6,892	8,197
Holland.....	2,542	2,964	4,091	5,032	6,021	7,106
England.....	4,088	4,569	3,165	3,871	4,014	4,020
Scotland.....			1,487	1,782	2,584	3,370
Ireland.....			297	285	412	600
Belgium... ..	2,881	2,681	2,829	3,110	3,367	3,607
Austria-Hungary	1,045	1,196	1,349	1,630	2,256	2,389
Spain.....	369	456	770	1,128	1,953	2,428
Denmark.....	834	1,071	1,030	1,375	1,320	1,692
Russia.....	467	620	625	1,011	1,037	1,597
Italy.....	883	792	938	1,235	1,197	1,380
Switzerland....	833	876	953	931	1,038	1,026
Finland.....	181	332	466	566	505	382
Norway.....	69	107	164	252	238	286
Portugal.....	68	46	44	119	13	43

(b) CONSUMPTION OF PURE POTASH (K_2O) CALCULATED IN POUNDS PER 100 ACRES ARABLE LAND.

Country	Arable land in acres	1895	1896	1897	1898	1899	1900
Germany.....	86,971,300	152.5	191.6	227.3	244.3	273.0	298.3
Holland.....	5,012,100	111.7	130.3	179.9	212.3	264.7	312.5
Sweden.....	8,622,000	129.3	146.2	175.5	195.2	176.2	209.5
Scotland.....	3,641,200	77.3	86.3	90.0	107.8	156.5	204.0
Belgium.....	5,232,800	121.3	112.9	119.2	131.0	141.8	151.9
Denmark.....	6,305,000	29.2	37.5	36.0	48.1	46.1	59.1
England.....	16,915,400	33.3	37.2	41.2	50.4	52.3	52.4
Norway.....	1,412,900	10.7	16.7	25.7	39.3	37.1	44.7
Switzerland....	5,258,700	35.0	36.8	40.0	39.0	43.5	43.0
United States...	348,212,300	21.5	24.1	29.5	32.7	32.2	42.2
Finland.....	2,755,100	14.5	26.3	37.3	45.3	40.4	30.6
Ireland.....	5,322,500	10.6	11.9	12.3	11.8	17.0	24.8
France.....	92,649,800	12.0	14.0	17.3	15.5	20.9	19.5
Spain.....	72,201,100	1.2	1.4	2.3	3.5	6.0	7.4
Italy.....	50,421,000	3.8	3.5	4.1	5.4	5.3	6.1
Austria-Hungary	99,416,900	2.3	2.7	3.0	3.7	5.0	5.3
Portugal.....	11,329,000	1.3	0.9	0.9	2.3	0.3	0.8
Russia.....	515,055,200	0.2	0.3	0.3	0.4	0.4	0.7

It is seen that Germany is the greatest consumer of these salts, and the United States the next in actual quantity used. Other countries use comparatively small quantities, but some of them use larger quantities per acre of land under cultivation than are used in this country.

436. Amount of Actual Potash Used in Different States.—The relative quantities of potash used in the different states are shown in the following table:

DATE OF COMPILATION, JULY 8, 1901.

State	Tons of total fertilizer consumed in 1900	Per cent. K ₂ O (Estimated)	Tons actual potash sold in the various states in 1899, as per agent's statement			
			Tons K ₂ O	For agricultural purposes	Chemical purposes	Total
NORTH						
Connecticut	22,500	5.0	1,125	565	14	579
Delaware	6,000	4.0	240	118	224	342
Illinois	25,000	1.0	250	659	659
Indiana	75,000	1.5	1,125	47	47
Maine	6,000	3.0	180	106	106
Massachusetts	30,000	5.0	1,500	3,099	275	3,374
Michigan	7,000	2.6	182	252	252
Missouri	7,000	0.5	35	20	14	34
New Hampshire	5,000	3.0	150
New Jersey	42,929	6.0	2,576	1,245	3	1,248
New York	125,000	4.0	5,000	8,096	3,360	11,456
Ohio	200,000	2.0	4,000	1,026	..	1,026
Pennsylvania	125,000	3.0	3,750	4,284	200	4,584
Rhode Island	5,000	4.0	200	140	140
Vermont	13,000	5.0	650
Wisconsin	200	2.0	4
Canada	4,000	3.0	120	86	86
Total	698,629		21,087	19,843	4,090	23,933
SOUTH						
Alabama	155,746	1.5	2,336	724	724
Arkansas	1,200	1.5	18
Florida	40,000	8.0	3,200	821	821
Georgia	412,755	2.0	8,255	4,895	4,895
Kentucky	32,600	3.0	978	79	79
Louisiana	25,000	0.8	200	398	398
Maryland	85,000	3.8	2,550	6,968	952	7,920
Mississippi	66,667	1.5	1,000	449	449
North Carolina	275,000	1.5	4,125	2,986	2,986
South Carolina	250,000	1.5	3,750	10,381	10,381
Tennessee	25,000	2.0	500	587	587
Texas	3,900	1.0	39
Virginia	200,000	2.0	4,000	4,535	4,535
West Virginia	25,000	2.5	625	1	1
Total	1,597,868		31,576	32,824	952	33,776
Grand total	2,296,497		52,663	52,667	5,042	57,709

The southern states, it is seen, use more than twice as much potash as the northern, and this is due chiefly to the application of this plant food to the cotton and sugar cane crops.

437. Changes in Potash Salts in Situ.—The deposits of potash salts are not all found at the present in the same condition in which they were first deposited from the natural brines. The layers of salt have been subjected to the usual upheavals and subsidences peculiar to geological history. The layers of salt were thus tilted and the edges often brought to the surface. Here they were exposed to solution, and the dissolved brine afterwards separated its crystallizable salts in new combinations. For instance, kieserit and the potassium chlorid of the carnallit were first dissolved and there was left a salt compound chiefly of potassium and sodium chlorids sylvinit. In some cases there was a mutual reaction between the magnesium sulfate and the potassium chlorid and the magnesium potassium sulfate, schönit, was thus produced. This salt is also prepared at the mines artificially. The most important of these secondary products however, from the agricultural standpoint, is kainit. This salt arose by the bringing together of potassium sulfate, magnesium sulfate, and magnesium chlorid, and was formed everywhere about the borders of the layers of carnallit wherever water could work upon them. In quantity the kainit, as might be supposed, is far less than the carnallit, the latter existing in immense deposits. There is, however, quite enough of it to satisfy all the demands of agriculture for an indefinite time. In fact for many purposes the carnallit can take the place of kainit without detriment to the growing crops. The relative positions and quantities of the layers of mineral matters in the potash mines, and the depth in meters at which they are found is shown in Fig. 43.⁷

438. Theory of Deposition of Potash Salts.—The conditions which obtained in the evolution of the earth's crust upon which the deposition of soluble salts depends, are of great interest to agriculture in so far as the laying down of the stores of phosphoric acid, nitrates and potash are concerned. Deposits of phosphoric

Maercker, Die Kalidüngung, 2nd Edition, 1893 : 3.

acid which are stored are mostly insoluble or difficultly soluble in water. On the other hand, the nitrates which are deposited are

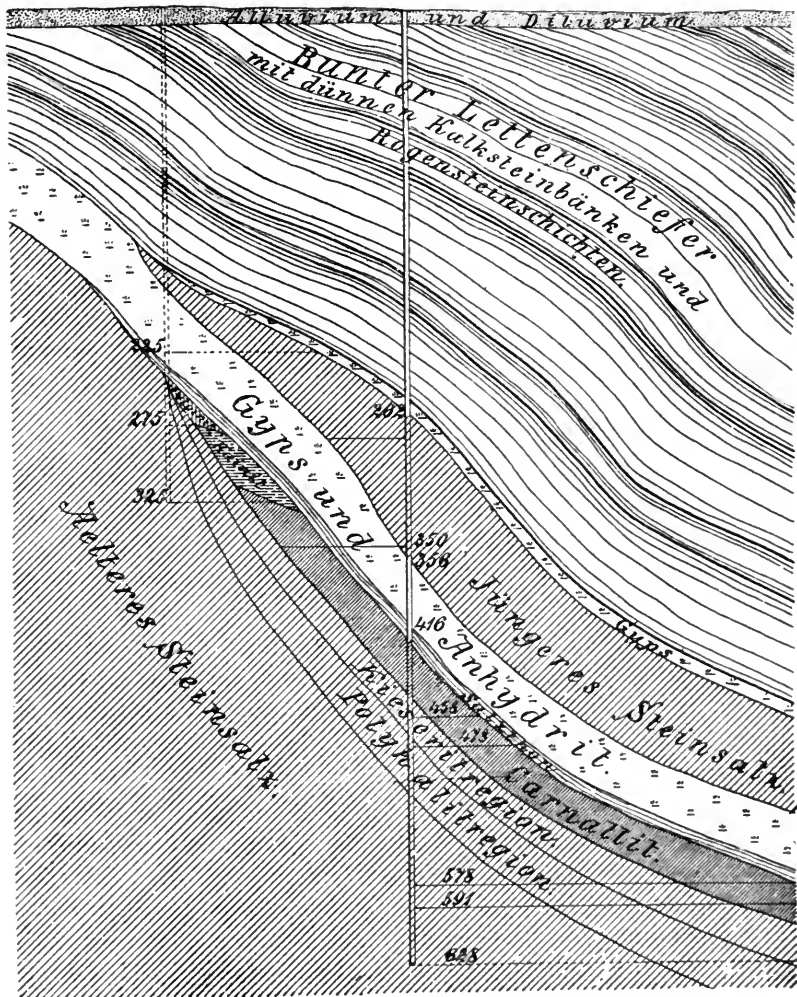


Fig. 43. Geological Relations of the Potash Deposits near Stassfurt.

very soluble in water and this is true, though to a less extent, with potash compounds. Nevertheless, all of these potash depos-

its have been deposited according to the conditions of concentration and temperature to which the original solutions have been subjected. The laws which govern the cooling, concentration and deposition of chemical compounds in different degrees of solubility are now well known. The theories of solution have been fully expounded and verified by actual demonstration.

It is evident that the depositions of potash salts must have come from the gradual concentration or cooling, or both, of the original solution. It is further evident that these original solutions were secured by the action of fresh or salt water upon rock deposits rich in potash. In going into solution the potash salts, in response to the law of equilibrium, have combined with different acids, producing salts of different degrees of solubility. The salts of the same solubility, obeying a well-known law, tend to be precipitated in certain given conditions of concentration and temperature. Thus, nature separates sometimes completely and sometimes incompletely, not only the similar salts of potash, but also other saline compounds whose deposition depends upon similar conditions. By the combined action of these forces the vast potash deposits which are found in different parts of the world but especially near Stassfurt, in Germany, have been produced.

It is well known that almost all chemical substances which exist in rocks, as incidental or principal constituents thereof are found in the water which comes in contact with these rocks, whether fresh or salt. It is, in fact, the accumulation of these dissolved portions which gradually transforms fresh into salt water. There are found in this solution, therefore, all the common metallic oxids in combination with all the common mineral acids.

The principal mineral bases are those of calcium, magnesium, potassium, sodium, iron, etc., and the principal acid bases are chlorine, sulfur, boron, carbon, bromine, iodine, etc. The deposits of these salts may be regarded as having arisen in two series; namely, the original deposit resting upon a foundation of rock salt and which consisted primarily of compounds of calcium or calcium in conjunction with magnesium and potash. The pure deposits of calcium sulfate are known as anhydrite and the compounds of calcium magnesium and potassium sulfate as polyhalite correspond-

ing in their pure state, to the formulae $2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. These deposits are found in alternate layers, having been intermingled with rock salt which diminishes in quantity as the deposits approach the surface. Above these calcium minerals are found other layers in which magnesium plays the principal part, consisting of kieserit $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and carnallit $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$. These may be regarded as the primary or original deposits. By the action of water of a less degree of concentration these primary deposits have been changed, in some instances, to those of a secondary character, thus potassium chlorid has evidently been derived by the action of water upon carnallit and kainit. $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ is evidently derived from carnallit and kieserit.

A study of these deposits both from the theoretic and practical point of view has been made by van't Hoff in which all the problems of a theoretic character relative to the depositions of these compounds are elaborated.⁸

Van't Hoff calls attention to the fact that in considering the natural depositions of salts of this kind, a commonly accepted principle; namely, that the least soluble salts in a mixture of this kind are the first deposited, is not necessarily correct.⁹ It is true that if the formation be considered as a whole, the deposits which take place naturally must be in harmony with the commonly accepted principle above stated, and, therefore, that a slightly soluble calcium salt would first appear and afterwards the combination of such a salt with more soluble sulfates, then the easily soluble magnesium sulfates, and finally comes the very soluble carnallit. This principle, however, assumes that all the substances are present in a saturated solution. It is easy to imagine, however, that such would not be the case and that a more difficultly soluble salt being present in small quantities would not, perhaps, be precipitated as quickly as a more easily soluble salt present in a saturated solution at the temperature of observation. Therefore, it would be quite impossible that there should be a solution so rich in magnesium sulfate, as van't Hoff states, and so poor in gypsum

⁸ Zur Bildung der ozeanischen Salzablagerungen, 1905.

⁹ Physical Chemistry in the Service of the Sciences, 1903 : 97.

that when concentrated, the more soluble magnesium salt would first be deposited. Thus, the actual composition of the salt under observation must be taken into consideration when applying the theory of the deposition of salt solutions. A study of the order in which these solutions have been deposited leads to a knowledge not only of the relative degree of saturation of the original salt in the solution but also to the conception of the temperature under which the deposits were laid down.

If, in the theoretic consideration of this problem some definite temperature, pressure and method of crystallization are assumed, it is easy to pass to a knowledge of the relative degree of concentration in the different constituents under those conditions. In sea water, naturally the amount of sodium chlorid present is of the first consideration, because that is always the most abundant of the mineral substances in solution. The next most important mineral constituents are the salts of magnesium and potassium, especially the chlorids and sulfates thereof, and the next series of salts to be considered are those of calcium. Van't Hoff, in order to give a clearer idea of this theory, expresses the proportion of the constituents in sea water, which are found to be, with the exception of calcium, the same everywhere, as follows: $100\text{NaCl} + 2.2\text{KCl} + 7.8\text{MgCl}_2 + 3.8\text{MgSO}_4$. Van't Hoff states that in a problem of this kind if only one salt is present the situation is very simple. When over two salts are present it is important to determine which will crystallize first and then when will the second salt begin to be deposited. This is illustrated by considering two common salts; namely, potassium and sodium chlorid in solution at 25° . If potassium chlorid be near the point of saturation it will be the first to separate into salt form and by further concentrating the solution the content of the sodium chlorid is gradually increased until the saturation point is reached and then it begins to come down. Further concentration does not change the present relation of the two salts in solution. They are both deposited at the same rate when the saturation point is reached and the evaporation continues, with a gradual deposit of the two salts until the water is all gone. If the experiment be started in the opposite condition of the sodium chlorid at saturation point.

the same result will be secured but in an inverse order. A solution which has been shaken for a long time with an excess of both salts so as to become thoroughly saturated will give the following composition: $100\text{H}_2\text{O} + 89\text{NaCl} + 39\text{KCl}$. (C Fig. 44).

Thus solutions which contain a greater ratio of sodium chlorid to potassium chlorid than $89 \times 58.5 : 39 \times 74.5$ will first deposit chlorid of sodium. In the opposite condition of the ratio potassium chlorid will first appear.

A consideration of this problem leads to the formation of the law which even in the most complicated cases governs the process of crystallization.

This law, as formulated by van't Hoff, shows that in depositing its contents, the solution gradually varies its composition away from that of a solution which is saturated with the substance being deposited at the moment and contains nothing but this substance. The principle becomes quite clear if the process which takes place during crystallization from an evaporating solution is reversed and water be continually added together with the salt which is being deposited.

Under these circumstances obviously the solution tends to become more and more a saturated solution of this salt alone, since the other constituents, whatever they may be, must gradually become relatively negligible in quantity.

Thus, if a solution which is practically that of sea water be considered corresponding to the formula for the salt in sea water, already given, it is evident that other salts could be added in order to change the degree of concentration. The principle, however, may be more briefly defined if the case of potassium chlorid, magnesium chlorid, and magnesium sulfate be first considered and only at the very end the chlorid of sodium which is always present in excess in sea water be taken into consideration.

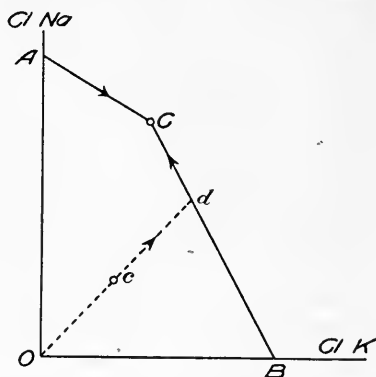


Fig. 44. Diagram Showing Law of Crystallization of Potash Salts.

Proceeding in a systematic manner, attention may first be called to the combination of potassium chlorid and magnesium chlorid, that is to say, a combination of these metallic oxids with a common acid and then a combination of magnesium chlorid and magnesium sulfate, that is a common base with different acids. If, however, the problem be stated in a general form, potassium sulfate which has not yet been mentioned in this connection, must be taken into account since this salt may be formed from the potassium chlorid and magnesium sulfate already in the solution. This gives a third combination of magnesium sulfate and potassium sulfate, that is, a combination of the same acid with two metallic bases and the last combination will be that of potassium sulfate and potassium chlorid, the same metallic oxids with different acids. In order to illustrate this problem graphically, van't Hoff gives a table of the solubilities of these bodies, in convenient form.

Saturation with	In mols. per 1000 mols. H ₂ O			
	K ₂ Cl ₂	MgCl ₂	MgSO ₄	K ₂ SO ₄
A. Potassium chlorid.....	44
E. Potassium chlorid and carnallit.....	5.5	72.5
F. Magnesium chlorid and carnallit.....	1	105
B. Magnesium chlorid.....	108
G. Magnesium chlorid and MgSO ₄ .6H ₂ O....	104	14
H. MgSO ₄ .7H ₂ O and MgSO ₄ .6H ₂ O.....	73	15
C. MgSO ₄ .7H ₂ O.....	55
J. MgSO ₄ .7H ₂ O and schönit.....	58.5	5.5
K. Potassium sulfate and schönit.....	22	16
D. Potassium sulfate.....	12
L. Potassium sulfate and potassium chlorid..	42	1.5

The explanation of these diagrams is best given in van't Hoff's words:—

“The presentation of the whole of this material graphically makes the understanding of it much easier. The rectangular axes in the plane of the paper can be retained and from their point of intersection at O (Fig. 45) the four single salts, potassium chlorid, magnesium chlorid, magnesium sulfate and potassium sulfate, can be laid off in the directions, A,B,C, and D, respectively. The four combinations which they form, two by two, fall then within the quadrants lying between the axes. We obtain in this way, a fashion of representing the facts something like Fig. 44 re-

peated four times. In this case, however, in three of the quadrants a complication arises from the existence of an intermediate compound. Between A, saturation with potassium chlorid, and D, saturation with potassium sulfate, there is only the point L, where the solution is saturated with both. Between A and

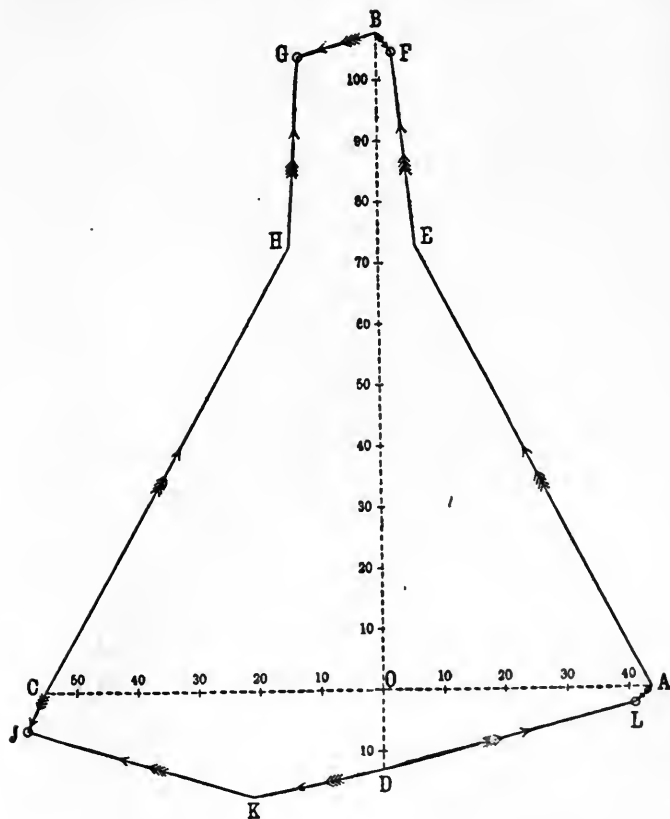


Fig. 45. Graphic Representation of Theory of Crystallization.

B, however, carnallit ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) appears, and thus two determinations are necessary, which have been added at E and F and stand for saturation with carnallit and potassium chlorid in the one case, and the same compound with magnesium chlorid in

the other. In the same fashion between B and C magnesium sulfate with six molecules of water of crystallization appears in GH and between C and D the mineral schönit ($K_2Mg(SO_4)_2 \cdot 6H_2O$) along JK. The progress of crystallization, using the same principle as before, is just as easy to follow, and is indicated by the arrows which in each quadrant are directed towards a so-called

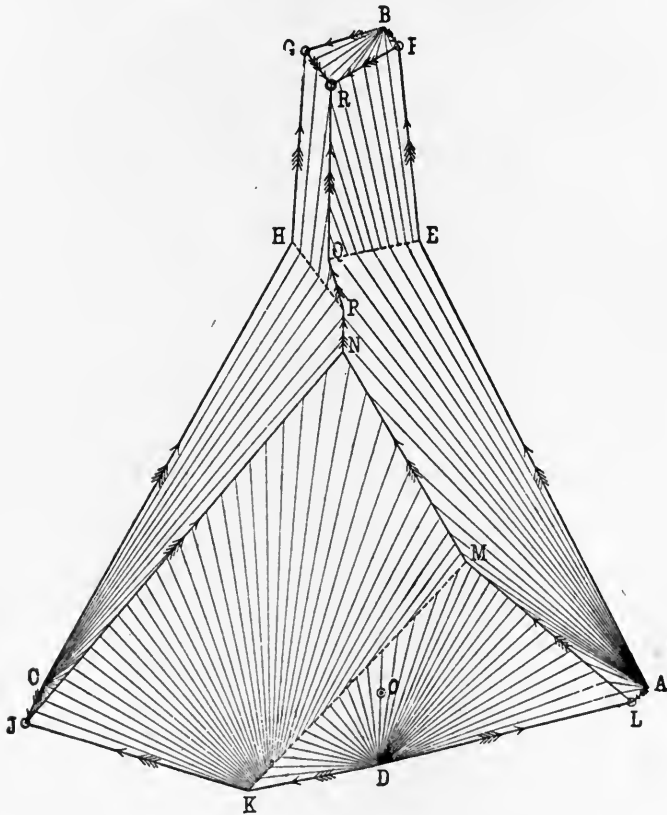
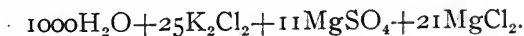


Fig. 46. Graphic Representation of the Deposition of Different Salts.

final point of crystallization. In this diagram these points are F, G, J, and L.

So far, however we have only considered a part of the possibilities, for solutions are entirely lacking which contain every-

thing, that is to say, chlorin and sulfuric acid, potassium and magnesium. The experimental treatment of this question may be best shown by means of an example. Let us start from L (Fig. 45), where the solution at 25° is saturated with potassium chlorid and potassium sulfate simultaneously. Taking care that both potassium salts are present in excess and in contact with the solution, we add magnesium in the form of chlorid or sulfate. The solution then takes up magnesium but remains still saturated with potassium sulfate and potassium chlorid. Finally its capacity for taking up magnesium becomes exhausted, and a solid magnesium salt is deposited. This in the case before us is schönit ($K_2Mg(SO_4)_2 \cdot 6H_2O$). After this, further addition of the magnesium salt will not lead to any being dissolved; the consequence will simply be an increase in the amount of schönit. The solution will retain its constant composition, since it is and remains saturated with potassium sulfate and potassium chlorid. We determine the composition of this solution by analysis, using a mixture which at 25°, after prolonged agitation, is seen to be in contact with all the three salts and is found to have attained a constant composition. The result is represented by the following formula:



Our task is thus finally limited to finding the solutions saturated with three salts and analyzing those solutions. Many such are *a priori* possible, if we consider the seven different compounds which have to be taken into account. The possible number would be:

$$\frac{7 \times 6 \times 5}{1 \times 2 \times 3} = 35.$$

As a matter of fact, however, only a few of these possibilities are realized, and when a solution obtained in the above manner is systematically evaporated at 25°, and the salt deposits are continually removed, the possibilities which are actually realized are found to be limited to four, in addition to the one described.

After potassium chlorid and schönit have come out, magnesium

sulfate with seven molecules of water of crystallization appears as an additional salt. The deposit having been removed, this hydrate of magnesium sulfate and potassium chlorid is now deposited until finally magnesium sulfate with six molecules of water of crystallization is added to these two salts as a new constituent. From this point onward the hexahydrate of magnesium sulfate with potassium chlorid crystallizes until carnallit makes its appearance. After this the hexahydrate of magnesium sulfate with carnallit constitutes the deposit until magnesium chlorid appears and now the solution dries up completely to a mixture of the three last named substances.

Collecting once more the quantitative measurements connected with these deposits, we have the following table:

Saturation with	In moles. per 1000 moles. H ₂ O		
	K ₂ Cl ₂	MgCl ₂	MgSO ₄
M. Potassium chlorid, potassium sulfate, schönit	25	21	11
N. Potassium chlorid, MgSO ₄ .7H ₂ O, schönit . . .	9	55	16
P. Potassium chlorid, MgSO ₄ .7H ₂ O, MgSO ₄ .6H ₂ O	8	62	15
Q. Potassium chlorid, carnallit, MgSO ₄ .6H ₂ O . . .	4.5	70	13.5
R. Magnesium chlorid, carnallit, MgSO ₄ .6H ₂ O . .	2	99	12

The next thing is to represent these numbers graphically, and when this has been done we are presented with a complete view of the whole process of crystallization.

To do this a third dimension is obviously required. We add a third axis passing through O, vertical to the former system of axes (Fig. 45), and along this we lay off the number of molecules. In practice this may be done conveniently by means of a model consisting of a piece of wood in which vertical needles are set at the proper places, with their lengths adjusted to the number of molecules. A horizontal projection on this model is shown in Fig. 46, whose border obviously coincides with the outline of Fig. 45, and whose points, M, N, P, Q, and R, represent the above data. This having been done, each pair of points representing saturation with the same two salts, for example, M and L, where in both cases saturation with the sulfate and chlorid of potassium exists, is connected by a line.

These lines divide the figure into areas, each of which corresponds to saturation with a definite salt, as follows:

EQPNMLA.....	Potassium chlorid
EQRF.....	Carnallit
FRGB.....	Magnesium chlorid
RGHPQ.....	$MgSO_4 \cdot 6H_2O$
PHCJN	$MgSO_4 \cdot 7H_2O$
JKMN.....	Schönit
KMLD.....	Potassium sulfate

The progress of crystallization is given in each area by lines which proceed away from the points which represent saturation with the body itself, as a single constituent. Thus in the potassium chlorid area, these lines proceed from A in all directions."

In the application of a theory of this kind to a solution containing a gram molecule of magnesium chlorid and a gram molecule of potassium sulfate the preliminary evaporation before the appearance of any deposit corresponds to motion from the origin in the vertical direction, until the area line immediately above it, that is, the potassium sulfate area is reached. In this condition, the potassium sulfate should separate theoretically, and in fact, this phenomenon actually occurs. Theoretically, the next movement would begin at D and move away from D until the limit KM is encountered and at this point the separation of schönit would begin. The actual experimental data in this case also correspond with the theory. If the salts, as they separate, are continuously removed, the deposit of schönit continues as indicated in the figure until the limit MN is reached at which point, theoretically a crystallization of potassium chlorid should take place. This theory is also corroborated by the experimental data.

When the point N is reached on the line MN, theoretically magnesium sulfate begins to be deposited. By consulting the table of the letters at the different points in order to understand just what they represent, the progress of crystallization can be followed theoretically until the complete deposit of the salts takes place. Thus, the figure, as worked out in detail, furnishes a means of comprehending the process of crystallization of these mixed salts, and, theoretically, of predicting in a very certain manner, the entire change which takes place.

In a similar manner, van't Hoff has worked out the influence of time and the variations of temperature and pressure on the

deposition of these salts. In the natural deposition it is noticed that there are often compounds found which do not appear in laboratory experiments but the deposition of which can be theoretically ascertained. By change of temperature, especially going above the fixed standard of 25° on which the previous predictions have been based, new combinations of minerals take place and minerals which are formed at 25° disappear. The dominant factors, therefore, in the order of crystallization and the rate of deposition, are temperature and concentration. The variations in pressure to which the salts are subjected doubtless have some influence but these influences are very minute when compared with those above mentioned.

The agricultural analyst who desires to study the causes which produce these deposits and the order in which the phenomena occur, is directed in the above epitome of van't Hoff's work to the principles which guided his investigations.

Further details of the method of procedure are found in the paper cited.

439. Potash from Feldspathic Rocks.—The question of the availability of potash in feldspathic rocks has been under discussion at intervals for many years. The fact that in all virgin soils potash was originally derived from the disintegration of the rocks is incontestable. It has, however, been generally supposed that such long periods of time were necessary in order to carry on the decompositions, that feldspar could not be made practical use of as a potash fertilizer. This impression has been confirmed by the fact that ground feldspar on digestion with water yields only extremely small amounts of potash to the solvent. The systematic investigations of Cushman¹⁰ have developed facts of importance in this connection.

Cushman has shown that a typical pegmatitic feldspar containing 9.3 per cent. of potash (K_2O) when ground to a 200-mesh powder, yielded the following amounts of potash to solution in water, under varying conditions:

¹⁰ Bureau of Chemistry, Bulletin 92, 1905; Office of Public Roads. Circular 38 : 1905.

	K ₂ O, per cent.
Digestion in distilled water	0.03
Grinding with water in a mill.....	0.32
Digestion in dilute solution of ammonia salts	0.25
Grinding with same solution.....	0.57
Digestion with limewater	0.50
Grinding wet with calcic sulfate.....	0.35
Grinding wet with lime.....	0.70
Removal of the alkali by electrolysis.....	0.50
Alternative grinding and electrolysis	3.50

These results indicate that the action of water alone, as well as the combined action of water and other substances found in the soil, carries on the decomposition of fine ground feldspar to a very considerable extent. The high yields of alkali that can be obtained by means of wet grinding and electrolysis indicate that the decomposition might readily go on to complete kaolinization of the feldspar, if any tendency were at work to remove the decomposition products from the surfaces of the particles upon which they are first formed. Since electrolysis does not produce decomposition but merely aids the water reactions by removal of the decomposition products, it would seem probable that in the soil this removal may be done by the plant roots themselves, thus leading to a continual and steady decomposition of the fine feldspathic particles. Until a comparatively recent time the fine grinding of rocks was a costly operation, but the development of improved methods used in the cement industry now makes it possible to grind rocks to extremely fine powders at low cost.

In 1850 G. Magnus observed that plants could be successfully grown and matured in ground feldspar, which apparently suffered decomposition during the process.¹¹ In 1887 Aitken in Scotland conducted successful plat experiments on a small scale, using Norwegian feldspathic rock rich in potash, ground to 120-mesh powder.¹² Peas and turnips were the crops used, and in all cases an increased yield was obtained as the result of the use of feldspar.

¹¹ *Journal für praktische Chemie*, 1850, **50** : 65.

¹² *Highland and Agricultural Society of Scotland, Transactions*, 1887, **19** : 253.

In 1889 the Maine State College Experiment Station successfully grew oats in plats using ground feldspar in connection with nitrate of soda and superphosphate.¹³ In 1890 Headden in Colorado carried on a similar set of experiments on oats.¹⁴ The conclusion was reached that the oat plant can use finely divided feldspar as a source of potash.

At about the same time Hensel in Germany was advocating the use of stone meal as a fertilizing agent. Conflicting reports have been made as to the results of these experiments, and in any case it would appear that the material used had not been ground fine enough to render it quickly available.

The investigations of Cushman have reopened the question and systematic experiments are under way which should settle this important question once and for all. Even should it appear that such material is directly useful as a fertilizer, the question as to its wide spread use will necessarily depend upon the cost involved in grinding and transporting it.

440. Cushman's Later Investigations.—Investigation of the availability of potash in feldspathic rocks has been continued by Cushman in connection with the experiments in the actual growing of crops.¹⁵ He finds that a cubic foot of granite weighs about 170 pounds and contains about 8.5 pounds of potash, and that 100 feet square and 100 feet in depth will contain about 8,500,000 pounds of potash. It is evident, therefore, that feldspathic rock which is accessible in the United States would afford an almost inexhaustible supply of potash if it could be utilized. Very large deposits of this feldspathic rock are found in various parts of the country, and these have been developed for building and other purposes in Maine, Connecticut, Pennsylvania and Maryland. The feldspathic rocks obtained from these mines have been ground to fine powders, chiefly for use in potteries.

Orthophyric feldspathic rock contains 16.8% of potash, but the feldspar from the sources above mentioned contains only from 8% to 10%.

Cushman says:

¹³ Annual Report of the Maine State College Agricultural Experiment Station, 1889 : 143.

¹⁴ Colorado Agricultural Experiment Station, Bulletin 65, 1901 : 28.

¹⁵ Bureau of Plant Industry, Bulletin 104, 1907.

“The question whether fine-ground feldspar can be used as a potash fertilizer has been a matter of controversy for many years. There is a large and widely scattered literature on the subject, an examination of which shows that the matter has been debated with much vigor and sometimes with prejudice and intolerance on both sides. It is easy to find the published records of a number of experiments, made by trained and thoroughly competent agriculturists, which tend to show that ground feldspar is an efficient potash fertilizer. On the other hand, a number of experiments seem to indicate that the potash is only slightly available, while others would appear to show that the ground rock is entirely useless. On account of the large interests involved in the settlement of this question it is not difficult to see why vigorous differences of opinion, and even unjust prejudice should have arisen. When, however, trained investigators reach opposite conclusions, based upon experimental evidence, we are forced to the opinion that while ground feldspar may be a useful fertilizer under certain conditions it is not so under others.”

Very full reference to the literature of the availability of rock potash is given by Cushman in the work above cited, and in addition to these data experiments were undertaken by him to test anew the value of the fine-ground rocks for this purpose. Tobacco was selected as the plant most suitable for the experiment, because it is one of those plants which requires a very large quantity of potash for its proper nourishment. Artificial soils were prepared having for a base coarse grained white sand and finely ground feldspar containing about 8 per cent. of potash. Seedlings were set out in this mixture and moistened from time to time with solutions of ammonium nitrate and ammonium phosphate in order to supply the necessary amount of nitrogen and phosphoric acid.

In addition to these field experiments others were made in a green house, in which the effect of potassium in the form of carbonate containing about 67 per cent. of potash was compared with the potash in fine-ground feldspar, containing about 8.3 per cent of potash.

In addition a third experimental plot was prepared, to which no potash was added. All three beds were supplied with a sufficient quantity of nitrogen for the purposes of crop growth in the form of ammonium nitrate.

After the harvesting of the crop the data were collected with the following results:

RESULTS OF GREENHOUSE EXPERIMENTS WITH TOBACCO PLANTS.

No. of plat.	Source of potash.	Actual weight of green crop. Pounds.	Estimated weight of green crop per acre. Pounds.	Actual weight of cured leaf. Pounds.	Estimated weight of cured leaf per acre. Pounds.
1	Potassium carbonate	154.0	30,800	5.70	1,140
2	Ground feldspar	155.0	31,000	6.30	1,260
3	128.5	25,700	5.30	1,060

Cushman calls attention to the fact that these yields are not equal to those obtained in the field under good conditions, but are satisfactory for a winter crop in a green house.

441. The Effect of Fineness of Grinding.—In the study of these experiments the theoretical contention on which is based the idea that the fineness of the grinding is to some extent the measure of the availability of the feldspar in feldspathic rocks was thoroughly tested. The conclusion is that the potash in these rocks is partially available even during the first season, but that the availability in the coarse particles is not very great, hence fineness of grinding is not only a necessary condition to the utilization of the potash, but time is also an important factor. It would be unwise in the present state of our knowledge to depend upon the finely ground potash alone for the production of a large crop. It is wiser to add during the first years at least a sufficient quantity of more available potash to supply the needs of the crop until the weathering of the finely ground rock has somewhat progressed.

The problem of cost is also an important factor in these investigations. Unless feldspar can be reduced to a fine powder, transported and sold at a small price per ton, it is evident that at least for the present it can not play any important role as a plant food.

442. Mills for Grinding.—The mills which are used for grind-

ing feldspar for the pottery would also be suitable for preparing it for agricultural purposes. Cushman says:

"For fertilizer purposes the fine grinding of feldspar could be done in iron mills similar to those which are used for grinding limestone in the cement industry. The only important points to consider would be the percentage of total potash present and the fineness of grinding. At the present time there are few data available on the cost of grinding feldspar to a 200-mesh powder, but with modern machinery there is little doubt that it can be done much more economically than would have been considered possible only a few years ago. Under the stimulus of the cement industry a great development has been made in recent years in the methods and art of fine grinding. The following table is of interest, as it shows at a glance what the potash in ground feldspar would cost if the percentage is compared with a cost of grinding varying from \$1 to \$10 per long ton.

PRICE PER POUND OF POTASH UNIT IN FELDSPAR.

Potash contained in the feldspar.	Cost of ground feldspar per ton (2,240 pounds).									
	\$1.	\$2.	\$3.	\$4.	\$5.	\$6.	\$7.	\$8.	\$9.	\$10.
3 per cent. . . .	\$.015	\$.030	\$.044	\$.059	\$.074	\$.089	\$.104	\$.119	\$.134	\$.149
4 per cent.011	.022	.033	.044	.055	.067	.078	.089	.100	.111
5 per cent.009	.018	.027	.035	.044	.053	.062	.071	.080	.090
6 per cent.007	.015	.022	.030	.037	.045	.052	.059	.067	.074
7 per cent.006	.012	.019	.025	.032	.038	.045	.051	.057	.063
8 per cent.005	.011	.017	.022	.028	.032	.039	.045	.050	.056
9 per cent.005	.009	.014	.019	.024	.029	.035	.039	.044	.049
10 per cent.004	.009	.015	.018	.022	.027	.031	.035	.040	.045
11 per cent.004	.008	.011	.015	.020	.023	.028	.030	.024	.040
12 per cent.004	.007	.011	.015	.018	.022	.026	.029	.033	.037
13 per cent.003	.007	.010	.014	.017	.021	.024	.027	.031	.034
14 per cent.003	.006	.010	.013	.016	.019	.022	.026	.029	.032
15 per cent.003	.006	.009	.012	.015	.018	.021	.024	.027	.030

The prices are given in cents per pound, so that if, for instance, rock carrying eight per cent. of potash could be delivered for \$9 per ton, the potash contained in it would be added to the land at a cost of 5 cents per pound. At \$5 per ton the cost per pound would fall to 28 mills. The figures are of course only applicable provided the potash in the ground material can be proved available as a plant food."

On this subject Cushman makes the following observation:

"It must be remembered that the only real measure of available potash is that which is made use of by the crop. It is not

likely that all the potash added, even in the form of soluble potash salts, is actually used, and the amount that can be supplied by ground rock is still an unknown quantity."

The quantity of feldspar ground in short tons and the cost of production is given in the following table for the years 1901-5 inclusive:

PRODUCTION AND VALUE OF FELDSPAR, 1901-1905.

Year	Crude.		[Short Tons]. Ground.		Total.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
1901	9,960	\$21,669	24,781	\$198,753	34,741	\$220,422
1902	21,870	55,501	23,417	194,923	45,287	250,424
1903	13,432	51,036	28,459	205,697	41,891	256,733
1904	19,413	66,714	25,775	199,612	45,188	266,326
1905	14,517	57,976	20,902	168,181	35,419	226,157

443. Possible Harmful Effects of Ground Feldspar.—"The question is frequently asked whether there is possible danger to the land in experimenting with the use of ground feldspathic rock. It is well known that in some cases, notably with tobacco, injurious effects are produced by the continued use of the soluble potash salts, particularly the sulphate and muriate. Feldspar grains of various sizes are normally present in many soils; it does not, therefore, seem possible that any harmful effect could follow the application of ground rock. As has been pointed out in an earlier portion of this paper, feldspar consists of the alkaline elements, soda, potash, and lime, combined with alumina and silica. After decomposition, hydrated aluminum silicate, the essential base of all clays, is left behind, the alkalies and the silica being set free in a condition in which they can be absorbed by the root action of plants. It would seem, therefore, that whatever the value of the results obtained no possible harm can follow the experimental use of ground feldspar in reasonable quantities."

444. Extract of Potash from Ground Rock.—"The discussion of the use of ground rock as a source of potash is not complete unless it includes the extraction of potash by chemical and electrical processes. If future experiments should demonstrate that fast-growing crops are dependent on very soluble forms of

potash the question of the extraction of this element from ground feldspar becomes a matter of importance.

The extraction of potash from rock has not as yet been accomplished on a commercial basis, but it has been done in the laboratory, and the method has been published in a recent bulletin.¹⁶ The full details of the investigation are too technical for insertion here, but if the processes described could be carried on at a cost low enough, the potash in ground rock could be rendered sufficiently soluble for all practical purposes. Briefly, the method consists in sliming the ground feldspar with water to which a small quantity of hydrofluoric acid has been added. This slime is placed inside a suitable wooden vessel and a current of electricity is passed through it. The alkali set free by the action of the acid is carried away by the electric current, while the acid appears to be used over and over again. Finally, by combining the acid and alkaline products, a material is obtained in which the potash which has been set free is soluble and available.

A number of methods for extracting potash from feldspathic rocks by means of fusions with various substances have been devised and even patented. In all of these methods, however, large quantities of by-products are formed which, though made from more or less costly material, are generally of no value. From laboratory investigations it would seem that the use of potash compounds to attack the feldspar would in some measure overcome this difficulty, since the potash used is just as valuable after the process is completed as it was before. Another method, which shows some promise of success consists in mixing the feldspar with lime and treating the mixture with live steam under pressure. By this means the potash is made easily acid soluble. It is hoped that further investigation will result in some method based on these principles for making the vast quantities of potash contained in feldspathic rocks completely available."

445. Conclusion.—"A careful reading of the foregoing pages will show that no claim has been made that ground feldspar is an efficient substitute, under all circumstances, for potash salts.

¹⁶ Bul. 28, U. S. Dept. of Agriculture, Office of Public Roads.

The effort has been to present all the evidence which could be collected, both for and against the use of ground feldspar as a fertilizer. The question is still open, and systematic and long-continued experimentation is the only possible method of obtaining conclusive information on the subject. The evidence so far obtained appears to indicate that under certain conditions and with certain crops feldspar can be made useful if it is ground sufficiently fine. On the other hand, it is highly probable that under other conditions the addition of ground feldspar to the land would be a useless waste of money. At the present stage of the investigation it would be extremely unwise for anyone to attempt to use ground rock, except on an experimental scale that would not entail great financial loss.

The subject must be approached conservatively, with due regard to business economy. Sensationalism and exaggeration invariably do harm. It is extremely unlikely that ground rock will ever entirely displace the use of potash salts for its availability must inevitably depend upon many modifying conditions, such as the nature of the soil, the amount of moisture present, the character of the other fertilizers used, and the varying root action of different crops. With tobacco the results so far obtained have been encouraging, but it is possible that this plant, which is a voracious feeder, can make use of the potash in fine-ground feldspar to a greater extent than any other fast-growing crops, such as potatoes and the cereals, some of which mature in practically sixty days and must therefore find their plant food in a highly available condition."

ORGANIC SOURCES OF POTASH

446. Tobacco Stems and Waste.—Until within a few years tobacco stems and other waste from factories, were treated as a nuisance in this country and burned or dumped into streams. By burning and saving the ash, the potash contained in the stems and waste is recovered in a form suitable for field use. The nitrogen contained in these waste materials, both in the form of nicotin and of albuminoids is lost. Ignition of this waste should not be practiced. It should be prepared for use by grinding to a fine powder. Applied to the soil in this condition the

powder may be useful as an insecticide as well as a fertilizer. Tobacco stems contain from 12 to 27 per cent. of moisture, and from 12 to 20 per cent. of ash. The composition of the stems from two celebrated tobacco-growing regions is subjoined:¹⁷

	Kentucky stems per cent.	Connecticut stems per cent.
Moisture.....	26.70	13.47
Organic and volatile.....	60.18	70.85
Ash	13.12	15.68

The ash calculated to the original substance has the following composition:

	Kentucky stems per cent.	Connecticut stems per cent.
Phosphoric acid.....	0.67	0.53
Potash.....	8.03	6.41

It is thus seen that about half the ash of tobacco stems is composed of potash. The stalks of the tobacco have almost the same composition as the stems, but the percentage of ash is not quite so great. In three samples analyzed at the Connecticut station the percentages of ash found in the water-free substance are 6.64, 7.00, and 7.46, respectively. The pure ash of the stalks is found to have the following composition:¹⁸

Constituents	Description of samples.	
	Cut Aug. 22, per cent.	Cut Sept. 17, per cent.
Silica	0.82	0.57
Iron and aluminum oxids	1.38	1.38
Lime	14.01	16.58
Magnesia	6.64	7.36
Potash	56.34	54.46
Soda.....	1.28	1.16
Sulfuric acid	8.06	6.75
Phosphoric acid	6.37	6.27
Chlorin	6.55	7.05
	<hr/>	<hr/>
	101.45	101.58
Deduct oxygen = chlorin.....	1.48	1.58
	<hr/>	<hr/>
	100.00	100.00

The leaves of the tobacco contain more ash than the stalks or stems, but the percentage of potash therein is less. In 18 samples

¹⁷ Connecticut Agricultural Experiment Station, Bulletin 97, 1889 : 7.

¹⁸ Annual Report of the Connecticut Agricultural Station, 1892 : 32.

analyzed at the Colorado station the percentages of moisture in the leaf varied from 6.08 to 28.00, and those of ash from 22.60 to 28.00.¹⁹ The percentages of potash in the ash varied from 15.20 to 26.30. In these data the carbon dioxide, sand, etc., are included while in those quoted from the Connecticut station they are excluded.

447. Cottonseed Hulls and Meal.—A considerable quantity of potash is added to the soil in cottonseed meal and hulls. The practice of burning the hulls cannot be recommended, although it is frequently done, for the incineration does not increase the quantities of phosphoric acid and potash, while it destroys the availability of the nitrogen. Nevertheless, the analyst will often have to deal with samples of the raw materials above mentioned, as well as with the ash of the hulls, in which the potash can be determined by some one of the standard methods to be described. In general it is found that the hulls of seeds and the bark and leaves of plants have a greater percentage of ash than the interior portions. In the case of cottonseed, however, an exception is to be noted. The cottonseed meal in the air-dried state has about seven per cent. of ash, while the hulls have only about three. When it is remembered, however, that the greater part of the oil has been removed from the meal it will be seen that in the whole seed in the fresh state the discrepancy is not so marked.

In the crude ash of the hulls the percentage of potash varies generally from 20 to 25, but in numerous cases these limits are exceeded. In 12 samples of cottonseed hull ashes examined by the Connecticut station the mean percentage of potash in the crude sample was 22.47, and the extremes 15.57 and 30.24 per cent., respectively.²⁰ In determining the value of the ash per ton the content of phosphoric acid must also be taken into account.

Cottonseed meal contains about 1.75 per cent of potash. Since the mean percentage of ash in the meal is seven, the mean content of potash in the crude ash is about 25.

¹⁹ Colorado Agricultural Experiment Station, Bulletin 10, 1890 : 13.

²⁰ Connecticut Agricultural Experiment Station, Bulletin 103, 1890 : 9.

448. Wood Ashes.—Unleached wood ashes furnish an important quantity of potash fertilizer. The composition of the ash of woods is extremely variable. Not only do different varieties of trees have varying quantities of ash, but in the same variety the bark and twigs will give an ash quite different in quantity and composition from that furnished by the wood itself. In general the hard woods, such as hickory, oak, and maple, furnish a quality of ash superior for fertilizing purposes to that afforded by the soft woods, such as the pine and birch trees.

The character of the unleached wood ashes found in the trade is indicated by the subjoined analyses. The first table contains the mean, maximum and minimum results of the analyses of 97 samples by Goessmann.²¹

	Composition of wood ashes.		
	Means	Maxima	Minima
Potash	5.5	10.2	2.5
Phosphoric acid.....	1.9	4.0	0.3
Lime.....	34.4	50.9	18.0
Magnesia.....	3.5	7.5	2.3
Insoluble.....	12.9	27.9	2.1
Moisture	12.0	28.6	0.7
Carbon dioxid and undetermined	29.9		

In 16 analyses made at the Connecticut station the data obtained are given below:²²

	Means	Maxima	Minima
Potash	5.3	7.7	4.0
Phosphoric acid.....	1.4	1.8	1.9

In 15 analyses of ashes from domestic wood-fires in New England, the following mean percentages of potash and phosphoric acid were found:

Potash.....	9.63
Phosphoric acid.....	2.32

In leaching, ashes lose chiefly the potassium carbonate and phosphate which they contain. Leached and unleached Canada ashes have the following composition:

²¹ Annual Report of the Massachusetts Agricultural Experiment Station, 1888 : 202.

²² Annual Report of the Connecticut Agricultural Experiment Station, 1889 : 110.

	Unleached per cent.	Leached per cent.
Insoluble	13.0	13.0
Moisture	12.0	30.0
Calcium carbonate and hydroxid.....	61.0	51.0
Potassium carbonate.....	5.5	1.1
Phosphoric acid.....	1.9	1.4
Undetermined.....	6.6	3.5

In the wood ashes of commerce, it is evident that the proportion of the potash to the lime is relatively low.

The number of parts by weight of the chief ingredients of the ash in 10,000 pounds of woods of different kinds is given in the table page 531, with the percentage composition of the pure ash, that is the crude ash deprived of carbon and carbon dioxide.

449. Statement of Results.—The bases which are found present in the ashes of wood and other vegetable tissues exist without doubt before incineration, chiefly in combination with inorganic acids. Even the phosphorus and sulfur which after ignition appear as phosphates and sulfates, have previous thereto existed in an organic form to a large extent. The silica itself is profoundly modified in the organism of the growing plant, and possibly may not exist there in the purely mineral form in which it is found in the ash. During the progress of incineration, with proper precautions, all the phosphorus and sulfur are oxidized and appear as phosphoric and sulfuric acids. The silica is reduced to a mineral state, and if a high heat be employed silicates are formed. The organic salts of lime, magnesia and other bases at a low temperature are converted into carbonates, and if a higher temperature be used, may appear as oxids. The organic compounds of alkalies will be found in the ash as carbonates. It would be useless, therefore, to try to state the results of ash analysis in forms of combination similar to those existing in the original vegetable tissues. It is not certain even that we can in all cases judge of the form of combination in which the different constituents exist in the ash itself. It is, therefore, to be preferred in a statement of ash analysis to give the bases in the form of oxids, and the sulfur and phosphorus in the form of anhydrides, and the chlorine in its elementary state. In this case an

POUNDS OF THE INGREDIENTS NAMED IN TEN THOUSAND POUNDS OF WOOD.

Potash	9.02	18.06	16.85	14.94	13.95	13.80	10.60	7.13	5.01	4.54	3.02	2.90	2.90	1.79
Phosphoric acid	5.72	9.55	6.96	1.15	5.98	5.83	2.49	3.19	1.24	.96	.92	1.09	1.09	.73
Lime	6.41	24.73	35.61	7.60	27.40	18.40	7.85	14.21	18.04	15.16	12.46	7.93	7.93	12.12
Magnesia	14.67	.49	5.28	.10	3.05	4.86	.90	2.94	2.03	.74	.10	.34	.34	1.17
	Dogwood.	<i>Platanus occi-</i>	<i>Q. obtusiloba</i>	<i>Ash.</i>	<i>Q. rubra</i>	Hickory.	<i>Q. alba</i>	<i>M. grandiflora</i>	<i>G. palustris</i>	<i>P. mitis</i>	<i>Picea nigra</i>	Chestnut.	<i>Castanea vesca</i>	Old field pine.
	<i>florida</i>	<i>dentatis</i>		<i>F. americana</i>		<i>loma-</i>								

THE PURE ASHES OF THE WOODS CONTAIN THE FOLLOWING PER CENTS. OF THE INGREDIENTS NAMED.

Potash	28.04	23.17	21.92	46.04	24.66	28.60	42.16	19.54	15.35	19.70	14.30	18.10	18.10	3.85
Phosphoric acid.	8.51	12.23	9.00	3.58	10.55	11.97	9.48	8.75	3.82	4.18	4.33	6.76	6.76	4.11
Lime	38.93	31.62	46.39	23.57	48.26	37.94	29.85	38.94	55.24	65.53	58.98	49.18	49.18	67.73
Magnesia	6.80	.62	6.88	.60	5.38	10.04	3.43	8.05	6.25	3.20	.50	2.11	2.11	6.54
	Dogwood.	<i>Platanus occi-</i>	<i>Q. obtusiloba</i>	<i>Ash.</i>	<i>Q. rubra</i>	Hickory.	<i>Q. alba</i>	<i>M. grandiflora</i>	<i>G. palustris</i>	<i>P. mitis</i>	<i>Picea nigra</i>	Chestnut.	<i>Castanea vesca</i>	Old field pine.
	<i>florida</i>	<i>dentatis</i>		<i>F. americana</i>		<i>loma-</i>								

equivalent amount of oxygen to the chlorin found must be subtracted from the total. If an attempt be made to combine the acid and basic elements, the chlorin should first be united with sodium, and any excess thereof with potassium, and the amount of base so combined calculated to oxid and deducted from the total of such base or bases present. The carbonic acid present should be combined first with alkalies after the chlorin has been supplied. The phosphoric acid should be combined first with the iron and afterwards with lime or magnesia. In all cases the percentages should be based upon the ash, after the carbon and sand have been deducted, or it is also convenient at times to throw out of the results the carbon dioxid and to calculate the other constituents to the ash free of that substance. In determining the quantities of mineral matters removed from soil by crops, the ash should be determined with great care, freed of carbon and sand, and the calculations made on the percentage thus secured. In all statements of percentages of the essential constituents of ash, as regards fertilizing materials, it should be specified whether the percentage is calculated on a crude ash, the pure ash, that is free of carbon and sand, or upon a basis excluding the carbon dioxid. For the purpose of fertilizer control the analyst and dealer will be satisfied, as a rule, with the determination of the percentages of phosphoric acid and potash alone. To the other constituents of an ash is not assigned any commercial value.

450. Fertilizing Value of Ashes.—Primarily, the fertilizing value of wood-ashes depends on the quantity of plant food which they contain. With the exception of lime, potash, and phosphoric acid, however, the constituents of wood-ashes have little, if any, commercial value. The beneficial effects following the application of ashes, however, are greater than would be produced by the same quantities of matter added in a purely manurial state. The organic origin of these materials in the ash has caused them to be presented to the plant in a form peculiarly suited for absorption. Land treated generally with wood-ashes becomes more amenable to culture, is readily kept in good tilth, and thus retains moisture in dry seasons and permits of easy drainage in

wet. These effects are probably due to the lime content of the ash, a property moreover favorable to nitrification and adapted to correcting acidity. Injurious iron salts, which are sometimes found in wet and sour lands, are precipitated by the ash and rendered innocuous or even beneficial. A good wood-ash fertilizer, therefore, is worth more than would be indicated by its commercial value calculated in the usual way.

451. Availability of Ash Potash.—Harcourt has determined the availability of the potash of wood-ashes by the citric acid method of Dyer.²³

It has been stated by those interested in the sale of potash fertilizers that the potash in wood-ashes is not all in an available form, *i. e.*, part of it is insoluble and is, therefore, of no use to the plant. To ascertain what truth there is in the statement, a number of ashes was treated by Dyer's method for determining availability of plant food. The following table gives the number of pounds of potash and the amount that would be immediately available in 100 pounds of the different ashes examined.

Name of ash	Pounds of potash in 100 lbs. ash	Pounds of potash available in 100 lbs. ash	Per cent. of potash available
White oak	9.39	7.64	82.33
Birch	8.58	6.82	79.48
Mixed ash	13.40	12.72	94.92
Walnut	4.62	4.61	99.87
Red oak	5.75	4.72	82.09
Poplar	10.42	8.78	84.26
White ash	16.88	15.24	90.20
Butternut	3.99	3.56	89.22
Willow	9.59	8.19	85.40
Average	87.50

According to this method nearly 80 per cent. of the total potash of the birch ash, and, practically, all that of the walnut ash, or an average of 87.5 per cent. of the potash of all the ashes examined was found to be immediately available. In other words, an average of the nine samples experimented with shows that all but 12.5 per cent. of the total potash would be in a form of which the growing plant could make use at once.

452. Molasses from Sugar-Beets.—The residual molasses re-

²³ Ontario Agricultural College, 23rd Annual Report, 1897 : 27.

sulting after the extraction of all the crystallizable sugar in beet-sugar manufacture is very rich in potash. The molasses contains from 10 to 15 per cent. of ash.

The composition of the ash varies greatly in the content of potash as well as of the other constituents.²⁴ The content of potassium carbonate varies from 22 to 55 per cent. and, in addition to this, some potassium sulfate and chlorid are usually present.

The following figures give the composition of a good quality of beet-molasses ash:

	Per cent.
Potassium carbonate.....	45.30
Sodium carbonate	13.86
Potassium chlorid	17.02
Potassium sulfate.....	8.00
Silica, lime, alumina, water, phosphoric acid, and undetermined.....	15.82

Thus, in 100 parts of such an ash over three-quarters are potash salts. The molasses may be applied directly to the soil or diluted and sprayed over the fields.

453. Kinds of Potash Fertilizers Derived from Beet-Molasses.—The by-products from the factories using molasses for any purpose contain varying amounts of potash, and this renders it uncertain in any given case, without a special analysis to determine the actual quantity of potash purchased.²⁵ The residue from the molasses distillery known as "Schlempekohle" is a very common potash product in the German markets. The residues of the still are evaporated and incinerated to a carbonaceous mass suitable for transportation and application to the soil. In this product the potash is chiefly in the form of carbonate, but notable quantities of chlorid and sulfate are also present. The potash mass above described is used also largely for the manufacture of commercial potash which utilizes the greater quantity of the chlorid and sulfate present. The residue is dried and sold also, as a potash fertilizer, but contains comparatively very little pot-

²⁴ Horsin-Déon, *Traité de la Fabrication du Sucre*, 2nd Edition, 1900 : 1001.

²⁵ Reitmair, *Wiener landwirtschaftliche Zeitung*, 1905, 55 : 844.

ash, and that mostly as a silicate. It is known as "Schlempekohlenschlam."

Another product is made by the evaporation and drying of the product, so as to avoid calcination and preserve the nitrogenous constituents intact. Such preparations are called "Chilinit," a name which smacks of fraud, since the nitrogen therein is not in the form of saltpeter, but is found chiefly as amids and other organic combinations.

454. Residue of Wineries.—The pomace of grapes after being pressed or fermented for wine production contains considerable quantities of potash as crude argol or acid potassium and lime tartrate. This material can be applied directly to the soil or first burned, when its potash will be secured in the form of carbonate.

The use of the winery refuse for fertilizing purposes has not assumed any commercial importance in this country.

455. Insoluble Potash in Plants.—Berthelot has called attention to the existence of plant tissues of insoluble alkaline compounds.²⁶ Since, in the estimation of potash, we often extract the potash without incineration, it is evident that any insoluble material of this kind, likewise, of lime, or other alkaline bodies, will not be included in the determination. In a sample of hay dried at 110° it was found, when finely ground and extracted with water, that 27.8 per cent. of the potash was soluble and 72.2 per cent. insoluble. On incineration the soluble matter was found to contain 81.1 per cent. of organic matter and 18.9 per cent. of ash. The organic matter contained:

	Per cent.
Carbon	49.4
Hydrogen	6.65
Nitrogen	2.20
Oxygen and undetermined	41.71

The ash contained:

Potash (K ₂ O)	5.95
Lime (CaO)	2.56
Silica (SiO ₂)	5.38
Alumina, phosphoric acid and analogues	0.76

Total	14.65
Carbonic acid, undetermined compounds and loss	8.65

Total 23.3 of ash
or mineral matter to 100 parts of organic matter.

²⁶ Comptes rendus, 1905, 141 : 793.

In like manner the insoluble portion was examined and by incineration yielded:

	Per cent.
Organic matter.....	95.94
Ash	4.06
Or, for 100 parts organic matter.....	4.21 of ash.

The organic matter had the following composition:

Carbon	49.51
Hydrogen.....	6.31
Nitrogen.....	2.21
Oxygen and undetermined.....	41.97

The ash was composed of:

Potash.....	0.13
Lime	0.62
Silica.....	2.31
Alumina, phosphoric acid, etc.....	0.41
Carbonic acid, different compounds and loss	0.74
Total	<u>4.21</u>

From the above it is seen that the soluble part contains the greater quantity of the mineral compounds, not only as was to be expected of potash, but also of lime and silica. Nevertheless, there exists in the plant a notable quantity of potash entangled in some compound insoluble in water, amounting to about two-tenths of the total potash per cent.

456. Forms in which Potash is Found in Fertilizers.—The chief natural sources of potash used in fertilizer fabrication are: First, the natural mineral deposits, such as Stassfurt salts; second, the ash derived from burning terrestrial plants of all kinds; third, organic compounds, such as desiccated mineral matters, tobacco waste, cottonseed hulls, etc.

All these forms of potash may be found in mixed fertilizers. While the final methods of analyses are the same in all cases the preliminary treatment is very different, being adapted to the nature of the sample. For analytical purposes, it is highly important that the potash be brought into a soluble mineral form, and that any organic matters which the sample contains be destroyed. If the sample be already of a mineral nature, it

may still be mixed with other organic matter and then it requires treatment as above, for it is not safe always to rely solely on the solubility of the potash mineral, and the solution, moreover, in such cases, is likely to contain organic matter. In some States, only that portion of the potash soluble in water is allowed to be considered in official fertilizer work. In these cases it is evident that the organic matter present should not be destroyed in the original sample, but only in the aqueous solution. Since, however, the potash occluded in organic matter becomes constantly available as the process of decay goes on, it is not advisable to exclude it from the available supply. It may not be so immediately available as when in a soluble mineral state, but it is not long before it becomes valuable. In the opinion of some investigators phosphorus, nitrogen, and potash are all more valuable finally when applied to the soil in an organic form. This fact is not irreconcilable with the theory already advanced that all mineral compound bodies are probably decomposed before they enter as component parts into the tissues of the vegetable organism.

It is highly probable, therefore, that the potash existing in organic compounds, finely divided and easily decomposed, is of equal, if not greater value to plant life than that already in a soluble mineral state. For analytical purposes the organic matter, when present, is destroyed, either by ignition at a low temperature, or by moist combustion with an oxidizing agent before the potash is precipitated. For agricultural purposes the plant food represented by the potash occluded in the organic substance is held with some degree of tenacity, preventing its leaching by heavy rains, and permitting its gradual release as required by the growing plant.

457. Quantity of Potash Removed by Crops.—The quantity of potash removed from the soil annually by the principal crops in the United States is equivalent to 2,500,000 tons of muriate of potash or 1,250,000 tons of potash.²⁷

The foregoing discussion of the sources and kinds of potash presented to the analyst is sufficient to clearly set forth the objects of the examination.

²⁷ Voorhees, *Journal of the Franklin Institute*, 1905, **160** : 211.

METHODS OF ANALYSIS**PREPARATION OF SAMPLE**

458. Destruction of Organic Matter by Direct Ignition.—The simplest and most direct method for destroying organic matter is by direct ignition. The incineration may be conducted in the open air or in a muffle and the temperature should be as low as possible. In no case should a low red heat be exceeded. By reason of the moderate draft produced in a muffle and the more even heat which can be maintained this method of burning is to be preferred. With the exercise of due care, excellent results can be obtained in an open dish or one partly closed with a lid. At first, with many samples, the organic matter will burn of its own accord after it is once ignited, and during this combustion the lamp should be withdrawn. The ignition in most cases should be continued in a platinum dish but should the sample contain any reducible metal capable of injuring the platinum a porcelain vessel should be used. The lamp should give a diffused flame to avoid overheating of any portions of the dish and to secure more uniform combustion. In using a muffle the heat employed should be only great enough to secure combustion and the draft should be so regulated as to avoid loss due to the mechanical deportation of the ash particles.

459. Ignition with Sulfuric Acid.—The favorable action of sulfuric acid in securing a perfect incineration may also be utilized in the preparation of samples containing organic matter for potash determinations. In this case the bases which by direct ignition would be secured as carbonates are obtained as sulfates. In the method adopted by the official chemists it is directed to saturate the sample with sulfuric acid and to ignite in a muffle until all organic matter is destroyed.²⁸ Afterwards, when cool the ash is moistened with a little hydrochloric acid and warmed, whereby it is more easily detached from the dish. The potash is then determined by any one of the standard methods. This method has several advantages over the direct ignition. Where any chlorids of the alkalis are present in the ash there

²⁸ Bureau of Chemistry, Bulletin 107, 1907 : 11.

is danger of loss of potash from volatilization. This is avoided by the sulfate process. Moreover, there is not so much danger in this method of occluding particles of carbon in the ash.

460. The Destruction of Organic Matter by Moist Combustion.

—In the process of ignition to destroy organic matter or remove ammonium salts in the determination of potash, there are often sources of error which may cause considerable loss. This loss, as has already been mentioned, may arise from the volatilization of the potash salts or mechanically from spattering. In order to avoid these causes of error de Roode has used aqua regia both for the destruction of the ammonium salts and for the oxidation of the organic matter at least sufficiently to prevent any subsequent reduction of the platinum chlorid.²⁹ The method consists in boiling a sample of the fertilizer, or an aliquot portion of a solution thereof with aqua regia. The proposed method has not yet had a sufficient experimental demonstration to warrant its use, but analysts may find it profitable to compare this process with the standard methods. The organic matter may also be destroyed by combustion with sulfuric acid, as in the kjeldahl method for nitrogen. The residue, however, contains ammonium sulfate and a large excess of sulfuric acid, and for both reasons would not be in a fit condition for the estimation of potash. It is suggested that the organic matter may also be destroyed by boiling with strong hydrochloric acid, to which from time to time, small quantities of sodium chlorate free of potash is added. Subsequently the solution is boiled with addition of a little nitric acid and the ammonium salts thus removed.

461. Qualitative Detection.—To detect the presence of potash in a mixture the aid of the spectroscope may be invoked. In the scale of the spectrum divided into 170 parts, on which the sodium line falls at 50, potassium gives three faint rather broad bands, two red, falling at 17 and 27, and one plum-colored band, near the extreme right of the spectrum, at 153. Potassium, however, does not give brilliant and well-marked spectral bands, such as are afforded by its associates, rubidium, caesium, sodium, and lithium. A convenient qualitative test which

²⁹ Journal of the American Chemical Society, 1895, 17 : 86.

for practical purposes will be quite sufficient, may be secured by dipping a platinum wire loop into a strong acid solution of the supposed potash compound, and viewing through a piece of cobalt glass, the coloration produced thereby when held in the flame of a bunsen. The red-purple tint thereby produced is compared with that coming from a pure potash salt similarly treated. If a fertilizer sample give no indication of potash when treated as above it may be safely concluded that it does not contain any weighable quantity.

For the estimation of the percentage of potash present in a given sample it may be safely assumed that all of value in agriculture will be given up to an aqueous or slightly acid solution if organic matter have been destroyed, as indicated in a previous paragraph. In the case of minerals insoluble in a dilute acid, the potash may be determined by some one of the processes given in the first volume.

The potash having been obtained in an aqueous or slightly acid (hydrochloric) solution, it may be determined either by precipitation as potassium platino-chlorid or as potassium perchlorate. The former method is the one which has been almost exclusively used by analysts in the past, but the latter one is coming into prominence, and by reason of the greater economy attending its practice and the excellent results obtained by some analysts, demands a generous consideration.

462. The Platonic Chlorid Method.—The principle of this method rests on the great insolubility of the potassium platino-chlorid in strong alcohol and the easy solubility of some of its commonly attending salts; viz., sodium, etc., in the same reagent. Before the precipitation of the potash it is customary to remove the bases of the earths, sulfates, etc. Barium chlorid and hydroxid, ammonium oxalate or carbonate, sulfuric acid, etc., are used in conjunction or successively to effect these purposes in the manner hereinafter described. The filtrate and washings containing the potash are evaporated to dryness and gently ignited to expel ammonium salts and in the residue taken up with water and acidulated with hydrochloric acid, the potash is precipitated

with platinic chlorid solution. The best methods of executing the analysis follow.

463. The Official Agricultural Method.—This method is based on the processes at first proposed by Lindo³⁰ and Gladding,³¹ and is given below as adapted to mixed fertilizers and mineral potash salts.³²

(1) *Preparation of reagents.*—(a) *Ammonium chlorid solution.*—Dissolve 100 grams of ammonium chlorid in 500 cubic centimeters of water, add from five to 10 grams of pulverized potassium-platinic chlorid, and shake at intervals for six or eight hours. The mixture is allowed to settle over night and filtered, and the residue is ready for the preparation of a fresh supply.

(b) *Platinum solution.*—The platinum solution used contains one gram of metallic platinum (2.1 grams of H_2PtCl_6) in every 10 cubic centimeters.

(2) *Methods of making solution.*—(a) *With potash salts and mixed fertilizers.*—Boil 10 grams of the sample with 300 cubic centimeters of water 30 minutes. In the case of mixed fertilizers add to the hot solution a slight excess of ammonia and then sufficient powdered ammonium oxalate to precipitate all the lime present. Cool, dilute to 500 cubic centimeters, mix and pass through a dry filter. In case of muriate and sulfate of potash, sulphate of potash and magnesia and kainit, dissolve and dilute to 500 cubic centimeters without the addition of ammonium and ammonium oxalate.

(b) *With organic compounds.*—When it is desired to determine the total amount of potash in organic substances, such as cottonseed meal, tobacco stems, etc., saturate 10 grams with strong sulphuric acid, and ignite in a muffle at a low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly in order to loosen the mass from the dish, and proceed as directed under (3)(a) below.

(3) *Determination.*—(a) *In mixed fertilizers.*—Evaporate 50 cubic centimeters of the solution made according to (2), cor-

³⁰ Chemical News, 1881, 44 : 77, 86, 97, 129.

³¹ Division of Chemistry, Bulletin 7, 1885 : 38.

³² Bureau of Chemistry, Bulletin 107, 1907 : 11.

responding to one gram of the sample, nearly to dryness, add one cubic centimeter of dilute sulfuric acid (1 to 1), evaporate to dryness and ignite to whiteness. As all the potash is in form of sulfate, no loss need be apprehended by volatilization of potash, and a full red heat must be maintained until the residue is perfectly white. Dissolve the residue in hot water, using at least 20 cubic centimeters for each decigram of K_2O , add a few drops of hydrochloric acid and platinum solution in excess. Evaporate on a water bath to a thick paste and treat the residue with 80 per cent. alcohol, specific gravity 0.8645, avoiding the absorption of ammonia. Wash the precipitate thoroughly with 80 per cent. alcohol both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 cubic centimeters of the ammonium chlorid solution (1) (a) to remove impurities from the precipitate, and repeat this washing five or six times. Wash again thoroughly with 80 per cent. alcohol, and dry the precipitate for 30 minutes at 100° . The precipitate should be perfectly soluble in water.

(b) *Muriate of potash*.—Dilute 25 cubic centimeters of the solution, prepared according to (2) (a), with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid, add 10 cubic centimeters of platinum solution and evaporate to a thick paste. Treat the residue as under (3) (a).

(c) *Sulfate of potash, sulfate of potash and magnesia, and kainit*.—Dilute 25 cubic centimeters of the solution, prepared according to (2) (a), with 25 cubic centimeters of water, acidify with a few drops of hydrochloric acid and add 15 cubic centimeters of platinum solution. Evaporate the mixture and proceed as directed under (3) (a), except that 25 cubic centimeter portions of ammonium chlorid solution should be used.

(d) *Water-soluble potash in wood-ashes and cotton-hull ashes*.—Use above method making the solution according to (2) (a), and pay special attention to the last sentence (3) (a).

464. Optional Method.—(1) *Preparation of reagent*.—*Platinum solution*.—The platinum solution used is the same as that described under the indo-gladding method.

(2) *Method of making solution*.—The solution is prepared as

directed under the lindo-gladding method, omitting in all cases the addition of ammonia and ammonium oxalate.

(3) *Determination*.—Dilute 25 cubic centimeters of the solution made as directed under (2), (50 cubic centimeters, if less than 10 per cent. of potassium oxid be present) to 150 cubic centimeters, heat to 100°, and add, drop by drop, with constant stirring, a slight excess of barium chlorid solution. Without filtering, add in the same manner barium hydrate in slight excess. Filter while hot and wash until the precipitate is free from chlorids. Add to the filtrate one cubic centimeter of strong ammonium hydrate, and then a saturated solution of ammonium carbonate until the excess of barium is precipitated. Heat and add, in fine powder, 0.5 gram of pure oxalic acid or 0.75 gram of ammonium oxalate. Filter and wash free from chlorids, evaporate the filtrate to dryness in a platinum dish, and ignite carefully over the free flame, below a red heat, until all volatile matter is driven off. Digest the residue with hot water, filter through a small filter and dilute the filtrate, if necessary, so that for each decigram of K_2O there will be at least 20 cubic centimeters of a liquid. Acidify with a few drops of hydrochloric acid and add platinum solution in excess. Evaporate on a water bath to a thick sirup and treat the residue with 80 per cent. alcohol (specific gravity 0.8645). Wash the precipitate thoroughly with 80 per cent. alcohol both by decantation and after collecting on a gooch or other form of filter. Dry for 30 minutes at 100° and weigh.

It is desirable, if there be an appearance of foreign matter in the double salt, that it should be washed according to the previous method with several portions of the ammonium chlorid solution of 10 cubic centimeters each.

(4) *Factors*.—For the conversion of potassium platinochlorid to KCl , use the factor 0.3071; to K_2SO_4 , 0.3589, and to K_2O , 0.1941.

465. Potash Methods Recommended by the Official French Commission.³³—By authority of law the President of the French Republic appointed a commission for the purpose of prescribing official methods of analyses of fertilizers.³⁴ This Commission was

³³ La Sucrerie indigène et coloniale, 1897, 49 : 645; 50 : 45.

³⁴ Grandeau, *Traité d'Analyse des Matières agricoles*, 3d Edition, 1897, 1 : 419.

composed of the following named chemists: Tisserand, Vasalière, Schloesing, Prillieux, Risler, Aimé Girard, Cornu, Grandeau, Liébaut, Joulie, Mamelle, Müntz and Marsais.

Perchloric Acid Method.—The preference is given by the French Commission to this method which is conducted according to the procedure given by Schloesing, which is substantially the one found on page 579. The method varies slightly when used with the different salts of potash, as, for instance, the sulfates and the chlorids. There is also a very slight difference in the manipulation where the potash is contained in a complex or mixed fertilizer. The above differences refer, however, solely to the preliminary treatment and to the elimination of the potash from its principal compounds.

Platinum Chlorid Method.—The French commission has also recommended the platinum method for the determination of potash in the form of double chlorids of potash and platinum. The method described does not differ in any essential points from that already given. Where it is advisable to estimate the soda also, the total chlorin is determined in the mixed chlorids, the potash estimated by the platinum method, the chlorin necessary to combine with it deducted from the total chlorin and the residual chlorin calculated to chlorid of soda.

Method of Corenwinder and Contamine.—The French commission has recommended also as one of the alternative methods the determination of potassium in salts and in refined potash compounds according to the variations of Corenwinder and Contamine, in which there is introduced into the process as a reagent, sodium formate. This method is regarded by the Commission as exact as that in which the perchlorate is used. In this process 25 grams of the salt to be examined is ignited in case it contains any organic matter or salts of ammonia, which must previously be destroyed or eliminated. After cooling, the melt is dissolved and the volume brought to one liter and the solution filtered. An aliquot part of the filtrate, conveniently 20 cubic centimeters, corresponding to five decigrams of the original material, is acidulated with hydrochloric acid, evaporated to dryness, and the saline residue weighed for the purpose of determining

what quantity of chlorid of platinum should be added in order that it will be in slight excess. The quantity of the platinum reagent used is calculated in such a way that it is sufficient to saturate the whole quantity of the salts present, which are for this purpose calculated as if they were the chlorid of sodium. The chlorid of platinum employed should contain in 100 cubic centimeters 17 grams of platinum. Each cubic centimeter of the solution is sufficient for each decigram of the weight of the saline residue obtained as above. After adding the platinum salts the mixture is placed in a capsule and evaporated with precautions to prevent the platinum salt from being heated beyond a temperature of 100°. Above this temperature the salts may form a little of the subchlorid of platinum which is insoluble in alcohol. After cooling, the mass is digested for several hours with 15 cubic centimeters of 95 per cent. alcohol, the capsule being placed under a small cover. During this time it is stirred from time to time with a glass rod and the supernatant liquid is poured into a small filter and the salt washed with alcohol until the filtrate becomes colorless. There is thus obtained as an insoluble residue a mixture of chloro-platinate of potassium with various quantities of soda, silicates and oxids of iron which may have been present in the original sample. By means of boiling water the mass remaining in the capsules is dissolved and poured upon the filter and the washing of the capsule is continued with boiling water until all of the chloro-platinate is dissolved, which is easily determined by the alcohol wash becoming colorless. The solution of chloro-platinate is received in a well glazed dish, containing no cracks, and is heated upon a sand bath to boiling and there is added to it in very small proportions some formate of soda dissolved in water. The capsules having been taken from the bath to avoid mechanical loss, formate of soda is added until the mixture is completely decolorized. Instead of doing this in an ordinary dish, an open flask or beaker may be employed. By this process the platinum present in the mixture is precipitated as a black powder, and in order to aggregate it, the mixture is evaporated to about one-half its volume and brought upon a small filter, bringing the platinum in by means of cold water slightly acidulated. When all the platinum

is brought together upon the filter the washing is finished by means of boiling water. Sometimes the finely divided platinum passes through the filter, which is easily detected by a gray metallic tint which the filtered liquid assumes. In this case it is necessary to allow it to settle for one or two days, decant the colorless supernatant liquid and add the deposited matter to the filter by means of cold water. Finally, the filter is dried and ignited and there is obtained in this way the weight of metallic platinum corresponding to that of potassium in the original sample, since 100 parts of platinum are equivalent to 47.57 of potash.

466. Method of Potash Determination of the Union of German Fertilizer Manufacturers.—The method of potash determination employed by the Union of German Chemists is the same as that recommended by the Potash Syndicate of Stassfurt, with only slight modifications.³⁵ The German manufacturers, however, use the atomic weight of platinum, 194.8, instead of 197.2, as employed by the syndicate. The factors, therefore, for conversion in the two cases are slightly different.

467. Methods Used at the Halle Station.—(1) *In Kainits and other Mineral Salts of Potash.*³⁶—Five grams of the prepared sample are boiled for half an hour in a half liter flask with from 20 to 30 cubic centimeters of concentrated hydrochloric acid and 100 cubic centimeters of water, and afterwards as much water added as is necessary to fill the flask about three-quarters full, and the sulfuric acid is then precipitated with barium chlorid. To avoid an excess of barium chlorid the solution used is of known strength and is added first in such quantity as would precipitate the sulfuric acid from a kainit of low sulfuric acid content. The mixture is then boiled, allowed to settle and tried with a dropping tube containing barium chlorid. If a further precipitate appear, a few drops more of barium chlorid solution are added, again boiled and allowed to settle. This is continued until barium chlorid gives no precipitation. After the barium chlorid gives no more precipitate a drop of dilute sulfuric acid is added to test

³⁵ Methoden zur Untersuchung der Kunstdüngemittel, 1903 : 21.

³⁶ Bieler und Schneidewind, Die agricultur-chemische Versuchsstation, Halle a/S, 1892 : 76.

for excess of barium. The operation is continued with the sulfuric acid until it no longer gives a precipitate of barium sulfate. By the alternate use of the barium chlorid and sulfuric acid the exact neutral point can soon be secured. When this point is reached the liquid is allowed to cool, the flask is filled to the mark, its contents filtered, and of the filtrate 50 cubic centimeters, equal to half a gram of the substance, removed for further estimation.

This quantity is evaporated on a water bath to a sirupy consistence in a porcelain dish with 10 cubic centimeters of platinic chlorid. The platinic chlorid solution should contain one gram of platinum in each 10 cubic centimeters. The residue is treated with 80 per cent. alcohol and, with stirring, allowed to stand for an hour. The precipitate is then collected on a gooch, either of platinum or porcelain, washed about eight times with 80 per cent. alcohol, and the potassium platinochlorid dried for two hours at 100° . After weighing, the precipitate is dissolved in hot water and the residue washed, first with hot water and then with alcohol. The crucible with the asbestos felt is dried at 100° and weighed. Any impurities which the double salt may have carried down with it are left on the filter and the weight of the original precipitate can thus be corrected. The weight of potassium platinochlorid is multiplied by 0.1927 and the product corresponds to the weight of K_2O in the sample.

(2) *Estimation of Potash in Guanos and Other Fertilizers containing Organic Substances.*—Ten grams of the substances are carefully incinerated at a low temperature in a platinum dish. After ignition the contents of the dish are placed in a half liter flask and boiled for an hour with hydrochloric acid and a few drops of nitric acid. The sulfuric acid can then be precipitated directly with barium chlorid, or better, allow the flask to cool, fill to the mark, filter and treat an aliquot part of the filtrate with barium chlorid as described above. The filtrate from the separated sulfate of barium is neutralized with ammonia and all the bases, with the exception of magnesia and the alkalies, precipitated with ammonium carbonate, and the mixture boiled, filled to the mark and filtered. From 100 to 200 cubic centimeters of this

filtrate are evaporated in a platinum dish. After evaporation the ammonium salts are driven off by careful ignition, the residue taken up with hot water and filtered through as small a filter as possible into a porcelain dish, the magnesia remaining in the precipitate. The filtrate is acidified with a few drops of hydrochloric acid, 10 cubic centimeters of platinic chlorid added and the further determination conducted as with kainit.

468. Dutch Method.—The process used at the Royal Agricultural Station of Holland is almost identical with that employed at Halle.³⁷

A. *Method for Stassfurt and other Potash Salts.*—The necessary reagents are:

1. A dilute solution of barium chlorid.
2. A solution of platinic chlorid containing one gram of platinum in 10 cubic centimeters. It must be wholly free from platinous chlorid and nitric acid, and partially freed from an excess of hydrochloric acid by repeated evaporations with water.
3. Alcohol of 80 per cent. strength by volume.

The methods of bringing the potash into solution and of precipitating the sulfuric acid are the same as for the Halle process described above.

To 50 cubic centimeters of the solution add 20 cubic centimeters of the platinum solution and evaporate the mixture nearly to dryness. Add a sufficient quantity of 80 per cent. alcohol and stir for some time. Allow to stand and then filter through a gooch dried at 120°. Finally wash with 80 per cent. alcohol dry at 120°, and weigh.

B. *Method for Potash-Superphosphate and other mixed Fertilizers.*—The reagents necessary are the same as under A, and, in addition, a saturated solution of barium hydrate and a solution of ammonium carbonate mixed with ammonia.

Boil 20 grams of the substance with water for half an hour, cool, make up to half a liter and filter. Boil 50 cubic centimeters of the filtrate, and add barium chlorid till no more precipitate forms. Mix with baryta water to strong alkaline reaction, cool, make up to 100 cubic centimeters and filter. Raise 50 cubic cen-

³⁷ Methoden von Onderzoek aan de Rijkslandbouwproefstations, 1894 : 6.

timeters of the filtrate to the boiling temperature and add ammonium carbonate solution till no more precipitate forms. Cool make up to 100 cubic centimeters and filter. Transfer 50 cubic centimeters of the filtrate to a platinum dish, evaporate and heat the residue, avoiding too high a temperature, till the ammonia salts are expelled. Dissolve the residue in water, filter, and treat the filtrate as described under A.

469. Swedish Methods.—The Swedish chemists determine the potash in mineral salts by the platinum chlorid process, but with certain variations from the processes already given. The manipulation is conducted as follows:³⁸

Pour about 300 cubic centimeters of hot water over one gram of the sample to be examined in a beaker, and filter after complete solution; add one cubic centimeter of hydrochloric acid, heat nearly to boiling, add dilute barium chlorid solution from a pipette or burette in a very fine stream, stirring slowly and carefully, till all sulfuric acid is completely precipitated, and only a trace of the precipitant is in excess. If the precipitation be conducted in the way given, the barium sulfate will come down in crystalline condition, and settle rapidly within a few minutes, and almost immediately after the precipitation is finished may be filtered clear. Bring the filtrate and washings from the barium sulfate into a liter flask; fill this to the mark, take out 50 cubic centimeters with a pipette, evaporate the greater portion on a water bath in a porcelain dish, transfer the residue by means of ammonia-free water to a beaker of 50 cubic centimeters capacity, add 10 cubic centimeters of platinic chlorid solution, stir well with a glass rod, evaporate on a water bath to a sirupy condition, allow to cool, and if the residue be too dry, add a few drops of water to allow the sodium platinochlorid to take up crystal water with certainty, stir well, add alcohol after a few minutes, mix carefully, leave the mixture standing for a while in the beaker covered with a watch-glass, stirring occasionally; finally, decant the solution, which must be of a dark yellow color, through a very small filter, wash the precipitate in the beaker repeatedly with small quantities of alcohol and decant; then transfer the precipi-

³⁸ Official Swedish Methods, translated for the Author by F. W. Woll.

tate to the filter, wash with alcohol, dry the filter and the precipitate at a gentle heat till all alcohol has evaporated, carefully transfer the contents of the filter to a watch glass placed on white glazed paper; dissolve the potassium platinochlorid still remaining on the filter in small quantities of boiling water, evaporate the filtrate on a water bath in an accurately weighed platinum dish to dryness and transfer to the same the main portion of the chlorid from the watch-glass. In order to obtain the salt free of the corresponding combinations of sodium, barium, calcium, and magnesium, which salts, although soluble in alcohol, may make the salt impure, before weighing treat the precipitate twice with small quantities of cold water, which will dissolve these impurities; evaporate the solution after addition of one cubic centimeter of platinic chlorid nearly to dryness on a water bath, treat the residue in the same way as given before, add the small quantity of potassium platinochlorid which is hereby obtained together with the main portion to the platinum dish, dry at 130° , and weigh. Only after having been treated in this way may the precipitated potassium platinochlorid be considered absolutely pure. The Stassfurt salts contain magnesia, often in large quantities, and as a consequence the potassium platinochlorid precipitated directly is likely to be contaminated therewith.

470. Methods for the Analysis of Carnallit, Kainit, Sylvinit, and Bergkieserit.—The chemists of the German Potash Syndicate use the following methods in the analysis of the raw products mentioned above.³⁹

(1) *Preparation of the Sample.*—It is advisable to take from a large, well mixed mass at least half a kilogram for the analytical sample, and this should be ground to a fine powder in a mill or mortar.

(2) *Estimation of the Potash by the Precipitation Method.*—In a half liter flask are placed 35.71 grams of kainit, hartsalz or sylvinit, or 30.56 grams of carnallit or bergkieserit, which are boiled with 350 cubic centimeters of water after the addition of 10 cubic centimeters of hydrochloric acid. After cooling, the

³⁹ Division of Chemistry, Bulletin 35, 1892 : 63.

Methods of Analyses of Potash Salts, Published by the Kalisyndikat, Leopoldshall-Stassfurt, 1906.

flask is filled to the mark with water, well shaken, and its contents filtered. Fifty cubic centimeters of the filtrate are treated in a 200 cubic centimeter flask with a solution of barium chlorid, the flask filled to the mark, well shaken, and its contents filtered. Twenty cubic centimeters of the filtrate, corresponding to 0.3571 or 0.3056 gram of the substance, as the case may be, are treated with five cubic centimeters of platinic chlorid solution and the potassium estimated according to the usual methods. When the perchloric acid method is employed, 13.455 grams of the carnallit or bergkieserit, or 15.7225 grams of kainit, sylvinit or hartsalz are dissolved in a 500 cubic centimeter flask and treated directly with barium chlorid. Twenty cubic centimeters of the filtrate, equal to 0.5382 or 0.6289 gram of the sample, as the case may be, are then treated with perchloric acid, as described further along.

(3) *Estimation of Potash (K_2O) in Raw Potash Salts.*—(a) For the determination of potash alone in carnallit, kainit, and sylvinit 100 grams of the well-mixed sample are put into a graduated flask holding one liter and dissolved by boiling with half a liter of water, acidulated with 10 cubic centimeters of hydrochloric. The purpose of adding hydrochloric acid is to bring any polyhalit that might be present in the salts into solution and which it is difficult to dissolve in pure water. After dissolving and cooling, the flask is filled up to the mark. The solution, after mixing, is filtered through a dry filter and 100 cubic centimeters of the filtrate, corresponding to 10 grams substance, are put into a half liter flask by means of a pipette. After the addition of 200-300 cubic centimeters of water the solution is heated to boiling and the sulfuric acid accurately precipitated with normal barium chlorid solution, containing 104 grams of the dry salt in one liter. The volume of the precipitate is calculated from the amount of barium solution used and from the specific gravity of the barium sulfate. After cooling, the flask is filled up with water as far above the mark as equals the volume of the calculated barium precipitate, and, after thorough mixing, the solution is filtered again through a dry filter. Fifty cubic centimeters of this filtrate, corresponding to one gram substance, are

evaporated upon the water bath with a sufficient amount of platinic chlorid. The residue of potassium platinochlorid is washed with 90 per cent. alcohol, dried at 120° , and weighed.

(b) If it be desired to determine separately the quantity of potash present in the form of sulfate and in the form of chlorid, as, for example, in kainit and in sulfate of potash, or if it is to be determined whether potassium sulfate is in combination with a proportionate amount of magnesium chlorid, as in kainit, or in combination with magnesium sulfate alone, as in schönit, it then becomes necessary to determine besides potash the percentages of chlorin, sulfuric acid, lime, magnesia, the total alkalis, water, and the residue insoluble in water. For this purpose 100 grams of the sample are dissolved, the solution is filtered, the filter washed, and the filtrate made up to one liter; a part of the liquid is taken for the determination of sulfuric acid, by precipitating with barium chlorid, and another part for the determination of lime and magnesia. For the determination of the alkali chlorids, 100 cubic centimeters of the solution, corresponding to 10 grams substance, are acidulated with hydrochloric, and, after heating to boiling, the sulfuric acid is completely precipitated with barium chlorid, with the precaution of using not more of the barium solution than is necessary for the complete precipitation. Fifty cubic centimeters of the filtered solution, corresponding to one gram substance, are evaporated to dryness in order to drive off the hydrochloric acid. Magnesium chlorid is decomposed by igniting with oxalic acid. After ignition, the residue is moistened with a little ammonium carbonate for the purpose of converting the calcium oxid that may have been formed into calcium carbonate. The alkali chlorids, which are entirely free of lime and magnesia, are weighed, and potassium chlorid is determined by means of platinic chlorid or perchloric acid. The amount of sodium chlorid is obtained by deducting potassium chlorid from the mixed chlorids.

Estimation of Water.—For the water determination five grams of the sample are ignited and the loss of weight is determined. The ignited mass is dissolved in water, and for the purpose of determining the quantity of magnesium chlorid that may have

been decomposed by the ignition, the percentage of chlorin is determined by titration. The difference in the contents of chlorin before and after ignition is subtracted from the loss in weight, after allowance has been made for the absorption of oxygen and for the loss of hydrogen. The rest is water. Or, in order to avoid the loss of chlorin, the sample is covered by a known quantity of freshly ignited burnt lime or lead oxid to absorb the chlorin from the magnesium chlorid.

Calculation of Composition.—The results obtained are calculated in the following manner: From the total amount of the sulfuric acid found, that portion is deducted which is combined with calcium as calcium sulfate; the rest of the sulfuric acid is divided into two equal parts for the purpose of calculating the contents of potassium sulfate and magnesium sulfate, according to the molecular proportion in which these salts are present in kainit and in schönit. If there be an excess of potash left uncombined with sulfuric acid, then it is in the form of potassium chlorid; likewise, the amount of magnesia, uncombined with sulfuric acid, is to be reckoned as magnesium chlorid. The result of this calculation will tell how much potash is in the form of kainit (K_2SO_4 , $MgSO_4$, $MgCl_2$, with $6H_2O$) and how much of it is in the form of schönit (K_2SO_4 , $MgSO_4$, with $6H_2O$) and how much in the form of potassium chlorid. The sodium is reckoned as sodium chlorid.

In the case of hartsalz, the water content of which is only about one-third of that in kainit, the potassium is calculated as chlorid. When longbeinit ($K_2SO_4, 2MgSO_4$) is present with kainit, the magnesia and lime present are credited as sulfates, the excess of sulfuric acid remaining being then reckoned as a potassium salt. Should a complete examination and identification of the various minerals present in a more complicated mixture of the crude salts be required, this cannot be performed from calculations founded simply upon a quantitative chemical analysis of the various constituents. In such a case for example the magnesium chlorid soluble in alcohol should be determined, as from this the proportion of carnallit may be reckoned. Further aid

will be obtained in separating the minerals with bromoform according to their varying specific gravities.

Calculations of the salts present in carnallit and bergkieserit are obtained in the following manner: The lime found is reckoned as sulfate, and the excess of sulfuric acid, after satisfying the lime, is then credited to magnesia. The remaining magnesium is stated as magnesium chlorid.

(c) In calculating the contents of potash, of potassium chlorid, and of potassium sulfate from the weighed potassium platinochlorid, the factors 0.1928, 0.3056, and 0.3566 are used, assuming that the atomic weight of platinum is 197.18.

(d) The two methods which have been described under *a* and *b*, and which are in common use in the Stassfurt potash industry, *i. e.*, the so-called precipitation method, and the oxalic acid method, give almost identical results. The first method, however, deserves preference on account of greater simplicity in cases where potash alone is to be determined. Finkener's method likewise gives results which agree well with the results obtained by the customary methods. It consists in evaporating the salt solution with a sufficient quantity of platinic chlorid without previously removing the sulfuric acid, reducing the potassium platinochlorid, and weighing the metallic platinum.

The following are the results of comparative analyses:

1. After the precipitation method 22.02 per cent. KCl
2. After the oxalic acid method 22.03 per cent. KCl
3. After Finkner's method 22.01 per cent. KCl

In another sample of carnallit the following results were obtained:

1. After the precipitation method 17.88 per cent. KCl
2. After the oxalic acid method 17.88 per cent. KCl

In a third sample of carnallit the content of potassium chlorid was as follows:

1. After the precipitation method 18.44 per cent.
2. After the oxalic acid method 18.38 per cent.

The German chemists object to precipitating the sulfuric acid and alkaline earths with barium oxid and ammonium carbonate, and afterwards the potash with platinic chlorid. The results ob-

tained with this method are, according to them, very inaccurate, and always too low. This is explained by the fact that it is impossible to precipitate sulfuric acid without the same time precipitating some of the potash, unless it be in an acid solution.

A separation of the alkaline earths, if potash alone is to be determined, is superfluous, for the reason that calcium and magnesium platinochlorid are soluble in 90 per cent. alcohol, even with more facility than sodium platinochlorid.

471. Methods for Concentrated Potash Salts.—In the preceding paragraphs have been given the methods used by the Stassfurt syndicate for the estimation of potash in the raw salts as they come from the mines. Following are the methods used by the same syndicate for the concentrated approximately pure compounds and the other salts which accompany them.⁴⁰

Potassium Chlorid.—The following process is used for the estimation of potassium and other constituents of the high grade chlorids of commerce. In a half liter flask are placed 7.6401 grams of the finely powdered sample, which is dissolved and made up to the mark. With salts which contain more than half a per cent. of sulfuric acid the preliminary conversion of the sulfates into the corresponding chlorin compounds, by precipitation with barium chlorid solution, is necessary. Twenty cubic centimeters of the above solution, corresponding to 0.3056 gram of the salt, are placed in a flat porcelain dish having a diameter of about 10 centimeters and, after the addition of five cubic centimeters of the platinic chlorid solution, evaporated on the water-bath with constant stirring until, after cooling, the sirupy liquid passes quickly into a fine crystalline condition. The evaporation can be carried on to dryness without risk in the use of the concentrated salts. In addition to the potassium chloroplatinate, the principal ingredient is the corresponding sodium salt, and this is more easily dissolved by alcohol when dry than when water is present. The residue is rubbed into a fine powder with a glass rod, mixed with 20 cubic centimeters of 96 per cent. alcohol, and brought onto a filter moistened with alcohol and dried at 120°.

⁴⁰ Analytical Methods for the Examination of Potash Salts, Published by the Kalisyndikat, Leopoldshall-Stassfurt, 1906.

and washed with strong alcohol, care being taken that the liquid does not touch the edge of the filter. The filtration can be carried on under a moderate pressure. The complete washing of the potassium platinochlorid can be easily accomplished upon the filter. By the use of hot alcohol the process may be greatly hastened. The filter and the precipitate, after as much of the alcohol wash has been removed as is possible, are dried at 120° to 130° to constant weight and weighed while still warm. One milligram of the potassium platinochlorid thus obtained corresponds to a tenth per cent. of potassium chlorid.

(2) *By Perchloric Acid.*—13.455 grams of the well ground sample are dissolved in water and made up to 500 cubic centimeters after the addition of from three to four cubic centimeters of the acid solution of barium chlorid, containing 122 grams of the crystallized salt and 50 cubic centimeters of strong hydrochloric acid in one liter. Twenty cubic centimeters of the filtrate ($=0.5382$ gram of the sample) are placed in a shallow glass or blue enameled porcelain basin of about 10 centimeters diameter. One and a half times the quantity of perchloric acid of 1.125 specific gravity necessary to decompose all the salts is added. The mass is then evaporated on the water-bath until the odor of hydrochloric acid disappears, and white fumes of perchloric acid begin to come off. After cooling, the residue is washed with 96 per cent. alcohol to which 0.2 per cent. of perchloric acid has been added. In washing, 20 cubic centimeters of the alcohol are first added to the basin and the residue is thoroughly rubbed down in the liquid, which is then decanted through a tared filter. The washing is repeated, several times by decantation and finally on the filter. The final washing requires pure alcohol (as little as possible) to remove free perchloric acid. The filter and residue are dried and weighed in the same manner as in the platinum process.

One milligram potassium perchlorate represents 0.1 per cent. of potassium chlorid.

Estimation of Sodium Chlorid.—For the estimation of the sodium chlorid which may present in the potassium chlorid, 12.5 grams of the latter salt are dissolved in a quarter liter flask with

25 cubic centimeters of boiling water after the addition of 90 milligrams potassium carbonate for the purpose of converting the magnesium and calcium compounds into carbonates. To the hot solution absolute alcohol is added, the flask well shaken and filled to the mark and again shaken for one minute. After filtration 100 cubic centimeters, corresponding to five grams of the salt, are evaporated to dryness in a porcelain or platinum dish after the addition of a few drops of concentrated hydrochloric acid in order to convert any potassium carbonate which may be present into chlorid. The residue is gently ignited and weighed. In this mixture of potassium and sodium chlorids the potassium chlorid may be estimated in the usual way and the sodium chlorid determined by difference, or the respective proportions of the two bases may be calculated after the determination of the total chlorin by precipitation with a standard solution of silver nitrate.

Estimation of Magnesium Chlorid.—In order to estimate the amount of magnesium chlorid in high-grade muriate of potash, 25 grams of the latter salt are dissolved in a half liter flask and treated with 10 cubic centimeters of a twice normal solution of potash-lye. The flask is filled to the mark with water, thoroughly shaken and its contents filtered. Fifty cubic centimeters of the filtrate are titrated with one-tenth normal sulfuric acid. The calcium compounds which remain in solution do not influence the result. The quantity of magnesium chlorid originally present corresponds to the number of cubic centimeters of the normal potash-lye which has disappeared in the operation. The reaction which takes place is represented by the following equation: $MgCl_2 + 2KOH = MgO_2H_2 + 2KCl$.

Sulfuric Acid in Muriate of Potash.—Fifty grams of the sample are dissolved in 500 cubic centimeters of water. After filtering, 200 cubic centimeters, equivalent to 20 grams of the sample, are acidified with one cubic centimeter of concentrated hydrochloric acid and precipitated at boiling temperature with barium chlorid. After standing from 15 to 18 hours the precipitate is separated by filtration and weighed in the usual manner.

Potassium Sulfate.—The quantity of potassium sulfate con-

tained in the high grade sulfates of commerce is determined in the following manner: In a half liter flask are placed 8.9275 grams of the finely ground sample which is dissolved in about 350 cubic centimeters of boiling water after the addition of 20 cubic centimeters of hydrochloric acid. The sulfuric acid is thrown out by the addition, drop by drop, of a barium chlorid solution, the contents of the flask being kept boiling meanwhile and thoroughly stirred. The barium chlorid solution is delivered from a burette with a glass stop-cock. From time to time the addition of the barium chlorid is stopped and the upper part of the liquid allowed to become clear by the subsidence of the barium sulfate. It is then noticed whether or not an additional drop of the barium chlorid solution produces a turbidity. A convenient method is to drop a small crystal of barium chlorid into the clear supernatant liquid. Any excess of barium chlorid is removed by the careful attention of sulfuric acid. After the precipitation is complete and the contents of the flask are cooled, it is filled up to the mark with water and its contents filtered. Twenty cubic centimeters of the filtrate, corresponding to 0.3571 gram of the original salt are precipitated by platinic chlorid in the usual manner and the resulting potassium platinochlorid collected and weighed. One milligram of the potassium platinochlorid thus obtained corresponds to one-tenth per cent. of potassium sulfate in the original salt. To the percentage of potassium sulfate thus found three-tenths per cent. are to be added for a correction when high-grade potassium sulfate is examined. If the sample be a high-grade sulfate of potassium and magnesium no correction should be applied.

Estimation of Potassium Chlorid and Potassium Sulfate in Calcined Manurial Salts.—In these salts 15.281 grams of potassium chlorid or 17.847 grams of potassium sulfate are dissolved in a half liter flask after the addition of 10 cubic centimeters of hydrochloric acid. The flask is filled to the mark and its contents filtered and 250 cubic centimeters placed in a half liter flask and treated with barium chlorid solution as indicated above. The rest of the operation is exactly as has been described. In each

case one milligram of the potassium platinochlorid corresponds to one-tenth per cent. of the desired salt.

By Perchloric Acid.—Dissolve 15.7225 grams of the sample in 100 cubic centimeters of boiling water, containing 30 cubic centimeters of concentrated hydrochloric acid, in a liter flask. The rest of the process is identical with that described above for muriate of potash, with the exception that a smaller excess of barium chlorid is required and that instead of 20 cubic centimeters of filtrate, 40 cubic centimeters are evaporated. One milligram of potassium perchlorate equals 0.1 per cent. of potassium sulfate. The addition of 0.3 per cent. should be made under the same conditions as are specified under muriate of potash.

Estimation of Magnesium Sulfate in Kieserit.—Ten grams of the finely powdered kieserit are boiled for one hour in a half liter flask two-thirds full of water. After cooling, from 50 to 60 cubic centimeters of double normal potash-lye and 20 cubic centimeters of a 10 per cent. neutral potassium oxalate solution are added, the flask filled to the mark, and after being well shaken and standing for a quarter of an hour, filtered. The reaction is represented by the formula $MgSO_4 + 2KOH = MgO_2H_2 + K_2SO_4$. Fifty cubic centimeters of the filtrate are then titrated with one-tenth normal sulfuric acid. To the percentage of magnesium sulfate found by this process two-tenths per cent. are to be added as a correction.

472. Preparation of Solutions.—I. *Preparation of the Platinic Chlorid Solution.*—The platinum scrap or recovered waste is dissolved in a porcelain basin on the water bath. Four times its weight of pure concentrated hydrochloric acid is added, and while warm nitric acid is gradually introduced. Use one part of nitric to four parts of hydrochloric acid. When the platinum has been dissolved, the solution is concentrated by evaporation until a drop taken upon a glass stirring rod quickly deposits crystals. On cooling the mass assumes a crystalline condition; it is then taken up with water and filtered. The solution of platinic chlorid is now diluted so that 10 cubic centimeters contain one gram of metallic platinum. Special care is necessary that the solution does not contain platinous chlorid or nitrous compounds.

The first may be changed into platinic chlorid by fuming hydrochloric acid and a little nitric acid. The nitrous compounds may be removed by the alternate addition of hydrochloric acid and water during evaporation. It has further to be noted, that by making use of platinum scrap from the laboratory, iridium compounds may be present. These may be removed by precipitation with ammonium chlorid and subsequent reduction.

The purity of the platinic chlorid may be best proved by conducting an analysis of potassium chlorid formed from pure materials of known composition.

2. *Perchloric Acid*.—An acid of 1.125 specific gravity should be used and preparations of this strength are now offered to the trade.

3. *The Barium Chlorid Solution*.—One hundred and twenty-two grams of the crystallized salt with 50 cubic centimeters of concentrated hydrochloric acid are dissolved in water, and made up to one liter.

4. *The Calcium Saccharate Solution*.—Four hundred and fifty grams of quicklime and 450 grams of sugar are dissolved in seven liters of water. After shaking thoroughly for half an hour the resulting precipitate is left over from two to three weeks. The solution is then filtered and a further 450 gram of sugar is added. The solution should preferably be stored and drawn off in a closed bottle with a burette attachment.

5. *Alcohol*.—For washing the potassium chloroplatinate precipitates, alcohol of at least 96 per cent. purity should be employed.

6. *Filters*.—The most serviceable filter for the platinic chlorid estimation of potash is the Swedish filter, Murktell 1 F. Many otherwise excellent filter papers show a gain in weight after treating with 96 per cent. alcohol and drying at 120°. This may amount to several milligrams for a nine centimeter filter. On this account it is advisable in taring a filter to omit moistening it with alcohol before placing in the drying oven.

473. **Lunge's Modification of Technical Methods**.—The technical methods for the determination of potash in the Stassfurt salts, which have just been described, are of great interest to agricultural chemists in all parts of the world since, practical-

ly all the potash used for fertilizing purposes comes from this region. The methods which are in vogue for the valuation of the product are both of a scientific and commercial importance. Lunge has tabulated these methods in convenient form for reference.⁴¹ The methods as described by Lunge are very nearly the same as those just given, but are modified in some particulars.

In the investigation of crude salt it is to be recommended that as large a sample as possible be used in order to eliminate any error which might arise from the unequal distribution of impurities in the crude product. The estimation of potash is conducted uniformly by the platinum method. The description for the method of complete analysis of raw salts is not suitable for this manual but belongs rather in the domain of mineral analyses. It is however, sometimes, of interest to the agricultural analyst to determine the quantity of chlorine and sulfuric acid in the raw salt by reason of the injurious effects which these bodies sometimes produce.

The methods for the complete analysis of these salts are given by Lunge in the article referred to above. The method for the analysis of crude salts for potash alone is as follows: In the case of carnallite and bergkieserite 30.56 grams of the salt and for kainite, sylvite and hartsalz 35.71 grams are boiled in a 500 cubic centimeter flask with about 300 cubic centimeters of water and the addition of 15 cubic centimeters of concentrated hydrochloric acid. After cooling, the flask is filled to the mark. The sulfuric acid in 50 cubic centimeters of the solution or of the filtrate is precipitated in a 200 cubic centimeter flask with barium chloride and after cooling, the flask is filled to the mark and 20 cubic centimeters of the filtrate are treated with a sufficient quantity of the platinum chloride solution in a flat porcelain dish of about 10 cubic centimeters diameter and, with frequent shaking, the mixture is evaporated on the water bath until the residue is of a sirupy consistence and fumes of hydrochloric acid are no longer evolved. On cooling, the mass solidifies to a crystalline cake.

The formulation of large crystals of sodium platinochloride is

⁴¹ *Chemisch-technische Untersuchungsmethoden*, 5th Edition, 1904, 1 : 534.

to be as carefully avoided as possible since these crystals interfere with the subsequent operation. The crystalline residue is rubbed to a powder with a broad glass rod and then treated with 20 cubic centimeters of alcohol and vigorously stirred and rubbed and the solution filtered through a warm filter previously dried to a constant weight at from 120° to 130° and moistened with alcohol. Care is to be taken that the liquid does not touch the edge of the filter. This operation is repeated two or three times upon the residue remaining in the dish until all the soluble platinum double salts are dissolved. Favorable results will be secured the sooner if at the time of the second treatment with alcohol the dish is heated until the alcohol is almost boiling. A less content of platinum chlorid is not secured in this way because by means of the first decantation by far the greater part of those bodies are removed which are apt to reduce a solution of potassium chlorid in alcohol. The well-washed precipitate is collected upon the filter and, after as complete as possible a removal of the alcohol by suction and by pressing between filter paper, dried at 120° to 130° , to constant weight. Usually 20 minutes are sufficient for that purpose and the mass is weighed while still warm. Before drying, the filter is carefully folded so as to avoid any loss of material in weighing. Each milligram of potassium corresponds to one-tenth per cent, of potassium chlorid or potassium sulfate.

474. The Barium Oxalate Method.—The principle of this process, worked out by Schweitzer and Lungwitz⁴² is based on the fact that in an ammoniacal solution, by means of barium oxalate, all the alkaline earths can be precipitated as oxalates, and sulfuric acid in similar circumstances can be thrown down as a barium salt and the iron and alumina as hydroxids. The reagents used to secure this precipitation are ammonia and barium oxalate.

For the determination of potash in a superphosphate the analytical process is conducted as follows. Ten grams of the superphosphate are mixed with half a liter of water and 15 grams of barium oxalate dissolved in hydrochloric acid.

⁴² Chemiker-Zeitung, 1894, 18 : 1320.

The mixture is boiled for 20 minutes and treated with some hydrogen peroxid to oxidize any ferrous iron that may be present. Afterwards the solution is made alkaline with ammonia. After cooling, it is made up to a given volume (half a liter) and filtered. An aliquot part of the filtrate is evaporated to dryness, ignited, extracted with hot water, and, after the addition of a few drops of hydrochloric acid, the potassium is precipitated with platinic chlorid, and collected and weighed in the usual manner: Or the ignited residue may be dissolved directly in dilute hydrochloric acid and the rest of the process carried out as indicated.

In kainit the process is conducted as follows: Ten grams of the powdered sample are treated with a hydrochloric acid solution of the barium oxalate containing 10 grams of the salt. The rest of the operation is conducted as described above. In the use of this method it is important that always enough of the barium oxalate solution be employed to fully saturate all the sulfuric acid which may be present.

475. Method of de Roode for Kainit.—All the potash contained in kainit, according to de Roode, passes readily into aqueous solution.⁴³ On evaporating this aqueous solution to a pasty condition with enough platinic chlorid to unite with all the halogens present, all the other bodies can be washed out of the potassium platinochlorid by ammonium chlorid solution and the pure platinum salt thus obtained, which is washed and dried in the usual way. De Roode therefore, asserts that it is quite useless to previously precipitate the solution of kainit with barium chlorid, ammonium oxalate, or carbonate. Before the addition of alcohol to the residue obtained by evaporation with platinic chlorid the sodium sulfate present renders the platinum salt sticky and difficult to wash, but the disturbing sodium compound can be readily removed by washing with ammonium chlorid solution.

The method of direct treatment has the advantage of avoiding the occlusion of potash in other precipitates and the danger of loss on ignition. The method as used by de Roode gives results

⁴³ Journal of the American Chemical Society, 1895, 17 : 85.

about one-tenth per cent. higher than are obtained by the official processes.

476. The Calcium Chlorid Method.—Huston has proposed the addition of calcium chlorid to the solution of a fertilizer in the determination of potash, in order to furnish sufficient calcium to form tricalcium phosphate with all the phosphoric acid present, and thereby permit the use of platinum dishes in the lindo-glad-ding method.⁴⁴ In testing this process de Roode found that when sufficient calcium chlorid was added to combine with all the phosphoric acid present and then ammonia added in excess and a portion of the solution filtered, no test for phosphoric acid could be obtained; but, that if in addition to the calcium chlorid and ammonia, some ammonium oxalate or carbonate was added, a filtered portion of the solution gave a test for phosphoric acid.⁴⁵ This is accounted for by the fact that the calcium phosphate, which is precipitated by the ammonia, is changed by the ammonium oxalate or carbonate into calcium oxalate or carbonate and ammonium phosphate, so that the very object for which the calcium chlorid was added is defeated by the addition of the ammonium oxalate or carbonate. In order to make the use of calcium chlorid effective it is necessary to filter the liquid from the precipitate formed by the calcium chlorid and ammonia and then add the ammonium oxalate or carbonate to the filtrate. This necessitates two separate filtrations and makes the proposed method of Huston as long as the old process.

477. Moore's Potash Method for Fertilizers as Modified by Veitch.—In reviewing the methods used and proposed for estimating potash in fertilizers Veitch has suggested that the losses now occurring may be partly or entirely overcome by using the method of Moore, provided, of course, any potash is occluded in the ammonia and ammonium oxalate precipitate in the lindo-glad-ding method.⁴⁶ The addition of other bases, as proposed by Hare

⁴⁴ Division of Chemistry, Bulletin 43, 1894 : 26.

⁴⁵ Journal of the American Chemical Society, 1895, 17 : 46.

⁴⁶ Journal of the American Chemical Society, 1905, 27 : 56.

Fünfter internationaler Kongress für angewandte Chemie ; Bericht, 1904, 1 : 486.

Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 429.

in the lime-water method, appears to be unnecessary except for the purpose of saving the platinum dishes from the effects of igniting phosphates in the presence of organic matter.

In order to determine the applicability of the method to this class of materials several modifications were tried, the purpose of which was to destroy organic matter and ammonium salts in the most expeditious manner. These were destroyed both by aqua regia and by igniting in porcelain dishes, the potash being taken up afterward in distilled water and also in water acidified with hydrochloric acid. In all cases the results have been given corrected and uncorrected for the undissolved foreign salts. In cases where the ignited residue was taken up only in distilled water the impurities in the precipitate were sometimes considerable. Comparisons were also made of washing with plain alcohol and with acidified alcohol. The results are given in the following table.

The samples represented mixtures of the commoner raw materials.

No.	
1759	Acid phosphate.
1761	Acid phosphate and cottonseed meal.
1762	Acid phosphate and muriate of potash.
1763	Acid phosphate and muriate of potash, cottonseed meal and nitrate of soda.
2119	Peruvian guano.
2120	Mixed fertilizer.
2911	Acid phosphate and potash salts.
2912	Dissolved animal bone and potash salts.

TABLE SHOWING PERCENTAGE OF POTASH IN FERTILIZERS.

Moore's Method

		Organic matter and NH_3 salts destroyed with $\text{HNO}_3 + \text{HCl}$				
		Acid alcohol		Plain alcohol		
No.	Official method.	K_2O + undiss. salts Per cent.	Corrected K_2O . Per cent.	K_2O + undiss. salts. Per cent.	Corrected K_2O Per cent.	Filt. on paper corrected. Per cent.
1759	4.98	5.10	5.01	5.25	5.17	5.31
1761	0.92	1.02	0.87	1.37	0.85	0.97
1762	0.70	0.68	0.62	0.99	0.67	0.87
1763	5.70	6.17	6.13	6.58	6.19	5.85
2119	3.88	4.00	3.96	3.74	3.71	3.92
2120	3.60	3.72	3.69	3.82	3.78	3.67
2911	3.96	4.04	3.99
2912	4.08	4.14	4.13

TABLE SHOWING PERCENTAGE OF POTASH IN FERTILIZERS.—Cont.

		Moore's Method			
		Ignited in porcelain			
		Dissolved in HCl		Dissolved in H ₂ O	
No.	Official method.	K ₂ O + undis. salts. Per cent.	Corrected K ₂ O. Per cent.	K ₂ O + undis. salts. Per cent.	Corrected K ₂ O. Per cent.
1759	4.98	4.96	4.92	4.84
1761	0.92	1.05	0.81	0.79
1762	0.70	...	0.92	1.43	0.79
1763	5.70	6.21	6.16	6.13	5.97
2119	3.88	3.47	3.44	3.50	3.49
2120	3.60	3.83	3.75	3.70	3.68
2911	3.96	4.01	3.83	2.09	2.08
2912	4.08	4.08	3.93	2.25	2.24

As a rule, the results are slightly higher by the moore method than by the official method; this is only noticeably so in case of sample 1763. From this it would appear that the flocculent precipitate of iron and lime phosphate has but little to do with the low results usually obtained. It is to be noticed that only when the acid alcohol is used may the impurities contained in the platinum precipitate be neglected. Where plain alcohol is used it is usually necessary to dissolve the potassium chlorplatinat, wash, and re-weigh the crucible to obtain the true weight of the potash.

It is obvious that after igniting the material it is not sufficient to treat it with water alone in order to dissolve the potash; such procedure does not always secure all the potash, some of it remaining undissolved, possibly in complex silicates or phosphosilicates, adhering to the dish. It was found that the potash so held could usually be readily recovered by dissolving the ignited material in the dish in dilute hydrochloric acid. This is not always true, however, the potash so held being dissolved but slowly in some instances, and while it appears that all potash may be recovered by prolonged treatment, the process is not considered to have any advantages over the official method.

478. Estimation of Potash by the Platinum Method in the Presence of Sulfates of the Alkalies and Alkaline Earths.—Regel

calls attention to the difficulties attending the ordinary method of determining potash in the presence of the sulfates of the alkalies and alkaline earths.⁴⁷ He modifies the method by precipitating the potash directly without previous precipitation with barium chlorid. This, however, is not a new variation, as Regel supposes, since it is the basis of the one proposed by Moore and practiced with such success in this country for many years. The precipitate of the platinum potash salt is washed in the usual manner. If sodium sulfate is present some of this is contained in the precipitate. In this case the precipitate is washed into a small beaker, the parts remaining on the filter being dissolved in hot water and powdered magnesium is added in excess. It is to be noticed that the magnesium, even in almost completely neutral solutions, reduces the double salt. Upon its introduction there is a notable evolution of heat and a decomposition of the neutral salt with a separation of black, finely divided metallic platinum. The precipitate of platinum is separated by filtration and any excess of magnesium removed by washing with dilute hydrochloric acid. The separated platinum is dried, ignited, and weighed. If magnesium sulfate or calcium sulfate is present in the original platinum precipitate, the method of separation is exactly the same as that just described except that five per cent. nitric acid is used instead of hydrochloric acid for the solution of any excess of sulfates. In this way calcium sulfate in the quantities in which it is present in potash salts is completely removed.

The reasons for using nitric acid are the following:

If the mixture of metallic platinum and the residual salts is treated with hydrochloric acid, the filtrate is clear. If, however, an attempt be made to wash out the hydrochloric acid with water there is obtained a deep black tinted filtrate containing dissolved platinum from which metallic platinum separates slowly. This phenomenon only occurs if the platinum salts are mixed with considerable quantities of potassium chlorid or calcium sulfate, a fact for which up to the present time no satisfactory explanation has been made. Since the separation of the platinum from the

⁴⁷ Chemiker-Zeitung, 1906, 30 : 684.

blackened filtrate doubtless occurs through the action of the oxygen of the air, it was sought to prevent the solution of the platinum beforehand by the use of a substance like nitric acid easily giving off oxygen.

479. Rapid Control Method for Potash Salts.—For rapid control work where great accuracy is not required, Albert recommends that the finely ground substance be placed in a liter flask and about 400 cubic centimeters of water added and three cubic centimeters of hydrochloric acid.⁴⁸ After boiling, barium chlorid is added, drop by drop, as long as a precipitate is produced. After cooling, the flask is filled to the mark and shaken and its contents filtered through a dry filter. An aliquot portion of the filtrate is evaporated with platinum chlorid solution in a smooth porcelain dish almost to dryness and the mass treated with alcohol, filtered through a weighed filter, and well washed with alcohol. The filter is then dried in an air-bath to a constant weight. For the different kinds of potash materials on the market the following proportions are recommended:

Kainit or Carnallit.—Twenty grams in one liter: Fifty cubic centimeters of the filtrate are evaporated with 40 cubic centimeters of platinic chlorid solution. The weight of potassium platinochlorid obtained $\times 19.3$ gives the per cent. of K_2O .

Sulfate of Potash.—Fifteen grams in one liter: Twenty cubic centimeters of the solution are evaporated with 15 cubic centimeters of platinic chlorid. The weight of potassium platinochlorid obtained $\times 64.33$ gives the per cent. of K_2O .

Potassium Chlorid.—Ten grams in one liter. Twenty-five cubic centimeters are evaporated with 15 cubic centimeters of platinic chlorid solution. The weight of the precipitate obtained $\times 77.2$ gives the per cent. of K_2O .

480. Weighing the Precipitate as Metallic Platinum.—Hilgard calls attention to the difficulty of weighing the double chlo-

⁴⁸ Zeitschrift für angewandte Chemie, 1891, 4 : 281.

rid of platinum and potash as such, although he acknowledges that in the gooch this weighing can be made with great accuracy.⁴⁹ He prefers to estimate the platinum in the metallic state and uses for this purpose a platinum crucible the inside of which, half way up from the bottom, is coated with a layer of platinum sponge, which is conveniently prepared by the decomposition of a few decigrams of the platinum double salt by inclining the crucible and rotating it during the progress of the reduction, which should require about a quarter of an hour. The platinum sponge produced in this way greatly favors the decomposition of the double salt for analytical purposes. The decomposition of the salt takes place quickly and quietly and at conveniently low temperatures.

When the decomposition is ended the crucible is strongly heated so as to hold the platinum sponge together sufficiently to prevent its being removed in the subsequent washing of the crucible by decantation. By the ignition at a high temperature necessary to secure this, the greater part of the potassium chlorid is volatilized. After cooling, a few drops of concentrated hydrochloric acid are placed in the crucible and if the slightest yellow color be shown the acid is evaporated and the ignition repeated, with the addition of a little oxalic acid. In most cases the slight yellow color produced comes from a trace of iron and will, therefore, appear again after the second ignition. The crucible is subsequently washed by repeated decantations, finally with boiling water, and after drying is ignited and weighed.

The advantage of this process is that without further trouble the reduced metal is completely freed of any salts of the alkaline earths, etc., which have been carried down with it and also from any of the uncombined sodium chlorid which may not have been washed out by the alcohol. In fact, the results obtained in this way are nearly always lower than those obtained through the direct weighing of the double salt, and the wash water which is first poured off contains, as a rule, traces of the alkaline earths and almost without exception some sodium chlorid. Correction

⁴⁹ *Zeitschrift für analytische Chemie*, 1893, **32** : 184.

for the filter ash is unnecessary because the ash is completely dissolved by the treatment received. The platinum sponge which is collected in the crucible in this way is removed in case it does not adhere to the sides and the crucible is then ready for the next operation.

481. Sources of Error in the Platinum Method.—In the comparative work done in the determination of potash by the members of the Association of Official Agricultural Chemists there has been noted, from year to year, marked differences in the data obtained by different analysts. Such differences often are due to personal errors, or a failure to accurately follow the directions for manipulation. Sometimes, however, they are due to sources of error in the processes employed. In the platinum method these sources of error have been long known to exist. Chief among these is the remarkable facility with which potash becomes incorporated with the precipitates of other bodies. The character and magnitude of some of these errors have been studied by Robinson.⁵⁰

Many precipitates occlude potash and hold it so firmly that it cannot be washed out with hot water although the potash compounds present in the precipitate are perfectly soluble. It appears to be a kind of molecular adhesion. Barium sulfate has this property of attaching potash molecules in a high degree, and ferric and aluminic compounds only to a slightly less extent. To reduce the losses, consequent on the conditions just mentioned, to a minimum, the sulfuric acid and earthy bases should be very slowly precipitated, with violent agitation, at a boiling temperature.

Another source of loss in the platinum method arises from the use of a solution of ammonium chlorid for washing the potassium platinochlorid precipitate. There is danger here, not only of the solution of the impurities present in the precipitate, but also of a double decomposition by means of which some ammonium

⁵⁰ Journal of the American Chemical Society, 1894, 16 : 364.

may be substituted for the potassium in the washed product. In the official method, moreover, there is danger of securing a final precipitate which may contain traces of calcium and magnesium sulfates when these bodies are abundantly present in the sample used for analysis. The careful analyst must guard against these sources of error, but it is probably true that he will never secure a practically chemically pure precipitate of potassium platinochlorid when working on the mixed fertilizers found in commerce.

482. Effect of Concentration on the Accuracy of Potash Analysis.—Winton has also studied the sources of error in the determination of potash as platinochlorid, especially with reference to the effect of the concentration of the solution at the time of precipitation.⁵¹

He finds that the method of precipitating in concentrated solutions and drying the potassium platinochlorid at 130° , depends for its accuracy upon the mutual compensation of three errors; viz., (1) due to the solubility of the potassium salt in 80 per cent. alcohol, (2) due to the presence of water in the crystals which is not driven off at 130° , and (3) due to the use of a factor based on the wrong atomic weight of platinum.

He finds, further, that the error due to the presence of water occluded in the crystals can be reduced to a minimum, and the process of drying greatly simplified, by adding the solution of platinum chlorid to the potash solution in a dilute condition, not exceeding one per cent. in strength. The potassium platinochlorid thus produced can be very effectively dried at 100° . The error due to the solubility of the salt in 80 per cent. alcohol can also be greatly reduced by using 95 per cent. alcohol. The error due to the wrong factor; viz., 0.3056 based on the old atomic weight of platinum, can be corrected by using the factor based on the recently determined atomic weight of platinum; viz., 195, which is 0.30688.

Since Winton's paper was published the atomic weight of plati-

⁵¹ Journal of the American Chemical Society, 1895, 17 : 453.

num has been reduced to 194.8, so that the factor on this basis is 0.3071.

483. Differences in Crystalline Form.—Winton has also observed a distinct difference in the crystals of potassium platinochlorid when obtained from concentrated and dilute solutions.⁵² When platinic chlorid is added to a concentrated solution of potassium chlorid, a large part of the salt which is formed is precipitated in a pulverulent state, the remainder being deposited on evaporation. After treating with alcohol, filtering, and drying, the double salt is found in the state of a fine powder which, when examined under the microscope, is found to consist largely of radiating crystals. The characteristic form is one having six arms formed by the intersection, at right angles, of three bars. Numerous globular cavities in the crystals are observed in which mother liquid is enclosed. For this reason the salt is not easily dried at 100°, but when so dried loses additional moisture at 130°, and still more at 160°. The total additional loss, after drying at 100°, from this cause may amount to as much as six-tenths per cent. of potassium chlorid.

When, however, the solution of the potassium salt is so dilute that no precipitate at all is formed on the addition of platinic chlorid, the double salt is all deposited, as well as formed slowly, during the evaporation and occurs exclusively as octahedra. These octahedra are comparatively free of cavities, and give up practically all their moisture when dried at 100°. A method of procedure, therefore, for potash determination, based on the above principle of the addition of the reagent to dilute solutions, and drying the double salt produced upon evaporation, after washing with 95 per cent. alcohol at 100°, and using the factor 0.3071 for potassium chlorid and 0.1941 for potassium oxid, gives good results and is regarded as better than any of the methods which prescribe the addition of platinic chlorid to highly concentrated potash solutions.

484. Factors for Potash Estimation.—The factor now in use by the official chemists to convert potassium platinochlorid into potash (K_2O) is 0.1941, and for potassium chlorid 0.3071.

⁵² Journal of the American Chemical Society, 1895, 17 : 453.

Wolfbauer gives the differences which may arise by computing the potash from its double platino chlorid by the different values assigned to the atomic weight of platinum.⁵³

The common factor used at that time to obtain potassium chlorid from potassium platinochlorid was based on the atomic weight 197.18 and is derived from the formula:

$$\frac{2(39.13 + 35.46)}{2 \times 39.13 + 197.18 + 6 \times 35.46} = \frac{149.18}{488.20} = 0.30557.$$

The variations arising from taking other assigned values for the atomic weight of platinum are shown in the following table:

Atomic weight of platinum	Determined by or calculated by	Factor for potassium chlorid from		Relation to factor 0.30557 in per cent.	
		Potassium platinochlorid	Platinum	Potassium platinochlorid	Platinum
197.18	Berzelius	0.30557	0.75658	100.00	100.00
197.88	Andrews	0.30517	0.75390	99.86	99.65
195.06	Haberstadt	0.30690	0.76468	100.44	101.07
194.87	Seubert and Clarke	0.30702	0.76555	100.47	101.20

The factor 0.3056 was regarded as the best for the computation from potassium platinochlorid and 0.7566 from platinum. It was also suggested that it is better to make the computation from the reduced platinum than from the double salt. Accepting the atomic weight of platinum as 194.8, the factor last given in the above table is almost correct.

485. Recovery of the Platinum Waste and Preparation of the Platinic Chlorid Solution.—(1) *By reduction in Alkaline Alcohol.*—All filtrates containing platinic chlorid, all precipitates of potassium platinochlorid and all residues of metallic platinum should be carefully preserved and the platinum recovered therefrom by the following process: The platinum residues are placed in a large porcelain dish. Since these residues contain a large amount of alcohol, they should be diluted with about one-third their volume of water, and when boiling treated with some sodium carbonate. The solid potassium platinochlorids should not be added until the liquid is boiling, and then only little by little. The heating on the water bath is continued until the liquid floating over the platinum sponge is quite clear and only slightly yellow.

⁵³ Chemiker-Zeitung, 1890, 4 : 1246.

The liquid is then poured off and the reduced platinum purified by boiling with hydrochloric acid and water. It is then dried and ignited to destroy any organic matter which may be present. It is advisable to boil the finely divided platinum once with strong nitric acid, and after this is poured off the solution of the platinum is effected in a large porcelain dish over a water bath by adding about four times its weight of hydrochloric acid, warming, and adding nitric acid, little by little. After the platinum is in solution the evaporation is continued until a drop of the liquid, removed by a glass rod, quickly solidifies. The crystalline mass which is formed on cooling is taken up with water and filtered, and then a sufficient amount of water added so that each 10 cubic centimeters will contain one gram of platinum. The specific gravity of this solution is 1.18 at ordinary temperatures. Special care must be taken that the solution contains neither platinous chlorid nor nitrogen compounds. If the first named compound be present it should be converted into platinic chlorid by treatment with fuming hydrochloric acid and a little nitric acid. The last mentioned compound may be removed by evaporating successively with hydrochloric acid and water. If the platinic chlorid be made from waste platinum, the danger of contamination with iridium must be considered. In such a case the platinum should be separated as ammonium platinochlorid, which can afterwards be reduced as above indicated. A convenient test of the purity of platinic chlorid solution is accomplished by the precipitation of a known weight of chemically pure potassium salt, and determining the quantity of platino-potassium chlorid produced.

(2) *By Reduction in Nascent Hydrogen.*—The platinum residues, filtrates containing platinum, etc., are collected in a large flask and evaporated in a large dish on a water bath, and reduced by means of zinc and hydrochloric acid to metallic platinum, the mass being warmed until all the zinc has been dissolved. The supernatant liquid standing over the spongy platinum is decanted and the spongy mass boiled twice with distilled water. The spongy platinum is then brought on a filter and washed till the filtrate shows no acid reaction. The filter and platinum sponge are next incinerated in a platinum dish and the

residue weighed. The weighed mass of pure platinum is dissolved in hydrochloric acid, with the addition of as little nitric acid as possible, and, after cooling, filtered. The filtrate is afterwards evaporated in a porcelain dish on a water bath to a sirupy consistence, taken up with water and filtered. To this filtrate enough water is now added to make the solution correspond to one gram of metallic platinum in 10 cubic centimeters.

486. Preparation of Chlorplatinic Acid by Electrolysis.—It has been noticed when using aqua regia to dissolve platinum that traces of nitric acid are removed with great difficulty, even by repeated evaporation. Weber has called attention to the fact that when working with as much as 100 grams of platinum, repeated evaporation to dryness of the solution is tedious and yields unsatisfactory results. If hydrochloric acid be used in the evaporation large quantities of material are necessary, while with water there is danger of decomposition of the chlorplatinic acid and consequent contamination with hydroxychlorplatinates.⁵⁴ To avoid these conditions the following method of preparing the platinum reagent is used.

Platinum scraps, or sponge, are dissolved in aqua regia, the excess of acid removed either by neutralization or evaporation, and the platinum solution reduced by zinc or alkaline formate, preferably the latter. The liquid is decanted from the precipitated platinum and the latter is warmed with a little dilute hydrochloric acid to remove iron. The platinum is transferred to the electrolytic apparatus, which is constructed as follows:

The apparatus (Fig. 47) is made of a cylindrical tube four centimeters in diameter and 35 centimeters long, ending in a narrow glass tube of about four millimeters bore, shaped in the form of a siphon. The anode consists of a thin disk of sheet platinum, closely fitting into the tube, and perforated with small holes. A short piece of platinum wire is welded to the disk and carried through the glass tube, as shown in the figure. The other end of the platinum wire ends in a glass tube which is carried to the top of the apparatus and filled with mercury. The platinum disk is about 30 centimeters from the top of the apparatus, and is placed at a point where the tube begins to be-

⁵⁴ Journal of the American Chemical Society, 1908, **30** : 29.

come narrow. The space below the anode is filled with glass beads to support the platinum disk. About five centimeters from the top of the tube three shoulders are moulded into the

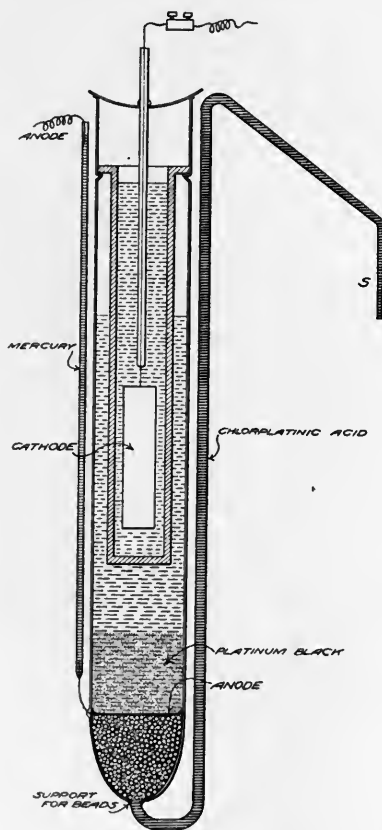


Fig. 47. Apparatus for Making Pure Chlorplatinic Acid.

tube and on these the cathode chamber is suspended, as shown in the figure. This chamber consists of a porous porcelain filter about 18 centimeters long and 25 millimeters in diameter. The cathode consists of a sheet of platinum from four to five centimeters long and from two to three centimeters wide, carrying a platinum wire passing through a glass tube as shown. This tube is suspended from a perforated watch glass which serves also as a cover for the apparatus. The whole apparatus is sus-

pended in a long cylinder when necessary so that it may be brought to any desired temperature by surrounding it with water. This outer tube is not shown in the figure and may be dispensed with when low currents are used. When the current rises to 10 amperes, the cooling jacket is essential to prevent the apparatus from becoming hot.

The reduced platinum to be treated is placed on the anode plate, and is washed with dilute hydrochloric acid until clean. The wash waters are drawn off through the siphon S. After washing, the platinum is covered with concentrated hydrochloric acid, in quantity sufficient to have it stand in the tube on a level with the end of S when the porous cylinder is inserted which is filled to the top with hydrochloric acid.

The current for electrolysis may be taken from a 120 volt direct current by inserting a number of incandescent lamps parallel with each other and in series with the cell. The cell may be run continuously on from eight to 10 amperes, and with this strength 64 grams of platinum may be dissolved in four or five hours. The theoretical quantity for 36 ampere hours is 65 grams. While the apparatus is in operation the hydrochloric acid travels from the cathode cell to the anode under the influence both of gravity and electric endosmosis. By adjustment of the height of hydrochloric acid in the anode cell the heavy layer of chlorplatinic solution as it is formed is delivered at the tip of the siphon S drop by drop, or the flow may be started by gentle suction at that point. The acid in the cathode chamber is replenished from time to time as it becomes necessary. Towards the end of the operation, when the amount of platinum remaining on the perforated disk becomes small, bubbles of chlorine commence to rise through the liquid, indicating that the current density is becoming too great. This is remedied by placing fresh acid upon the platinum black and decreasing the current.

In concentrating the solution of chlorplatinic acid prepared in this way, chlorine is passed through it for a short while to insure freedom from platinous compounds in case any have been formed during the electrolysis.

THE ESTIMATION OF POTASH AS PERCHLORATE

487. **General Principles.**—By reason of the great cost of platinum chlorid, analysts have sought for a reagent of a cheaper nature and yet capable of forming an insoluble compound with potash. Phosphomolybdic and perchloric acids are the reagents which have given the most promising results.⁵⁵ The principle of the method with the latter salt is based on the insolubility of potassium perchlorate in strong alcohol containing a little perchloric acid and the comparative easy solubility of the other bases usually associated with potassium in water. The French chemists have stated that magnesia, when present in considerable quantities, interferes with the accuracy of the results. Since in soil analysis considerable quantities of magnesia are often found, this base, according to the French chemists, should previously be removed when present in any considerable quantity, by the process described in the first volume. Kreider, however, as will be seen further on, working in the presence of magnesia, did not notice any disturbing effects caused thereby. The method is applicable to the common potash salts of the trade and with certain precautions to mixed salts. As will be mentioned later on, sulfuric acid should be previously removed and this is likely to introduce an error on account of the tendency of barium sulfate to entangle particles of potash among its molecules and thus remove them from solution. The barium sulfate should be precipitated slowly and in a strongly acid (nitric or hydrochloric) solution. The loss, which is inevitable, is thus reduced to a minimum and does not seriously affect the value of the numbers found. It is important to have an abundant supply of pure perchloric acid, and as this is not readily obtainable in the market the best methods of preparing it are given below. The method, while it has not been worked out extensively, is one of merit, and seemingly is worthy of fair trial by analysts. The process is by no means a new one, but was first proposed by Sérullas,⁵⁶ and prominently called to the attention of analysts by Schloesing,⁵⁷

⁵⁵ Wiley, *Principles and Practice of Agricultural Analysis*, 2nd Edition, 1906, 1 : 414, 421.

⁵⁶ *Annales de Chimie et de Physique*, 1831, [2], 46 : 294.

⁵⁷ *Comptes rendus*, 1871, 73 : 1269.

Kraut,⁵⁸ and Bertrand.⁵⁹ The method was fully developed by a committee appointed by the French agricultural chemists in 1887.⁶⁰

Wense has also described an improved method of estimating potash as perchlorate after the removal of sulfuric acid and also a process of preparing perchloric acid by distilling potassium perchlorate with sulfuric acid in a vacuum.⁶¹ He was also the first who proposed the plan of rendering potassium perchlorate insoluble in alcohol by dissolving a little perchloric acid therein. The best approved methods now known of preparing the perchloric acid and conducting the analysis will be described in the following paragraphs.

488. Schloesing's Modification of Sérullas' Process.—Dumas called attention to certain phenomena which took place at Cherbourg in consequence of flooding a large portion of land with sea water as a means of defense during the Franco-German war and the effect which this flooding had upon subsequent vegetation.⁶² Peligot was also interested in the discussion. Chevreul called attention to the difficulty which he had experienced in determining potash and soda, or rather the chlorids of potash and soda, by means of platinum chlorid.

In view of this difficulty, Schloesing proposed the use of perchloric acid, which he states was first proposed by Sérullas who was negligent in not citing in his paper the data of analysis which are the most efficacious means of determining the merits of a method.⁶³ The chief cause of the failure of the method proposed by Sérullas is the difficulty of getting perchloric acid in sufficient quantities and in a pure state. To Roscoe is awarded the credit of having devised a means of procuring the acid in abundance and in a state of purity. The process of Sérullas, according to Schloesing, is one of the most precise when pure perchloric acid furnished by the perchlorate of ammonia is employed. The method proposed for conducting the analysis is as follows: In

⁵⁸ *Zeitschrift für analytische Chemie*, 1875, **14** : 152.

⁵⁹ *Moniteur scientifique*, 1881, **23** : 961.

⁶⁰ Grandeau, *Traité d'analyse des matières agricoles*, 3rd Edition, 1897, **1** : 419.

⁶¹ *Zeitschrift für angewandte Chemie*, 1891, **4** : 691 ; 1892, **5** : 253.

⁶² *Comptes rendus*, 1871, **73** : 1080.

⁶³ *Comptes rendus*, 1871, **73** : 1269.

a mixture of chlorids or nitrates of potash and soda in solution, perchloric acid is added and the mixture evaporated on a sand bath until it is almost dry. The degagement of white fumes is a sign that perchloric acid is in excess and that the formation of the salt is complete. When the white fumes have ceased to come over, the mass is cooled and the perchlorate of potash is washed several times with small quantities of alcohol of 36°. The more abundant the soda, the more perchlorate of potash is retained in its crystals. For this reason it is advisable to dissolve with heat in the least quantity of water possible the perchlorates when they are almost washed, and to evaporate to dryness. Two washings with alcohol will then finish the purification of the salt. With a few drops of water the perchlorate which is retained upon the filter is dissolved and received into a capsule, evaporated again to dryness and heated to 250°. The salt is then absolutely dry and fit to weigh. The alcoholic solution of perchlorate of soda is evaporated, the salt is afterwards decomposed by heat, taken up by water and evaporated in a platinum capsule. The chlorid of soda thus obtained very often contains some trace of perchlorate. In order to have an exact estimate it is necessary to transform it into sulfate. In place of decomposing the perchlorate of soda by heat, it may be treated directly by sulfuric acid.

The paper gives data showing the exactitude of the reaction and describes the preparation of perchlorate of ammonia, which is the reagent employed to furnish the perchloric acid.

489. Caspari's Method for Preparing Perchloric Acid.—A hessian crucible about 15 centimeters high is filled with moderately well compressed pure potassium chlorate and gradually heated in a suitable furnace until the contents become fluid.⁶⁴ The heat must then be carefully regulated to avoid loss by foaming due to the evolution of oxygen. The heat is continued until oxygen is no longer given off and the surface of the liquid becomes encrusted, which will take place in from one and a half to two hours.

After cooling, the contents of the crucible are pulverized and

⁶⁴ Zeitschrift für angewandte Chemie, 1893, 6 : 68.

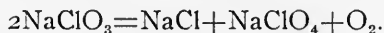
heated, with vigorous stirring, to boiling, with one and a half times their weight of water. By this process the potassium chlorid which has formed during the first reaction is dissolved and is thus removed. The residual salt is washed with additional quantities of cold water and finally dried. To remove the potassium base from the crude potassium perchlorate obtained as above, recourse is had to hydrofluosilicic acid. The reaction is represented by the following formula: $2\text{KClO}_4 + \text{H}_2\text{SiF}_6 = \text{K}_2\text{SiF}_6 + \text{HClO}_4$. In order to effect this decomposition the potassium perchlorate is dissolved in seven times its weight of hot water and an excess of hydrofluosilicic acid added to the boiling solution. A porcelain dish may be used. The boiling is continued, with addition of water to compensate for evaporation, for about an hour until particles of potassium perchlorate can no longer be detected.

On cooling, the gelatinous potassium silicofluorid is deposited and the perchloric acid separated therefrom as completely as possible by decantation. The residue is again boiled with water and a little hydrofluosilicic acid and the clear liquor thus obtained added to the first lot. The second boiling may generally be omitted. Finally, any residual perchloric acid may be removed on an asbestos felt under pressure. The clear liquid thus obtained is evaporated on a steam-bath to the greatest possible degree of concentration and allowed to stand in a cool place for 24 hours, whereby is effected the separation of any remaining potassium silicofluorid or potassium perchlorate. The residual liquid when filtered through an asbestos felt should give a perfectly clear filtrate. In order to throw out the last traces of hydrofluosilicic acid and any sulfuric acid present, an equal volume of water is added, and while cold small quantities of barium chlorid are successively added until the barium salt is present in a very slight excess. The clear supernatant liquid is poured off after a few hours and evaporated until the acid is all expelled and white fumes of perchloric acid are noticed. Any potassium perchlorate still remaining will now be separated and, in the cold, sodium perchlorate will also be separated in crystals. The clear residue is again diluted with an equal volume of water and any barium

salts present carefully removed with sulfuric acid. The mass is allowed to stand for one or two days, and is then filtered through paper and is ready for use. The removal of the barium with sulfuric acid may be omitted, the filtrate being diluted with an equal volume of water and allowed to stand for one or two days to permit the deposition of the last traces of barium silicofluorid and barium sulfate. The purity of the acid obtained depends chiefly on the purity of the hydrofluosilicic acid at first used. Hence to get good results this acid must be free from foreign bodies. If an absolutely pure product be desired, the acid above obtained must be distilled in a vacuum.

490. Method of Kreider.—Kreider has worked out a simpler method of preparing perchloric acid which will make it easy for every analyst to make and keep a supply of this admirable yet unappreciated reagent. This method is conducted as follows:⁶⁵

A convenient quantity of sodium chlorate, from 100 to 300 grams, is melted in a glass retort or round-bottom flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly evolved, and kept at this temperature till the fused mass thickens throughout, indicating the complete conversion of the chlorate to the chlorid and perchlorate, which requires from one and one-half to two hours; or the retort may be connected with a gasometer and the end of the reaction determined by the volume of oxygen expelled, according to the equation



The product thus obtained is washed from the retort to a capacious evaporating dish, where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well distributed heat, will be present in but small amount. It is then evaporated to dryness on the steam-bath, or more quickly over a direct flame, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilization of the remaining

⁶⁵ American Journal of Science, 1895, 149 : 443.

liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water and its removal from the dish, without moistening and reheating, is impossible.

After triturating the residue, easily accomplished in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker, where there is less surface for the escape of hydrochloric acid and from which the acid can be decanted without disturbing the precipitated chlorid. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chlorid, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a gooch, through which it may be rapidly drawn with the aid of suction, and the residue re-treated with the strongest hydrochloric acid, settled, and again decanted, the salt being finally brought upon the filter, where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chlorid, the latter, after washing, may be removed by water or by mechanical means, with precautions not to disturb the felt, which is then ready for the remainder. Of course, if water is used, the felt had better be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only an inconsiderable amount of perchlorate, when tested by first heating to expel the free acid and then treating the dry and powdered residue with 97 per cent. alcohol, which dissolves the perchlorate of sodium, but has little soluble effect on the chlorid.

The filtrate, containing the perchloric acid with the excess of hydrochloric acid and the small per cent. of sodium chlorid which is soluble in the latter, is then evaporated over the steam-bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium

determinations. Evidently the acid will not be chemically pure, because the sodium chlorid is not absolutely insoluble in hydrochloric acid; but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate, and unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent. alcohol, and its presence is, therefore, unobjectionable. One cubic centimeter of the acid thus obtained gives on evaporation a residue of only 0.036 gram, which is completely soluble in 97 per cent. alcohol.

Caspari's acid under similar treatment gave a residue in one case of 0.024 gram and in another 0.047 gram. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure, and, as Caspari has shown, without great loss, providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. In these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium, and thus on evaporation a residue insoluble in 97 per cent. alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chlorid, after treating with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, is well digested with 97 per cent. alcohol, which dissolves the sodium perchlorate, but leaves the chlorid, as well as any potassium salt insoluble. By giving the alcohol time to become saturated, which is facilitated by stirring, it is found on filtering and evaporating that an average of about 0.2 of a gram of sodium perchlorate is obtained for every cubic centimeter of alcohol and that the product thus obtained is comparatively free of chlorids, until the perchlorate is nearly all removed, when more of the chlorid seems to dissolve. This treatment with alcohol is continued until on

evaporation of a small portion of the latest filtrate only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate begins to crystallize, when the heat is removed and the contents quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. When the distillation is terminated at the point indicated, the distillate will contain most of the alcohol employed, but in a somewhat stronger solution, so that it requires only diluting to 97 per cent. to fit it for use in future preparations. The salt is then evaporated to dryness on the steam-bath and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

One cubic centimeter of the acid prepared in this way on evaporation gave a residue in one case of 0.0369 gram, and in another 0.0307 gram, completely soluble in 97 per cent. alcohol. The residue was then ignited and the chlorine determined by silver from which the equivalent of perchloric acid in the form of salts was calculated as 0.0305 gram. By neutralizing the acid with sodium carbonate, evaporating, igniting in an atmosphere of carbon dioxide till decomposition was complete, collecting the oxygen over caustic potash, allowing it to act on hydriodic acid by intervention of nitric oxide, titrating the iodine liberated with standard arsenic and calculating the equivalent of perchloric acid, after subtracting the amount of acid found in the form of salts, the amount of free perchloric acid per cubic centimeter proved to be 0.9831 gram.

The whole process, even when the separation with alcohol is necessary, can not well require more than two days, and during the greater part of that time the work proceeds without attention.

491. Keeping Properties of Perchloric Acid.—By most authorities it is asserted that perchloric acid is a very unstable body and is liable to decompose with explosive violence even when kept in the dark. It is probable that this tendency to spontaneous decomposition has been exaggerated. It is not even mentioned by Gmelin.⁶⁶

⁶⁶ Hand-Book of Chemistry, Translated by Watts, 1859, 2 : 317.

The most concentrated aqueous acid has a specific gravity of 1.65, is colorless, fumes slightly when exposed to the air, and boils at 200°. It has no odor, possesses an oily consistence and has a strong and agreeably acid taste. It reddens litmus without bleaching it and is slowly volatilized at 138° without decomposition. It is unaffected by exposure to the light, even the sun's rays. It is not decomposed by hydrosulfuric, sulfurous, or hydrochloric acids, nor by alcohol. Paper saturated with the strong acid does not take fire spontaneously, but it deflagrates with red-hot charcoal.

The acid prepared by the method of Kreider has approximately the composition of the di-hydrate, $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$. It is usually a little more dilute than is shown by the above formula. The di-hydrate is quite stable and the more dilute acid can be kept for an indefinite time. Kreider has kept the acid for six months and noticed no change whatever in its composition. Acid containing one gram of perchloric acid in a cubic centimeter has been kept three months with perfect safety. There is no reason why the strong aqueous acid should not be made a regular article of commerce by dealers in chemical supplies, under proper restrictions for storage and transportation.

The strong acid made in the laboratory of the Bureau of Chemistry by the Kreider method has not given the least indication of easy or spontaneous decomposition.

492. The Analytical Process.—The perchlorate process cannot be applied in the presence of sulfuric acid or dissolved sulfates. This acid, when present, is to be removed by the usual methods before applying the perchloric acid. Phosphoric acid may be present, but in this case a considerable excess of the reagent must be used. The process, as originally proposed by Caspari and carried out by Kreider is as follows:⁶⁷

The substance, free from sulfuric acid, is evaporated for the expulsion of free hydrochloric acid, the residue stirred with 20 cubic centimeters of hot water and then treated with perchloric acid, in quantity not less than one and one-half times that required by the bases present, evaporated, with frequent stirring,

⁶⁷ American Journal of Science, 1895, 149 : 446.

to a thick, sirup-like consistency, again dissolved in hot water and evaporated, with continued stirring, till all hydrochloric acid has been expelled and the fumes of perchloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more of the reagent. The cold mass is then well stirred with about 20 cubic centimeters of wash alcohol (97 per cent. alcohol containing 0.2 per cent. by weight of pure perchloric acid); with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settled, and again decanted. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 cubic centimeters of hot water and a little perchloric acid, when it is evaporated once more, with stirring, until fumes of perchloric acid rise. It is then washed with one cubic centimeter of wash alcohol, transferred to the asbestos, preferably by a policeman to avoid excessive use of alcohol, and covered finally with pure alcohol; the whole wash process requiring from 50 to 70 cubic centimeters of alcohol. It is then dried at about 130° and weighed.

The substitution of a gouch for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below and seemed to hold the finer particles of the perchlorate very satisfactorily.

A number of determinations were made of potassium chlorid unmixed with other bases or non-volatile acids and the data obtained are recorded in the following table:

Potassium chlorid used. Grams	Volume of filtrate. Cubic centimeters	Potassium perchlorate found. Grams	Error on potassium perchlorate. Grams	Error on potassium chlorid. Grams	Error on potash. Grams
0.1000	54	0.1851	0.0008—	0.0004—	0.0003—
0.1000	58	0.1854	0.0005—	0.0002—	0.0002—
0.1000	51	0.1859	0.0000	0.0000	0.0000
0.1000	50	0.1854	0.0005—	0.0002—	0.0002—
0.1000	48	0.1859	0.0000	0.0000	0.0000
0.1000	52	0.1854	0.0005—	0.0002—	0.0002—

Considerable difficulty, however, was experienced in obtaining satisfactory determinations of potassium associated with sulfuric and phosphoric acids. As Caspari has pointed out, the sulfuric acid must be removed by precipitation as barium sulfate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed, but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with, fairly good results may justly be expected. Below is given a number of the results obtained:

Compounds used. Gram	Volume of filtrate. Cubic centi- meters.	Potassium per- chlorate found. Grams	Error on potassium per- chlorate. Grams	Error on potassium chlorid. Grams	Error on potash. Grams
Potassium chlorid=0.10					
Calcium carbonate=0.13	50	0.1887	0.0028+	0.0014+	0.0005+ ¹
Magnesium sulfate=0.13	82	0.1875	0.0016+	0.0008+	0.0005+ ¹
Ferric chlorid =0.05	80	0.1861	0.0002+	0.0001+	0.0001+ ²
Magnesium sulfate=0.05	80	0.1843	0.0016-	0.0008-	0.0005- ²
Manganese dioxid=0.05	92	0.1839	0.0020-	0.0010-	0.0006- ²
Sodium phosphate=0.40	60	0.1854	0.0005-	0.0002-	0.0002- ²

¹ The residue showed phosphoric acid plainly when tested.

² Only traces of phosphoric acid found in the residue.

In the last three experiments of the above table the amount of perchloric acid was about three times that required to unite with the bases present, and the phosphoric acid subsequently found with the potassium was hardly enough to appreciably affect the weight, although its absolute removal was found impossible.

That the magnesia does not produce any disturbing effect, as is supposed by the French chemists, Kreider has proved by the following test: One hundred and fifty milligrams of magnesium carbonate were treated with perchloric acid, evaporated till fumes of perchloric acid appeared, and cooled, when the magnesium perchlorate crystallized: But on treating it with about 15 cubic centimeters of 97 per cent. alcohol containing 0.2 per cent. of perchloric acid, a perfectly clear solution was obtained. If therefore, a sufficient excess of acid be used, no interference will be caused by the presence of magnesium.

While it is true that the potassium perchlorate obtained may

be contaminated with a trace of phosphoric acid, if the latter be present in large quantity no fear of contamination with magnesia need be entertained if a sufficient quantity of the perchloric acid be used.

493. Removal of the Sulfuric Acid.—The practical objection to the removal of the sulfuric acid in the form of barium sulfate rests on the fact of the mechanical entanglement of some of the potash in the barium salt. Unless special precautions are observed a noticeable amount of the potash will be found with the barium sulfate.

Caspari has succeeded in reducing this amount to a minimum by the following procedure:⁶⁸ The solution of barium chlorid is prepared by dissolving 127 grams of crystallized barium chlorid in water, adding 125 cubic centimeters of 35 per cent. hydrochloric acid, and bringing the total volume up to one liter with water.

Five grams of the substance from which the sulfuric acid is to be removed are boiled with 150 cubic centimeters of water and 20 of strong hydrochloric acid. While the solution is still in ebullition it is treated, drop by drop, with constant stirring, with the barium chlorid solution above mentioned, until a slight excess is added. This excess does not cause any inconvenience subsequently. After the precipitation is complete the boiling is continued for a few minutes, the mixture cooled and made up to a quarter of a liter with water. No account is taken of the volume of the barium sulfate formed, since, even with the precautions mentioned, a little potassium is thrown down and the volume of the barium sulfate tends to correct this error. With a solution from which the sulfuric acid had been removed as above indicated, Caspari found a loss of only one milligram of potassium perchlorate in a precipitate weighing over 800 milligrams.

494. Estimation of Potash in Crude Potash Salts by Means of Perchloric Acid.—The potash in the raw salt may also be determined by perchloric acid as described below.⁶⁹ In the case of

⁶⁸ *Zeitschrift für angewandte Chemie*, 1893, 6 : 73.

⁶⁹ Lunge, *Chemisch-technische Untersuchungsmethoden*, 5th Edition, 1904, 1 : 536.

carnallit or bergkieserit 13.455 grams, and in the case of kainit, sylvinit and hartsalz 15.7225 grams are dissolved in about 300 cubic centimeters of water with 15 cubic centimeters of concentrated hydrochloric acid in a 500 cubic centimeter flask. The solution is heated to the boiling point and the sulfuric acid precipitated by barium chlorid. In this case a slight excess of barium chlorid is without any hurtful influence upon the exactness of the process, since chlorid of barium is converted into barium perchlorid by the perchloric acid and this salt is easily soluble in alcohol. For the complete precipitation of sulfuric acid there are required, in the case of carnallit, from 24 to 40 cubic centimeters, and, in the case of kainit, from 65 to 80 cubic centimeters of normal barium chlorid solution, containing 122 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, and 50 cubic centimeters of concentrated hydrochloric acid in one liter. After cooling, the flask is filled to the mark and its contents filtered through a dry, double folded filter of about 18 centimeters diameter. When filtered, 20 cubic centimeters are evaporated in a flat, dark-blue glazed porcelain dish of about 10 centimeters diameter with five cubic centimeters of perchloric acid of 1.125 specific gravity until the odor of hydrochloric acid has disappeared and white clouds of perchloric acid are evolved. The residue is treated with about 20 cubic centimeters of 96 per cent. alcohol and carefully rubbed in order to break up the mass into as fine particles as possible. After standing for a short time the supernatant liquid is filtered through a filter prepared as in the platinum method given above or through a gooch.

The rubbing of the potassium perchlorate is repeated twice more, but not with pure 96 per cent. alcohol, but with alcohol to which 0.2 per cent. of perchloric acid has been added. Finally, in order to remove the perchloric acid, the filter and the precipitate thereon are washed with a spray of 96 per cent. alcohol, using as little thereof as possible and drying and weighing as in the platinum method. In this process one milligram of potassium perchlorate, corresponds to 0.10 per cent. of potassium chlorate or of potassium sulfate in the raw material.

495. Influence of Carbonates.—In the method of determining

potash by perchloric acid Schenke calls attention to the influence of large quantities of carbonate of lime in requiring that larger quantities of perchloric acid be used in order to secure complete transformation of the lime salts into perchlorate. In each case it is necessary that such a quantity be used that the addition of additional quantities of perchloric acid to the hot concentrated filtrate no longer gives the odor of hydrochloric acid.⁷⁰

Further, it is recommended to add 15 cubic centimeters of alcohol to the warm pasty residue obtained upon evaporation, since the solid cooled residue is very incompletely, or at least difficultly, soluble in alcohol. If the material under investigation contains large amounts of lime as for instance marl, residues from filter presses, etc., it is advisable to separate as much as possible of this lime from the solution before precipitating the potash. In the estimation of potash, according to the perchlorate method, in strongly acid, especially sulfuric acid, solutions the long time required is the chief objection. In such cases it is quite important that there shall be two evaporations and incinerations in a platinum dish. In order to save as much time as possible, the process is carried on as follows:

Either sulfuric acid or fuming nitric acid may be used for the solution. The solutions are evaporated carefully to dryness over a small free flame, and thus the ammonium salts driven off. The residue is at first gently, and afterwards gradually more strongly heated until a distinct red heat is reached. This incineration does not need to be carried on so carefully as in the case of heating of the alkaline chlorids, since the alkaline sulfates, even when kept for a short time at a low red heat, do not lose any alkali. The ignited sulfates in order to avoid any loss in consequence of any shrinking on cooling, are carefully covered and after cooling are digested with hot water with continued rubbing and with a little hydrochloric acid. In all two or three cubic centimeters, of a five per cent. solution will dissolve all soluble material. The contents of the dish are then washed into a measuring flask and after heating, treated with a slight excess of a 10 per cent. barium chlorid solution. If there is only a slight precipitate of barium sulfate the separation of it by filtration

⁷⁰ Die landwirtschaftlichen Versuchs-Stationen, 1908, 68 : 61.

may be omitted, and after cooling and adding a few drops of alcoholic phenolphthalein solution the precipitation of the phosphate and other salts is accomplished in the same flask by means of milk of lime, free of alkali, which is added until a strong red colored saturated solution of calcium hydroxid is secured. Milk of lime does not dissolve the barium sulfate and the filtrate contains therefore no trace of sulfuric acid. After standing about half an hour the potash is determined in an aliquot part of the filtrate after acidifying with hydrochloric acid and a slight concentration thereof on the water bath with about five cubic centimeters or more of 20 per cent. perchloric acid.

Finally, special attention must be called to the fact that on account of the very slight solubility of barium salts in alcohol only a very small excess of the 10 per cent. chlorid of barium solution should be used for the precipitation of the sulfuric acid and only about two cubic centimeters of the five per cent. hydrochloric acid should be used for the solution of the ignited salts since with larger quantities of hydrochloric acid more milk of lime is necessary for saturation and a large quantity of the lime salts will thus be incorporated in the precipitate of the potassium perchlorate.

496. Applicability of the Process.—Experience has shown that sulfuric acid is the only substance which need be removed from ordinary fertilizers preparatory to the estimation of the potash by means of perchloric acid. The fact that this process can be used in the presence of phosphoric acid is a matter of great importance in the estimation of potash in fertilizers, inasmuch as these fertilizers nearly always contain that acid. The fact that the French chemists noticed that magnesia was a disturbing element in the process, as has been indicated in volume first, probably arose from its presence as sulfate. Neither Caspari nor Kreider has noticed any disturbance in the results which can be traced to the presence of magnesia as a base.

If ammonia be present there is a tendency to the production of ammonium perchlorate, which is somewhat insoluble in the alcohol wash used. Solutions containing ammonia before treating by the perchlorate method for potash should be ren-

dered alkaline by soda-lye and boiled. With the precautions above mentioned, the method promises to prove of great value in agricultural analysis, effecting both a saving of time and expense in potash determinations.

497. Accuracy of the Process.—The perchlorate method was tried in conjunction with the platinum method on the two samples of potash fertilizer prepared and distributed by the official reporter on potash for 1893.⁷¹ One of the samples was of a fertilizer which had been compounded for the Florida trade and contained bone, dried blood, and potash, mostly in the form of sulfate. The other sample consisted of mixed potash salts, sulfate, chlorid, double salt, kainit, and about five per cent. of the sulfates of calcium, potassium, and magnesium.

The results obtained by Wagner and Caspari on the two samples follow :

	Sample No. 1. Per cent. potash	Sample No. 2. Per cent. potash
By the platinum method	13.25	37.98
By the perchlorate method	13.09	37.82

In transmitting their results these chemists say: "In the course of our work the fact was again clearly and distinctly brought out that the improved perchlorate method is decidedly superior to the old platinum chlorid method as regards rapid execution and simplicity of manipulation. This superiority is especially perceptible in the analysis of mixed fertilizers containing phosphoric acid. For this reason the laborious and time-taking separation of the alkalis, which is necessary in the platinum method, is entirely avoided."⁷² In the presence of organic matter containing nitrogen it is advisable to previously destroy the nitrogenous materials in order to avoid the danger of their transformation into ammonia during the progress of the analysis.

The perchlorate method, on the whole, appears to be almost as accurate as the platinum process, requires less manipulation and can be completed in a shorter time and at less expense for reagents. In spite of these advantages, however, the use of the method has not obtained to any extent in this country, and in so far as the author knows, is not employed in any official or commercial laboratory in the United States.

⁷¹ Division of Chemistry, Bulletin 38, 1893 : 57.

⁷² Division of Chemistry, Bulletin 38, 1893 : 56.

PART FOURTH

MISCELLANEOUS FERTILIZERS AND INSECTICIDES

498. **Classification.**—Nitrogen, phosphoric acid, and potash are the most important of the plant foods both from a commercial and physiological point of view. They are the chief constituents of the most important fertilizers and manures, but are by no means the sole essential elements of plant nutrition. Lime, magnesia, soda, sulfur, chlorin and many other elements are found constantly in plants and must be regarded as normal constituents thereof. It is the purpose here, however, to speak only of those substances which are used as fertilizers and which constantly or occasionally are subjected to chemical examination for determining their commercial or agronomic value. These bodies may be conveniently divided into two classes; viz., mineral and organic. Among those of mineral nature may be mentioned lime, gypsum, marls, wood ashes, common salt, and ferrous sulfate; among those of organic nature may be included guano, hen manure, stall manure, composts, and muck or peat.

499. **Forms of Lime.**—By the term lime is meant the product obtained by subjecting limestone or other lime carbonates to the action of heat until the carbon dioxide contained therein is expelled. The resulting lime, CaO , when exposed for some time to the air, or at once on the addition of water, is converted into the hydrate CaO_2H_2 , known as slaked lime. On longer exposure to the air, the hydrate gradually absorbs carbon dioxide and becomes converted into carbonate. In whatever form lime is applied to the soil, it is found in the end, as carbonate. A distinction should also be made between lime obtained from mineral substances and that got from organic products such as shells. Strictly speaking this is not a weighty matter, inasmuch as limestones are sometimes but little more than aggregations of fossil shells. Practically, the distinction is made, and some farmers prefer shell lime to that of any other kind. Gas lime, that is

lime which has been used for the purification of illuminating gas made from coal, is hardly to be considered in this connection, since it may contain very little even of the hydrate. In this case the lime has been converted largely into carbonate and sulfid.

500. Application of Lime.—For many reasons it is important that the lime be transported to the field before it has had time to be converted into hydrate. The transportation costs less in this state and it can be handled with far less inconvenience than when slaked. The lime should be placed in small piles and left thus, best covered with a little earth, until thoroughly slaked. It is then spread evenly over the surface. The quantity used per acre depends largely on the nature of the soil. Stiff clays and sour marsh lands require a larger dressing than loams or well aerated soils. From three to six thousand pounds per acre are the quantities usually employed. When the lime is once thoroughly incorporated in the soil it is rapidly converted into carbonate, but while in the caustic state it may act vigorously in promoting the decay of organic matter and may prove injurious in promoting the decomposition of ammonium salts with attendant loss of nitrogen.

501. Action of Lime.—The benefits arising from the application of lime to agricultural lands, although in many cases great, do not arise from any distinct fertilizing action of its own. Plants need lime for growth and need plenty of it, but, as a rule, any soil which is good enough to grow crops will contain enough lime to furnish that constituent of the crops for many years. Its action is both mechanical and chemical. By virtue of the latter property it renders available for plant food bodies already existing in the soil, but existing in such shape as to be unavailable for plants. The supply of plant food available for the crops of one year is increased, but this increase is at the expense of the following years. Lime is a stimulant. There is a common proverb that "lime enriches the father but beggars the son." Nevertheless, a limestone country is usually a fertile one and soils containing plenty of lime naturally, are nearly always rich soils. It is said that the trees and plants which farmers pick out as indicative of rich land are nearly always those which prefer lime soils.

The mechanical action of lime on soils tends to lighten heavy clays and loams and to render firmer and more consistent the light and shifting sandy soils. When a lump of clay is stirred up in a bucket of rain water the water becomes muddy and remains that way for many days. If, however, to the bucket of muddy water a little lime water be added the suspended particles of clay begin to flocculate and soon the water is clear and the clay falls to the bottom, nor does it again make the water muddy for a long time when stirred up with it. The flocky character of the precipitate is tenaciously retained and it is necessary to knead the clay for some time to induce it to reassume its original heavy character. An action like this takes place when lime is added to heavy soils so that the soil becomes more porous and assumes a better tilth on cultivation. With sandy soils an altogether different action takes place. In making mortar, as is well-known, sand is stirred in with water and lime and after being exposed to air for a while the mixture becomes hard and firm, the firmness increasing with age. This is due to the fact that when the mortar dries the lime begins to absorb carbon dioxide from the air and is converted into grains of carbonate which adhere strongly to neighboring sand grains and to each other so that the whole soon gets to be a solid mass. Something like this takes place in the soil and the sand grains are to some extent bound together. The increased firmness of the soil thus gained is often of considerable advantage.

Besides these actions, which are more or less mechanical, lime exerts a chemical action on many soil constituents. Feldspar and other common rocks contain potash, and this potash is in such a form as to be inaccessible to plants. These rocks exist in the shape of small particles in many soils and on them lime exerts a decomposing action, setting the potash free. Lime also hastens the decomposition of the nitrogenous organic matter and at the same time renders the soil more retentive of the products formed. The conversion of ammonia, resulting from the decomposition of such organic matter into nitrites and nitrates, is not easily accomplished without a proper amount of calcium carbonate. The microorganisms producing this change, which is known as nitri-

fication, apparently require its presence for neutralizing the acid formed. In general, it may be said that the presence of lime hastens the destruction of organic matter.

It is difficult to say just what soils will be improved by liming and what will not, and it is a matter which must be settled by experiment in each case. As a rule, heavy clays and loams are benefited, yet of two such soils, apparently identical, one may not be affected in any marked degree while the other may readily respond to treatment. Sandy soils are often improved but sometimes not. Sour, boggy lands, are usually improved by the addition of enough lime to neutralize their undue acidity. Marsh grasses and plants are more tolerant of acid in the soil than tame grasses are, so that in unlimed soil the former run out the latter. The application of lime alone to a very poor soil does not pay.

The particles of lime resting in the soil are partially dissolved by the next rainfall after application, or by the soil moisture, forming lime water, and the lime is distributed in this form through the soil to some extent. It all probably soon becomes converted into carbonate as ground air is usually quite rich in carbon dioxide. Indeed, for many soils, it is immaterial whether lime be applied as lime or as carbonate, granting, of course, that the latter be ground to a fine powder. Economy is in favor of the lime, however, not only because it needs no grinding, but because it is lighter than the corresponding amount of carbonate, making a saving in transportation. The difference is quite considerable, 56 pounds of lime being equivalent in effect to 100 pounds of carbonate. For these reasons as well as because it possesses some valuable properties not shared by the carbonate, it is probable that for most localities lime is to be preferred to any form of ground oyster shells, ground limestone, marble dust or the like.

One of these valuable properties not possessed by limestone, is said to be that of acting as a fungicide and insecticide. As a rule, fungi prefer acid reaction in the substances in which they grow, so that the strongly alkaline properties of lime may make a limed soil unsuitable for their growth.

502. Preferable Form of Lime.—Burned lime or slaked lime as has already been said, is to be preferred to lime carbonate where

quick action in neutralizing a free acid or aiding in decomposition is the object in view. In a soil rich in ammonia compounds the powdered lime carbonate is preferable in order to avoid loss of the nitrogen compounds. Burned lime also exists in a finer state of subdivision than is usually found in the ground rock or shells. If the final effect desired is the amelioration of the physical state of the soil and the promotion of nitrification there is little difference in value between the burned and unburned lime.

503. Analysis of Lime.—Lime, which is prepared for use as a fertilizer is rarely submitted to a chemical examination. It is easy to see, however, that such an examination is of some importance. If the real value of a sample be dependent on the content of lime, the actual quantity present as determined by analysis, must fix the value for agricultural purposes. The more important things to be determined are the quantities of lime, and of slaked lime, of undecomposed calcium carbonate, and of insoluble matter. It will be also of interest to determine the respective quantities of lime present as oxid, hydrate, and carbonate. If any question be raised in the case of slaked lime in respect of its origin, it can usually be answered by an examination of the unburned or unslaked residues. In perfectly slaked lime containing no débris, the analyst will be unable to discover whether it has been made from limestone, marble or shells. The lime used for agricultural purposes should be reasonably free of magnesia, and should not be air-slaked before transportation to the field. In dry air-slaking, a considerable quantity of carbonate may be formed.

504. The Analytical Process. (1) *Insoluble and Soluble Constituents.*—A representative sample of the lime having been secured, it is reduced to a powder and passed through a half millimeter mesh sieve or ground to a fine powder in an agate mortar. Two grams of this sample are digested with an excess of hydrochloric acid, for two hours with frequent stirring, filtered, the residue washed with hot distilled water until chlorin is all removed, and dried to constant weight. The lime, magnesia, silica,

and other constituents of the filtrate, are determined by the usual processes of mineral analysis.⁷³

(2) *State of Combination of the Lime.*—In a lime containing only small quantities of magnesia the lime carbonate may be determined by estimating the carbon dioxide by any one of the reliable processes in use.⁷⁴ In every case sufficient acid must be employed to combine with all the bases present. Tartaric or hydrochloric acid may be used. From the volume or weight of the carbon dioxide obtained the quantity of calcium carbonate may be calculated. Since magnesium carbonate is more easily decomposed by heat than the corresponding calcium compound, any residual carbonate in a well-burned sample is probably lime. The total percentage of lime in the sample is to be determined in the usual way by precipitation as oxalate and weighing as carbonate or oxid. The lime existing as oxid can be determined by exposing a weighed sample in an atmosphere of aqueous vapor until all the lime is slaked. After drying at 100° the increase in weight is determined and the calcium oxid calculated from the formula, $\text{CaO} + \text{H}_2\text{O} = \text{CaO}_2\text{H}_2$.

If now the total lime be represented by a ; the lime combined as carbonate by b ; and that present as oxid by c ; the quantity x existing as hydrate may be calculated by difference from the equation

$$x = a - (b + c).$$

The total lime as oxid and hydroxid may also be separated from that present as carbonate by solution in sugar.⁷⁵ One gram of calcium oxid is completely soluble in 150 cubic centimeters of a 10 per cent. sucrose solution. Magnesia, iron and alumina do not interfere with the determinations.

505. Gypsum or Land Plaster.—This substance is highly prized as a top dressing for grass and for admixture with stall manure for the purpose of fixing ammonia. Its value in both cases de-

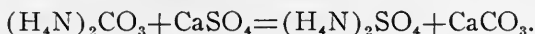
⁷³ Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 402, 405, 434, 512.

⁷⁴ Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 380, 436.

⁷⁵ Stone and Scheuch, Journal of the American Chemical Society, 1894, 16 : 721.

depends upon its percentage of hydrated calcium sulfate. The quantity of gypsum of all kinds mined in the United States in 1906 was 1,540,585 short tons. Of this amount only 62,671 short tons were sold as land plaster.⁷⁶ In the same time there were imported into the United States 440,586 short tons. If the same proportionate part of this were used for fertilizing purposes, it may be said that the annual consumption of land plaster in the United States at the present time for agricultural uses is 80,294 short tons.

Gypsum, being a very soft mineral, is easily ground and should be in the state of a fine powder when used for fertilizing purposes. It is soluble in about 500 parts of rain water, so that when applied as a top dressing it is carried into the soil by rain. Its favorable action is both as a plant food and mechanically in modifying, in an advantageous way, the physical constituents of the soil. It is also valuable for composting and for use in stables by reason of its power of fixing ammonia by the formation of lime carbonate and ammonium sulfate:



506. Analysis of Gypsum.—For agricultural purposes it will be sufficient to determine the quantity of sulfuric acid, and to calculate therefrom the amount of calcium sulfate in the sample: Or the lime may be determined and the quantity of sulfate calculated therefrom.

(1) *Insoluble Matter.*—In the conduct of the work the sample of gypsum is rubbed to an impalpable powder in an agate mortar. The sample, about one gram, is dissolved in a large excess of dilute hydrochloric acid, the digestion being continued at near the boiling-point, with frequent stirring, for at least two hours. The solution is made alkaline, filtered, and the residue washed and dried to constant weight.

(2) *Sulfuric Acid.*—The washings and filtrate from the above determination are made up to a definite volume with water and divided into two equal parts. The sulfuric acid is estimated in one part by adding to it sodium carbonate until the acidity is nearly neutralized. The sulfuric acid is then thrown down at near boiling temperature by the gradual addition of barium

⁷⁶ Burchard, *Mineral Resources of the United States, 1906* : 1073.

chlorid solution. The barium sulfate formed is separated, washed, dried, and weighed in the usual manner.

(3) *Iron and Alumina*.—To the other half of the solution a little nitric acid is added and boiled to convert any ferrous into ferric iron. On the addition of ammonia the iron and alumina are separated as hydroxids, collected on a gooch, washed, dried, ignited, and weighed as oxids.

(4) *Lime*.—In the filtrate the lime is thrown out as oxalate, and separated and weighed in the usual way as oxid. One part of CaO is equal to 2.4286 parts of CaSO₄.

(5) *Moisture*.—Two grams of the sample are dried to constant weight at 80°.

(6) *Water of Crystallization*.—The residue from the above drying is heated to 150°, until a constant weight is obtained. The loss represents water of crystallization.

(7) *Carbonates*.—The carbon dioxide is evolved by the usual process, and calculated to calcium carbonate.

507. Solution in Sodium Carbonate.—Gypsum is also easily decomposed by boiling with a solution of about 10 times its weight of sodium carbonate. The calcium, by this operation, is converted into carbonate and can be collected on a gooch, washed, and estimated as usual, but in this case it will contain all the insoluble matters, from which the lime can be separated by solution in hydrochloric acid.

In the filtrate from the above separation the excess of sodium carbonate is removed by the addition of hydrochloric to slight acidity, and the sulfuric acid estimated as described in the preceding paragraph.

Pure gypsum has a composition represented by the following formula: CaSO₄.2H₂O.

It contains:

	Per cent.
Sulfur trioxid	46.51
Lime	32.56
Water	20.93

A commercial sample of ordinary gypsum should have about the following composition:⁷⁷

⁷⁷ Frankland, *Agricultural Chemical Analysis*, 1883 : 240.

	Per cent.
CaSO ₄ ·2H ₂ O	88.15
CaCO ₃	3.50
Fe ₂ O ₃ and Al ₂ O ₃	1.50
Insoluble	2.80
Organic matter	0.50
Water and undetermined	3.55

Fine ground gypsum in the arid regions of the United States, especially when transported during the hot months, loses one molecule of its crystal water, and this often leads to disagreements respecting weight.⁷⁸

Hilgard also calls attention to the fact that soils naturally impregnated with gypsum are not productive. It is, however, very useful as a dressing to soils containing "black alkali" (carbonate of soda), converting the carbonate of soda into sulfate, a far less injurious ingredient. After solution in water it penetrates the soil and effects changes in its zeolitic constituents, setting potash free and thus increasing the stores of plant food.⁷⁹

508. Common Salt.—Common salt is highly esteemed in many quarters as a top dressing for lawns and meadows, and also for cultivated crops. Its action is chiefly of a mechanical and catalytic nature, since it does not form a notable percentage of the mineral food of plants. On account of its affinity for moisture it is also said to have some value as a condenser and carrier of water in times of drouth. On account of its great cheapness, selling often for less than \$10 a ton, its use in moderate quantity entails no great expense. Its ability, however, to pay for its own use in the increased harvest is of a doubtful character when it is applied at a cost of more than a few dollars per acre. In the chemical examination of a sample of common salt which is to be used as a fertilizer, a complete analysis is rarely necessary. When desired it can be conducted according to the usual methods of mineral analysis. For practical purposes the moisture, insoluble matter, magnesia and chlorin should be determined and the quantity of sodium chlorid calculated from the latter number. Traces of iodine or bromine which may be present are of no consequence.

⁷⁸ Hilgard, Letter to Author, 1907.

⁷⁹ Soils, 1906 : 43.

The moisture is determined by drying two grams of the well-mixed and finely powdered sample to constant weight at 100°. The chlorine is obtained by precipitation of an aliquot part of a solution of the salt by set silver nitrate, using potassium chromate as indicator.

In the determination of insoluble matter it should not be forgotten that a little gypsum may be present, and this should be dissolved by rubbing to a finer powder and by repeated digestion in water. The magnesia and lime are separated and determined in the usual manner. If the quantity of gypsum present be sufficient to warrant it, the sulfuric acid may be separated and weighed in the manner already described. Common salt, when present in the soil in proportions greater than 0.1 per cent., is injurious to vegetation. The presence of salt in any greater quantities in a soil renders it barren. In Texas the irrigation of rice fields with slightly brackish water has had the effect of rendering the fields unfit for rice growing. Salt is often used to kill weeds, and it is extremely doubtful if its use as a fertilizer is ever really indicated.

509. Green Vitriol.—When iron is used as a fertilizer it is sometimes applied as ferrous sulfate. The value of iron in a soil is incontestable, and by reason of the fact that fertile soils are always well aerated, the iron present in the arable layer is found in the ferric state. When green vitriol is applied to the soil it undergoes gradual oxidation and appears finally in a more highly oxidized form as ferric hydrate. Iron acts directly on the plant in promoting the development of the chlorophyll cells, and is also found in almost all parts of the vegetable organism. A too great quantity of ferrous sulfate is destructive of plant growth, in which respect it resembles common salt. It should, therefore, be applied with due regard to the dangers which might arise from an excessive quantity. It is not likely, however, that when applied in a finely powdered state at the rate of from one to two hundred pounds per acre it would ever prove poisonous to vegetation.

In the analysis of a sample of green vitriol it will be sufficient to determine the moisture, water of crystallization, iron, and

sulfuric acid. The moisture may be ascertained by drying the finely powdered sample over sulfuric acid for a few hours. The water of crystallization is separated by exposing the sample to a temperature of 285° for two hours. The iron may be determined by oxidizing to the ferrous state by boiling with nitric acid and then precipitating with ammonia, and proceeding as directed for iron analysis. The sulfuric acid is separated as barium sulfate and determined as already directed.

510. Pyrites.—The existence of iron pyrites in a soil in any notable quantity is injurious. The pyrites, which is sulfid of iron, FeS_2 , is converted into copperas, (ferrous sulfate or green vitriol) in which state before passing to a state of higher oxidation, it is quite injurious. Iron pyrites is easily recognized by its crystalline form and golden luster. It has often been mistaken for gold, and to this fact is due its common name, "fool's gold." It often occurs in globular masses in marls, and in this state is known as "sulfur balls." When heated, pyrites takes fire and burns with a pale blue flame (sulfur flame), and the iron is converted into ferric hydrate.

511. Stall Manures.—There are no definite methods to be described for the analysis of that large class of valuable fertilizer produced in the stable and pen, and which collectively may be called stall manures. The methods of sampling have already been described, but only patience and tact will enable the collector to get a fair representation of the whole mass.⁸⁰ These manures are a mixture of urine, excrement, waste fragments of fodder, and the bedding used for the animals. With them may also be included the night soil and waste from human habitations and the garbage from cities. All of these bodies contain valuable plant foods, and the phosphoric acid, potash, and nitrogen therein are to be determined by the methods already given for these bodies when they occur in, or are mixed with, organic matter. In general, stall manures are found to have a higher manurial value than is indicated by the amount of phosphorus, potash, and nitrogen which they contain. Through them there

⁸⁰ Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1908, 2 : 16.

is introduced into the soil large quantities of humus bodies whereby the physical state of the soil is profoundly modified and its adaptability to the growth of crops, as a rule, increased. The addition of active nitrifying ferments to stall manures is also advantageous, since they often contain active denitrifying organisms derived from straw and similar sources whose activity is checked by the proper treatment to secure progressive nitrification. Stall manures, however, may in many cases prove to be injurious to a crop, as for instance, when they are applied in a poorly decomposed state and in a season deficient in moisture.

It is essential, therefore, that the bedding of animals be in a finely divided state, whereby not only are the absorptive powers of the organic matter increased, but also the conditions for their speedy decay favored. To avoid the loss of ammonia arising from decomposing urine, it is advisable to compost the stall manure with gypsum or to sprinkle it from time to time with oil of vitriol.

In the analysis the moisture may be estimated by drying to constant weight at 100° or at a lower temperature in a vacuum. The potash and phosphoric acid are determined as usual, with previous careful incineration, and the nitrogen secured by the moist combustion process.

The organic matter of farmyard manure in many cases exerts a very beneficial effect on the texture of the soil, and in addition serves as a source of humus, which still further improves fertility. For these reasons the actual returns from the application of such manures are often much greater than would be expected from the total quantity of plant food which they contain.

There is no other virtue in stall manure than is found in its content of plant food and its effects on soil texture.

512. Hen Manure.—This fertilizing substance is a mixture of the excrement of the fowl yard with feathers, dust, and other débris. Measured by the standard applied to commercial fertilizers, hen manure has a low value. As in the case of other farm manures, however, it produces effects quite out of proportion to the amount of ordinary plant foods which it contains.

In a sample examined at the Connecticut station the percentages of its chief constituents were found to be the following:⁸¹

Water	51.84
Organic and volatile matters	24.27
Ash.....	23.89

The organic matter contained 0.61 per cent. of nitrogen as ammonia and the ash 0.97 per cent. of phosphoric acid, and 0.59 per cent. of potash, all calculated to the original weight of the sample. The percentage of water in this sample is undoubtedly higher than the average, so that it can hardly be taken to represent the true composition of this manure. The potash, phosphoric acid, and nitrogen are to be determined by some one of the standard methods already described, the two former after careful incineration.

513. Guanos and Cave Deposits.—The principal constituents of value in these deposits are nitrogen and phosphoric acid. The other organic matters are also of some value, but have no commercial rating. The nitrogen may be present in all its forms; viz., organic, ammoniacal, amid, and nitric, and for this reason is well suited not only to supply nourishment to the plant in the earlier stages of its growth, but also to cater to its later wants. In guano deposits in caves, due usually to the presence of bats, similar forms of fertilizers are found and the soluble constituents due to decay and nitrification are protected from the leaching to which they would be subjected in the open air.

In some localities in the United States a few open deposits are found, but the humidity of our climate, except in the arid regions of the West, has prevented the immense open deposits of guano that characterize some of the arid islands of the Pacific Ocean.

Many bat guanos examined in the laboratory of the Bureau of Chemistry have been found to contain potash, in one case 1.78 per cent. It is suggested, therefore, that the analyst do not omit to examine each sample qualitatively for this substance and to determine its amount when indications point to its presence in weighable proportions. In the many samples of bat guano of American origin which have been analyzed in the last

⁸¹ Connecticut Agricultural Experiment Station, Annual Report, 1888, : : 80.

few years, some very rich in plant food have been found. In one instance the total percentage of nitrogen present was 10.11 per cent. In some cases the phosphoric acid is high, but rarely in conjunction with a high content of nitrogen. In one instance where the total phosphoric acid reached 14.53 per cent., the content of nitrogen was 4.87 per cent.

In respect of the process of analysis there are no especial directions to be given. The phosphoric acid may be determined as given below, and the potash by the usual methods. The total phosphoric acid and potash are determined only after the destruction of the organic matter.

In old cave deposits the processes of decay and nitrification seem to have long been completed and very little power of inducing nitrification in culture solutions seeded from these samples has been found.

514. French Official Method for Total Phosphoric Acid in Guanos.—To determine the phosphoric acid in guanos, the method officially adopted by the French agricultural chemists may be used.⁸²

Two grams of the sample are rubbed up in a porcelain crucible with a decigram of slaked lime to prevent the possible reduction of the phosphoric acid by the organic matter. The mixture is slightly moistened with a few drops of water, dried on a sand-bath, and afterwards heated to redness, best in a muffle, until organic matter is destroyed. The contents of the crucible are detached and placed in a flask of 200 cubic centimeters capacity. The crucible is well digested twice with some hydrochloric acid to dissolve any adhering fragments, and finally washed with hot water, the acid and water being added to the flask. The contents of the flask are boiled for 15 minutes and then poured into a flat-bottom dish, the flask well rinsed three or four times with small quantities of water, and the liquor and washings evaporated to dryness to render the silica insoluble. The residue is taken up by a mixture of 10 cubic centimeters each of hydrochloric acid and water, heated for a few minutes and filtered, and the dish well washed with successive small portions of water,

⁸² Sidersky, *Analyse des Engrais*, 1901 : 61.

but the total volume of the filtrate and washings should not exceed 80 cubic centimeters. In this filtrate the phosphoric acid may be determined by any one of the approved methods.

515. Waste Leather.—This material belongs probably to that class of nitrogenous substances which has a small immediate value for plant nutrition. The chief manurial value of the waste is found in its nitrogenous content. The value of this for available plant food has been investigated by Lindsey.⁸³ A complete resumé of the literature of the subject is also given by him.

A good way of identifying leather waste is by the process proposed by Dabney.⁸⁴ It depends on the color produced in a solution of iron phosphate by the tannin compounds derived from the leather. The reagent is prepared by dissolving a freshly made precipitate of iron phosphate from 10 grams of ferric chlorid in 400 cubic centimeters of an aqueous solution of 40 grams of glacial phosphoric acid. A gentle heat promotes the solution of the phosphate.

In the case of a fertilizer supposed to contain leather, about one gram of the material is treated with 30 cubic centimeters of water and a few drops of sulfuric acid. The mixture is boiled and poured on a filter. To a portion of the filtrate some of the solution of iron phosphate is added, and the mixture made alkaline with ammonia. If leather be present in the sample, a purple or wine color will be developed. Lindsey could easily detect the leather when it was added in 10 per cent. quantities by the above method, and he regards this method as superior to the microscope, which is unreliable in the case of finely ground material.

While leather, as such, decays slowly, and, therefore, is not at once available for the nourishment of plants, it acquires greater utility after digestion in sulfuric acid. Artificial digestion experiments with leather previously treated with sulfuric acid show that, approximately, 70 per cent. of the nitrogen pass into solution. Such a prepared leather has, therefore, an available co-

⁸³ Agricultural Science, 1894, 8 : 49, 98.

Massachusetts Agricultural Experiment Station, Twelfth Annual Report : 285.

⁸⁴ North Carolina Agricultural Experiment Station, Bulletin 3.

efficient in respect of nitrogen not much inferior to most organic bodies.

In comparative trials with sodium nitrate it was demonstrated that nitrogen in leather, previously dissolved in sulfuric acid, has a rank of about 60 when it is rated at 100 in the soda salt.

For the estimation of the nitrogen in leather the moist combustion process is to be preferred.

516. Hair and Horn.—Waste hair and horn also have a high nitrogen content, and in certain circumstances this may become valuable for manurial purposes. To this end, however, a treatment similar to that prescribed for leather is imperative. In the natural state, hair and horn decay so slowly as to be of little consequence for plant food within any reasonable time in so far as practical agriculture is concerned. The preliminary digestion of these substances with sulfuric acid brings a large proportion of their nitrogen within reach of the growing crop.

517. Analysis of Wood Ashes.—The only kinds of ashes used extensively for manurial purposes are those derived from the burning of hard woods. The ash of soft woods, such as the pine, is too poor in plant foods to warrant its transportation to any great distance for manurial purposes. The methods of incineration of organic bodies for the purpose of obtaining and estimating their mineral contents will be fully discussed in the third volume of this work.

It is important in ash analysis to know whether there be enough of iron present to combine with all the phosphoric acid. For manurial purposes it will be found sufficient to determine the percentages of potash and phosphoric acid alone. For hygienic purposes it is advisable to examine the ash qualitatively and, if necessary, quantitatively for zinc, lead, copper, boric acid, and other bodies of a similar character which may be naturally present in the ash, or may have been added to the organic substance from which it was prepared for preservation or other purposes. The methods of making these special investigations will be discussed in the succeeding volume. At present will be given, however, not only the methods for detecting phosphoric

acid and potash, but also for a complete analysis of an ash in so far as its usual constituents are concerned.

518. Carbon, Sand, and Silica.—The earlier official agricultural methods prescribe the following procedure for the determination of the unburned carbon, and the sand and silica:⁸⁵

Five grams of the ash are treated in a beaker, covered with a watch-glass with 50 cubic centimeters of hydrochloric acid of 1.115 specific gravity, and digested on the water bath until all effervescence has ceased. The cover is removed and the liquid evaporated to complete dryness to render the silica insoluble. The residue is moistened with two or three cubic centimeters of hydrochloric acid and taken up with about 50 cubic centimeters of water, allowed to stand on the water bath a few minutes, filtered, and thoroughly washed. The filtrate and washings are made up to a quarter of a liter for analysis. The residue is washed from the filter into a platinum dish and boiled about five minutes with 20 cubic centimeters of a saturated solution of pure sodium carbonate; afterwards a few drops of pure sodium hydroxid solution are added and the liquid allowed to settle, and it is then decanted through a tared gooch. The residue is boiled with sodium carbonate solution and decanted as before, a second and a third time, and finally brought upon the felt and thoroughly washed, first with hot water, then with a little dilute hydrochloric acid, and finally with hot water until free of chlorids. The residue in the gooch is dried at 110° to constant weight, giving the carbon and sand. It is then incinerated and the weight of the sand determined, the difference giving the carbon. It is advisable to examine the sand with a microscope to determine if it be pure. The alkaline filtrate and washings from the carbon and sand are acidified with hydrochloric, evaporated to dryness, and the silica separated and determined in the usual way.

Instead of determining soluble silica directly from the sodium carbonate solution, as above, another portion of the ash may be treated with hydrochloric acid and evaporated to dryness as before described, filtered on an ordinary filter, washed, burned,

⁸⁵ Division of Chemistry, Bulletin 43, 1894 : 390.

and weighed, giving the weight of silica plus sand, from which the weight of sand is deducted to obtain soluble silica. It is inadmissible to separate the soluble silica from the residue after it has been ignited.

Instead of limiting the quantity of hydrochloric acid used for moistening the dried residue, as suggested above by the official chemists, enough should be employed to fully saturate the mass. The weight of pure ash is obtained by subtracting from the weight of the sample used the sum of the weights of carbon, sand, and carbon dioxide.

519. Ferric Phosphate and the Alkaline Earths.—The ferric phosphate, lime, magnesia, and manganese are determined in an aliquot part of the first hydrochloric acid solution and washings obtained above. Fifty or 100 cubic centimeters may be used, corresponding to one or two grams of the original ash. The accurately measured quantity of the solution is carefully treated with ammonia until the precipitate formed on its addition becomes permanent on shaking. Ammonium acetate and acetic acid are then added until the mixture has assumed a strongly acid reaction. The separation of the ferric phosphate precipitate is promoted by gentle warming, and it is separated by filtration without unnecessary delay. If the precipitate be not large the sample contains no manganese and alumina in weighable quantities, and if the filtrate be not red, the precipitate is washed with hot water containing a little ammonium nitrate. It is then ignited and weighed as $\text{Fe}_2\text{P}_2\text{O}_8$ and the quantity of ferric oxide computed therefrom. If, however, the precipitate be large, it is well washed as above and then dissolved in as small a quantity as possible of hydrochloric acid, and the solution is again precipitated as above by the addition of ammonia, ammonium acetate, and acetic acid. The ferric phosphate obtained by the second precipitation is treated exactly as above described.

In case, however, any weighable quantities of manganese or alumina are present it will not do to weigh the precipitate of ferric phosphate directly even after a second precipitation. Also if the filtrate at first obtained have a red color, the precipitate

may contain basic ferric phosphate. In this latter case it should be ignited and weighed, then dissolved in hydrochloric acid and the ferric oxid estimated in the solution and from the difference the quantity of combined phosphoric acid calculated.

The separation of the iron from the phosphoric acid may be accomplished by adding tartaric acid to the hydrochloric acid solution of the iron phosphate above obtained and then ammonium chlorid and ammonia. The mixture is placed in a flask and ammonium sulfid added. The flask is closed, placed in a warm place and allowed to stand until the supernatant liquid is clear and of a pure yellow color without a trace of green. The iron is separated by filtration, washed, dissolved, and estimated in the usual way.

If manganese and alumina be present the iron and manganese are separated from the phosphoric acid and alumina by the processes just given for the separation of iron from phosphoric acid. In the filtrate the alumina and phosphoric acid are separated as follows: The filtrate is evaporated in a platinum dish after the addition of an excess of pure sodium carbonate until no ammonia is set free by a further addition of the carbonate. Some nitric acid is then added and the evaporation continued to dryness. The residue is fused and after cooling softened with water, washed into a small beaker, some hydrochloric acid added, warmed, and filtered. Ammonia is added until the reaction is alkaline. If no precipitate be produced no alumina is present. In this case more nitric acid is added, the solution again evaporated and the phosphoric acid determined by the usual methods.

In case a precipitate is formed, showing the presence of alumina, nitric acid is added until the precipitate is dissolved, and then in slight excess and after evaporation the phosphoric acid separated by molybdic solution and determined as usual. From the filtrate the excess of molybdic acid is removed by hydrogen sulfid and the alumina determined in the filtrate: Or the alumina may be determined directly in the hydrochloric acid solution of the melt above obtained as aluminum phosphate by adding sodium phosphate, ammonia and acetic acid. The aluminum phosphate is separated by filtration and determined in the usual man-

ner. The phosphoric acid is then determined in another aliquot part of the original filtrate from the first solution of the ash.

Since most ashes contain an excess of phosphoric acid above the quantity required to combine with the iron it is preferable to proceed as described in the next paragraph.

520. Modified Method.—The principle of the method rests on the assumption that all the phosphoric acid may be removed from the solution by the careful addition of iron chlorid. Any excess of iron is then removed by ammonium acetate and the manganese, lime, and magnesia are separated in the filtrate. The percentage of iron is determined by reduction of the iron in another portion of the solution and titration with potassium permanganate. The process as conducted by McElroy is as follows:⁸⁰

Moisture.—If the ash contain much carbon the water is best determined by drying in vacuo to avoid oxidation.

Sand, Silica, and Carbon.—Place a portion of the ash in a weighed platinum dish, weigh, and cover the sample with hydrochloric acid of 1.115 specific gravity. Evaporate to dryness on the water bath, and then heat for 15 minutes at 105° to 110° in an air bath. Repeat the treatment with acid and drying: Finally cover with a third portion of acid and digest on the water bath for an hour or two. Filter into a weighed gooch and wash the residue free of chlorids. The gooch is best weighed with the dish to avoid the necessity of transferring the silica which may adhere to the sides of the former. Dry at a few degrees above the boiling temperature of water and weigh. Where the ash contains much charcoal the drying is best done in a vacuum at from 60° to 70°. The increase in weight found represents sand, silica, and carbon: Burn and reweigh. The loss is carbon.

Another portion of ash is treated as before except that it is filtered through a paper filter. The filtrate is united with that of the previous sample in a graduated flask. When the washing is completed the filter is placed in the dish, a weak solution of caustic soda added, and the mixture heated on the water bath for some time. Decant while hot through a fresh filter and re-

⁸⁰ Manuscript, Unpublished.

treat the residue in the dish with another portion of alkali. Finally wash with hot water till the alkaline reaction disappears, then with weak hydrochloric acid, then with water until chlorids disappear. The washed mass on the filter is transferred to a platinum dish and ignited. The weight obtained represents sand.

Separation of Phosphoric Acid.—The united filtrates from the two determinations are placed in a graduated flask and made up to the mark. An aliquot portion of this solution representing half a gram of the original ash or any other convenient quantity is transferred to a beaker and a solution of ferric chlorid added until ammonia produces a brown precipitate in the mixture. Neutralize with ammonia and hydrochloric acid alternately until the liquid is as little acid as it can be and still remain clear. Add from 10 to 20 cubic centimeters of a solution of sodium acetate (1:10) and bring to a boil. The liquid should be quite dilute. Filter and wash free of chlorids with boiling water containing some sodium acetate.

Manganese.—Make the filtrate faintly alkaline with ammonia and add ammonium sulfid. Any manganese sulfid which may form is separated by filtration, treated with dilute acetic acid and the resulting solution, which should be clear, heated to boiling, nearly neutralized with caustic soda, and mixed with bromin water. The resultant manganese dioxid is to be filtered into a gooch, ignited and weighed as Mn_3O_4 .

Lime.—Reacidify the filtrate from the manganese sulfid with acetic acid, heat to boiling and add ammonium oxalate: Allow to stand over night, filter through a gooch and wash with water containing acetic acid. The calcium oxalate can be weighed as such, but it is preferable to dry thoroughly and then heat in a small bunsen flame until a change can be noted passing over the precipitate. If this is carefully done the residue will be calcium carbonate. In any case, the result is to be checked by igniting over the blast-lamp to constant weight and weighing the lime thus obtained.

Magnesia.—In the filtrate the magnesia can be determined by sodium phosphate in the usual manner. In very accurate work the calcium oxalate obtained as directed above can be dissolved

and reprecipitated, and the magnesia in the filtrate added to that in the first filtrate.

Iron.—For iron another aliquot portion of the original solution is used, acidified with sulfuric, evaporated to drive off hydrochloric acid, rediluted and passed through the jones reductor. The filtrate is titrated with potassium permanganate solution in the usual manner.

Alkalies.—For the alkalies another aliquot portion is precipitated while hot with barium chlorid and barium hydrate, filtered, and ammonia and ammonium carbonate added to remove the excess of barium salt. Refilter, evaporate to dryness in a platinum dish, and ignite gently to expel all ammonia salts; repeat this operation after taking up with water and finally heat to constant weight. The weight obtained represents a mixture of potassium and sodium chlorids, with usually carbon derived from impurities in the ammonia. A little magnesia is often present. The potassium is estimated by means of platinum solution, and the potassium chlorid found deducted from the total weight gives the sodium chlorid. The carbon is usually unweighable, though it often looks as if present in considerable quantity. It may be estimated, however, by dissolving the mixed chlorids in weak hydrochloric acid and filtering through a gooch before making the potassium estimation. The estimation of the magnesia remaining with the mixed chlorids may be effected by evaporating the alcoholic solution remaining after the precipitation of the potassium to dryness, redissolving in water, placing the solution in a flask provided with gas tubulures, introducing hydrogen, and placing in the sunlight. The platinum is soon reduced, leaving the liquid colorless. Heating facilitates the reaction. Displace the hydrogen by a current of carbon dioxid, filter, concentrate the solution and precipitate the magnesia by sodium phosphate in the usual manner.

Phosphoric Acid.—It is best to determine the phosphoric acid directly in an aliquot part of the first filtrate from the hydrochloric acid solution of the ash obtained as described under the determinations of sand, silica and carbon. When there is not enough of the material for this, the precipitate of ferric phosphate

may be dissolved and the phosphoric acid determined after separation with ammonium molybdate.

Sulfuric Acid.—Fifty cubic centimeters of the original hydrochloric acid filtrate, obtained as described under the determinations of sand, silica and carbon, are heated to boiling, and the sulfuric acid thrown out by the gradual addition of barium chlorid. During the precipitation the mixture is kept at the boiling temperature, but taken from the lamp and the precipitate allowed to settle from time to time until it is seen that an additional drop of the reagent causes no further precipitate. The barium sulfate is collected, dried, and weighed in the usual manner.

Chlorin.—Dissolve from one to five grams of the ash in nitric acid in very slight excess, or in water. If the solution be made in nitric acid the excess must be neutralized if the chlorin be determined volumetrically; and if the solution be in water, nitric acid must be added if the determination be gravimetric.

The volumetric determination is accomplished in the usual manner with a standard silver nitrate solution, using potassium chromate as indicator. The gravimetric determination is effected by precipitation with silver nitrate, collecting, washing, and drying at 150° the silver chlorid obtained.

Carbon Dioxid.—The carbon dioxid is most conveniently estimated in from one to five grams of the ash, according to its richness in carbonates, by the apparatus described in Volume I or some similar device.⁸⁷

521. Early Official Method for Determinations of the Alkalies.—Evaporate the filtrate and washings from the sulfuric acid determination, paragraph 519 in a porcelain dish to dryness, re-dissolve in about 50 cubic centimeters of water and add milk of lime, or barium hydroxid solution, which must be perfectly free from alkalies, until no further precipitation is produced, and it is evident there is an excess of calcium hydroxid or barium hydroxid present; boil for two or three minutes, filter hot, and wash thoroughly with boiling water, precipitate the lime and baryta from

⁸⁷ Wiley, Principles and Practice of Agricultural Analysis, 2nd Edition, 1906, 1 : 380.

the filtrate with ammonia and ammonium carbonate, filter, evaporate the filtrate to dryness in a porcelain dish, and drive off the ammonia salts by heat below redness.⁸⁸ When cold, re-dissolve in 15 or 20 cubic centimeters of water, precipitate again with a few drops of ammonia and ammonium carbonate solution, let stand a few minutes on the water bath and filter into a tared platinum dish and evaporate to dryness, expel the ammonia salts by heating to just perceptible dull redness, weigh the potassium and sodium chlorids obtained and determine the potassium chlorid with platinic chlorid as usual.

The potassium may also be determined by the perchlorate method, or the total chlorin be determined volumetrically, and the relative percentages of potassium and sodium chlorids calculated by the usual formula: Or multiply the weight of chlorin in the mixture by 2.1035, deduct from the product the total weight of the chlorids and multiply the remainder by 3.6358. The product expresses the weight of the sodium chlorid contained in the mixed salts. The indirect method is only applicable when there are considerable quantities of alkalis present and where they exist in approximately molecular proportions. It is, therefore, a process rarely to be recommended in ash analysis.

522. Latest Official Methods for the Determination of Inorganic Plant Constituents.⁸⁹—1. *Preparation of Sample.*—The material must be thoroughly cleaned from all foreign matter, especially from adhering soil. It is to be ground and preserved in carefully stoppered bottles.

2. *Determination of Carbon-Free Ash.* (a) *Preparation of calcium acetate.*—Dissolve 20 grams of pure calcium carbonate in pure acetic acid, and dilute to one liter. Evaporate 20 cubic centimeters of the solution in a platinum dish, ignite gently, then strongly, to constant weight. The dish must be weighed quickly. This gives the calcium oxid in 20 cubic centimeters.

(a') *Alternative Method.*—Dissolve marble in hydrochloric acid, evaporate, and dry to render silica insoluble, dissolve with water and a little acid, and precipitate iron and aluminum in the

⁸⁸ Division of Chemistry, Bulletin 43, 1894 : 391.

⁸⁹ Bureau of Chemistry, Bulletin 107, 1907 : 21.

usual way: The calcium is then precipitated with ammonia and ammonium oxalate in hot solution, the precipitate washed well, dried, ignited and weighed. It is then dissolved and diluted so that 100 cubic centimeters contain 1.1 grams calcium oxid.

It is best to test the purity of this reagent by making blank determinations with it.

(b) *Preparation of Ash.*—Moisten from 10 to 20 grams of the substance with 40 cubic centimeters of calcium acetate solution, dry on a water bath, and ignite, gently at first, then more vigorously. The quantity of calcium acetate used should be sufficient to prevent fusion of the ash. Some form of apparatus must be used to prevent volatilization, either Shuttleworth's or Tucker's, or an ordinary platinum dish may be used, fitted with a cover, like that described by Wislicenus. The weight of the ash must be corrected for lime, carbon dioxide and carbon.

(c) *Determination of Carbon Dioxide.*—Using the ash prepared in (b), liberate the carbon dioxide with hydrochloric acid in any of the usual forms of apparatus, determining the carbon dioxide evolved either by increase of weight of potash bulbs or loss of weight of the apparatus. The former method is preferred.

(d) *Determination of Carbon, Sand and Silica.*—The residue from the carbon dioxide determination is transferred to a beaker or evaporating dish, evaporated to dryness and thoroughly dried and pulverized to render silica insoluble. The dry residue is moistened with from five to 10 cubic centimeters of hydrochloric acid, taken up with about 50 cubic centimeters of water, allowed to stand on the water bath for a few minutes, filtered through a parchment-paper filter (S. and S. "hardened" filters), and thoroughly washed. The solution and washings are to be made up to 250 cubic centimeters or other convenient volume and preserved for analysis. This is solution A.

The residue is washed from the filter (which may be used again) into a platinum dish and boiled about five minutes with 20 cubic centimeters of a saturated solution of pure sodium carbonate, a few drops of pure sodium hydroxide solution are added, the solids are allowed to settle, and the liquor decanted through a tared gooch. The residue in the dish is boiled

with sodium carbonate solution and decanted as before, and the process repeated a third time, after which the residue is brought upon the filter and thoroughly washed, first with hot water, then with a little dilute hydrochloric acid, and finally with hot water until free from chlorids. The gooch and contents are dried to constant weight at 110° , and the combined weight of carbon and sand determined. After incineration the loss in weight gives the carbon. It is advisable to examine the residue under the microscope to ascertain if it is really sand. The alkaline filtrates and washings are to be united, acidified with hydrochloric acid, evaporated to dryness, and the silica separated and determined in the usual way.

Alternate Method.—Instead of determining directly the silica dissolved by the sodium carbonate solution, as described above, another portion of the ash may be treated as in 2(c) and (d), and the residue of silica, sand, and carbon filtered on an ordinary filter, washed, burned, and weighed, giving the combined weight of silica and sand, from which the weight of sand found in 2(d) is to be deducted to obtain the silica. It is inadmissible to separate the soluble silica from the residue after ignition.

Subtract carbon, carbon dioxide, and calcium oxid added in the form of calcium acetate from the ash, and calculate results as carbon-free ash.

3. *Determination of Manganese, Calcium, and Magnesium.*—To an aliquot of solution A, corresponding to from 0.5 to two grams of ash, add a quantity of pure ferric chlorid solution, more than equivalent to the phosphoric acid which may be present, neutralize with ammonia, dissolve the precipitate in a very slight excess of hydrochloric acid, add one or two grams of sodium acetate and boil one or two minutes, filter at once and wash with boiling water. If necessary, dissolve the precipitate in hydrochloric acid and reprecipitate as above. Evaporate the filtrate and washings to about 50 cubic centimeters and determine manganese, calcium, and magnesium as in the analysis of soils.⁹⁰ The quantity of calcium found must be corrected for the calcium added.

⁹⁰ Bureau of Chemistry, Bulletin 107, 1904 : 15, (c), (d), (e).

4. *Determination of Phosphoric Acid.*—(a) In an aliquot portion of the hydrochloric acid solution, corresponding to 0.2 to one gram of ash, determine the phosphoric acid by any of the methods described for total phosphoric acid in fertilizers.

(b) The determination can also be made directly in the plant substances after incineration as prescribed in the methods for phosphoric acid, in fertilizers using sufficient material to give from 0.2 to one gram ash in the aliquot portion of the solution used for the phosphoric acid determination.

5. *Determination of Sulfuric Acid.*—Heat an aliquot of solution A, corresponding to from 0.5 to one gram of ash, to boiling and add barium chlorid solution in small quantities until no further precipitation is produced, and proceed in the usual manner to determine the barium sulfate.

6. *Determination of Chlorin.*—Determine the chlorin as silver chlorid, either gravimetrically or by one of the standard volumetric processes, in a nitric acid or aqueous solution of the ash. Nitric acid may be used as the solvent in 2 (c) and the solution employed for this purpose.

7. *Potassium in Plants.*—Potash may be determined as directed under fertilizers for potash in organic compounds, using sufficient plant material to get from 0.5 to one gram ash in the aliquot portion of the solution used for the potash determination.

8. *Sulfur in Plants.—Peroxid Method.—Provisional.*—Place from 1.5 to 2.5 grams of material in a nickel crucible of about 100 cubic centimeters capacity and moisten with approximately two cubic centimeters of water. Mix thoroughly, using a nickel or platinum rod. Add five grams of pure anhydrous sodium carbonate and mix. Add pure sodium peroxid, small amounts (approximately 0.50 gram) at a time, thoroughly mixing the charge, after each addition. Continue adding the peroxid until the mixture becomes nearly dry and quite granular, requiring usually about five grams of peroxid. Place the crucible over a low alcohol flame (or other flame free from sulfur) and carefully heat with occasional stirring until contents are fused. Should the material ignite, the determination is worthless. After fusion remove the crucible, allow to cool somewhat, and cover

the hardened mass with peroxid to a depth of about 0.5 centimeters. Heat gradually, and finally with full flame until complete fusion takes place, rotating the crucible from time to time in order to bring any particles adhering to the sides into contact with the oxidizing material. Allow to remain over the lamp for ten minutes after fusion is complete. Cool somewhat, place warm crucible and contents in a 600 cubic centimeter beaker and carefully add about 100 cubic centimeters of the water. After violent action has ceased, wash the material out of the crucible, make slightly acid with hydrochloric acid (adding small portions at a time), transfer to a 500 cubic centimeter flask, cool, and make to volume. Filter and use a 200 cubic centimeter aliquot for determination of sulfates by precipitating with barium chlorid in the usual manner.

9. *Chlorin in Plants (Provisional)*.—Saturate five grams of the sample in a platinum dish with 20 cubic centimeters of a five per cent. solution of sodium carbonate, evaporate to dryness, and ignite as thoroughly as possible. Extract the residue with hot water, filter and wash. Return it to the platinum dish, ignite to an ash, dissolve in nitric acid, and determine the chlorin by the usual method.

523. Stating Results of Fertilizer Analysis.—There is much difference of opinion respecting the manner in which the results of fertilizer analyses should be expressed. The matter may be looked at from two points of view, first, the strictly scientific expression for the use of scientific men alone, and, second, well known terms for the use of farmers. Inasmuch as the object of the inspection of fertilizers, that is, fertilizer control, is to acquaint the farmers with the character of the goods they purchase, it is evident that the method of expressing the results of analyses when exercised for the control and sale of fertilizers should be in terms easily understood by the farmer. In the United States it has been a very common method of expression to use the terms "potash," "phosphoric acid" and "ammonia" in designating the three important constituents of fertilizers. The farmers of this country, as a rule, are well acquainted with the meaning of these terms. By potash the potassium oxid

(K_2O), by phosphoric acid phosphoric anhydrid (P_2O_5), and by ammonia the total nitrogen expressed as ammonia, namely, H_3N , are meant. This latter constituent is also very frequently expressed "nitrogen as ammonia." In some parts of the country it is customary to calculate the phosphoric acid as tricalcium phosphate. In this form the name which is very commonly employed is "bone phosphate" or "bone phosphate of lime" whether it be made from bone directly or from phosphate rocks.

In some of the States the origin of the nitrogen is also required to be placed upon the label and also its character, namely, nitrogen as nitrates, nitrogen as organic matter, etc., or, if certain forms of organic matter be used, namely, leather or hair, this fact is also required to be stated. There is also a very strong movement in the United States to secure the expression of results of analyses of fertilizers in the elemental form, namely, nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), etc. There is also some influence brought to bear in the United States to report the results of the analysis of fertilizers in their ionic form.

The whole matter of the uniform notation of the results of the analyses of fertilizers in the United States is complicated by the large number of State laws requiring a certain form of expression. Even if the agricultural chemists of the country should agree upon a common form it would require legislation in many States to make it effective.

524. Objections to the Elemental System.—The objections to the elemental system of nomenclature may be summarized as follows as applying to the United States.⁹¹

1. The proposed elemental system is used only by one State; the common form, namely, K_2O potash, P_2O_5 phosphoric acid, and N nitrogen or H_3N ammonia, is used by nearly all the other States and by many foreign countries. The adoption of the elemental system will produce confusion among the States, and even if adopted by all the States would not be in harmony with the practice of other countries.

⁹¹ Fraps, Preliminary Report on the Unification of Terms, Bureau of Chemistry, Unnumbered Circular, 1905 : 4.

2. The common system of notation mentioned above is incorporated in the fertilizer laws of 27 of the States. Any change would require legislative action to ratify it in all of these States.

3. A change in the terms which are commonly used will cause confusion in the minds of a multitude of farmers, manufacturers and dealers who are acquainted with the terms now in use.

4. The apparent decrease of 20 per cent. in the amount of potash and 50 per cent. in the amount of phosphoric acid which would result from the adoption of the new system would require a great deal of explanation to make it clear to the farmers.

5. The use of the double system of notation for fertilizers in order to introduce the new system is undesirable and would result in confusion.

525. Advantages of the Elemental System.—Hopkins recommends reporting all analyses, as far as possible, on the uniform basis of chemical elements as follows:⁹²

For fertilizers :

Nitrogen (N).
Phosphorus (P).
Potassium (K).

For soils :

Nitrogen (N).
Phosphorus (P).
Potassium (K).
Calcium (Ca).
Magnesium (Mg).
Iron (Fe).

For soils :

Sulfur (S).
Inorganic carbon (C).
Organic carbon (C).
Aluminum (Al).
Manganese (Mn).
Sodium (Na).
Chlorin (Cl).
Silicon (Si).
Insoluble matter.
Hydrogen and oxygen.

The hydrogen and oxygen may be reported "by difference," or, if desired, they can be computed in the usual manner by calculating the oxygen necessary to form oxids with certain of the determined elements and adding to this the loss in ignition (after deducting the amount of volatile elements determined). Silicon (Si) can be reported if determined separately from the insoluble matter. Of course, in ultimate analyses, by the fusion

⁹² Bureau of Chemistry, Preliminary Report on the Unification of Terms, Unnumbered Circular, 1905 : 2.

method, the insoluble matter disappears. It will be seen that there is no difficulty whatever in reporting soil analyses by this method. This has already been demonstrated and illustrated by the Ohio experiment station.⁹³

In considering the different forms of nitrogen we can report nitrate nitrogen, ammonia nitrogen, and organic nitrogen; and, if necessary, we can also distinguish between organic and inorganic sulfur and between organic and inorganic phosphorus, as we do between organic and inorganic carbon. A complete analysis of potassium chlorid would be reported:

	Per cent.
Potassium	52
Chlorin	48
	<hr/>
Total	100

Whereas under the old system we have:

	Per cent.
Potash (K_2O)	63
Chlorin (Cl)	48
	<hr/>
Total	113
Less oxygen replaced by chlorin	13
	<hr/>
	100

One of the reasons for adopting this system is to secure ultimate uniformity. At the present time there is no uniformity.

Nitrogen.—A majority of the States already report nitrogen as N, but several States report it as NH_3 , and the Bureau of Soils reports it as NO_3 , NH_3 , and N.

Phosphorus.—The Bureau of Soils reports phosphorus as PO_4 , P_2O_5 , or P. Illinois reports it as P, and all other States as P_2O_5 .

Potassium.—The Bureau of Soils and the State of Illinois report potassium as K, and all other States, also the Bureau of Soils, report it as K_2O .

The various State laws with few exceptions permit the use of "equivalents" in addition to the required statement of analysis. Thus a uniform statement giving both N and NH_3 , P and P_2O_5 , K and K_2O could be used by all manufacturers, and it

⁹³ Ohio Agricultural Experiment Station, Bulletin 150, 1904 : 131.

would be acceptable in almost every State under the present laws. If this double statement were prepared in the simplest form it would not be objectionable, and it would not require any immediate or special legislation, excepting in one or two States. The following form is suggested:

	Per cent.		Per cent.
Nitrogen	1.4	= Ammonia	1.7
Available phosphorus	6.4	= Available phosphoric acid.....	14.4
Insoluble phosphorus.....	0.6	= Insoluble phosphoric acid	1.4
Total phosphorus	7.0	= Total phosphoric acid	15.8
Potassium	3.9	= Potash.....	4.7

526. Ingredients Expressed as Ions.—The expressions of the results of fertilizer analyses in the ionic nomenclature is practiced by the Bureau of Soils. One of the advantages of this system is to secure an expression of analytical data in a manner conformable to the present leading theory of the constitution of matter. This method of expression is open to the same criticism as that applied to the elemental system. It has the merit however, not possessed by the elemental system, of being more in accord with modern theories.

527. General Conclusion.—It appears therefore as the general consensus of opinion in the United States that the present system for the expression of the results of fertilizer analyses and also of the same elements as determined in the soil should be as follows: Nitrogen N; phosphoric acid P_2O_5 ; potash K_2O ; silica SiO_2 ; soda Na_2O ; lime CaO ; magnesia MgO ; ferric oxid Fe_2O_3 ; alumina Al_2O_3 ; sulfur trioxid SO_3 ; carbon dioxid CO_2 . This would not preclude the additional statement of the data in either elemental or ionic form as described.

METHODS OF ANALYSIS OF INSECTICIDES AND FUNGICIDES

528. Kinds of Insect Pests.—Various groups of insects act harmfully on plants, or animals, or as pests in households, or granaries; and require special methods of treatment to kill them.⁹⁴ Among these classes of insects may be mentioned internal feeders, subterranean insects, insects affecting stored products, house-

⁹⁴ Haywood, Manuscript Communication to the Author, 1908.

hold pests, and animal parasites. The insects which principally injure plants however, and for which insecticides are most often applied are external feeders, which include "biting" and "sucking" insects.⁹⁵

Biting insects are those which actually eat some part of the solid substance of the plant as the leaf, bark, flower, etc. For these some poisonous substance is used, which can be sprayed on the parts of the tree attacked and then be eaten by the insect in its food.

Sucking insects, are those which live by sucking the plant juices from leaf, bark, fruit, etc. For these insecticides must be used which kill the insect either by their causticity, by smothering, through closing the breathing pores, or by filling the air around the insect with poisonous fumes.

Classification of Insecticides.—From the above it will be seen that insecticides may be classified according to the group of insects upon which they act, in the following manner:

Insecticides used against

1. External feeders:
 - (a) Biting insects.
 - (b) Sucking insects.
2. Internal feeders.
3. Subterranean insects.
4. Insects affecting stored products.
5. Household pests.
6. Animal parasites.

Since the methods used in combating, as well as the insecticides used against, internal feeders and household pests are extremely varied, it does not seem best to consider these classes of insecticides in this section.

Following are descriptions of the composition, adulteration and methods of analysis of the principal commercial insecticides under the various groups enumerated above, such as the chemist is usually called upon to examine. Those insecticides which are home-made and do not require analysis by the chemist are not included.

⁹⁵ Marlatt, Department of Agriculture, Farmers' Bulletin 127, 1901 : 7.

Insecticides for External Biting Insects.—This group of insecticides includes paris green, green arsenoid, arsenate of lead, london purple, etc.

529. Paris Green.—Paris green is supposed to be copper-acetoarsenite and to contain 31.29 per cent. copper oxid, 58.65 per cent. total arsenious oxid and 10.06 per cent. acetic acid. On account of its method of manufacture it may contain small amounts of dust (determined as sand), small amounts of sodium sulfate, and larger or smaller amounts of free arsenious oxid. The following constituents therefore are usually determined in the complete analysis of a sample of paris green: Moisture, sand, sulfuric acid calculated as sodium sulfate, total arsenious oxid, total copper oxid, soluble arsenious oxid and acetic acid by difference.

Analyses of Paris Green.—Moisture.—Dry one to two grams for eight to 10 hours at 105° to 110°, and calculate the loss as moisture.⁹⁶

*Total Arsenious Oxid. Method I.*⁹⁷—*Solutions Required.*—(a). *Starch Solution.*—Use a starch solution which is prepared by boiling two grams of starch with 200 cubic centimeters of distilled water for about five minutes.

(b) *Standard Iodin Solution.*—Prepare a standard iodine solution in the following manner:—Dissolve 12.7 grams of powdered iodine in about 250 cubic centimeters of water to which has been added about 25 grams of chemically pure potassium iodide, and make up the whole to a volume of two liters. To standardize this solution, weigh one gram of chemically pure dry arsenious oxid, transfer to a 250 cubic centimeter flask by means of about 100 cubic centimeters of a solution containing two grams of sodium hydroxide in each 100 cubic centimeters, and boil until all arsenious oxid goes into solution. Make up to a volume of 250 cubic centimeters and use 50 cubic centimeters for analysis. Concentrate this portion of 50 cubic cen-

⁹⁶ Bureau of Chemistry, Bulletin 107, 1907 : 25.

⁹⁷ Smith, Journal of American Chemical Society, 1899, 21 : 769.

Haywood, Journal of the American Chemical Society, 1900, 22 : 568,

timeters by boiling in a 250 cubic centimeter flask to half its volume, and allow to cool to about 80°. Add an equal volume of concentrated hydrochloric acid and three grams of potassium iodid, mix, and allow the whole to stand for 10 minutes to reduce the arsenic oxid formed by boiling the alkaline arsenite to arsenious oxid. Dilute the solution with cold water and add an approximately tenth-normal solution of sodium thiosulfate, drop by drop, until the solution becomes exactly colorless. This end point is easy to read without the aid of starch. Make this solution slightly alkaline with dry sodium carbonate, using a drop of methyl orange to read the change, and then make slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate on the bottom are acted on by the hydrochloric acid. Add sodium bicarbonate in excess and run in the solution of iodine drop by drop, using starch water to read the end reaction. Sometimes the solution becomes dark toward the end of the titration. This change must not be confused with the final dark-blue color given by the iodine-starch.

From the number of cubic centimeters of iodine solution and the weight of arsenious oxid used determine the value of each cubic centimeter of iodine in terms of arsenious oxid.

Determination.—Transfer two grams of paris green to a 250 cubic centimeter flask by means of about 100 cubic centimeters of a two per cent. sodium-hydroxid solution. Boil this mixture for five to 10 minutes, or until all the green particles have changed to red cuprous oxid, then cool it to room temperature and make the volume up to 250 cubic centimeters. Filter the well-shaken liquid through a dry filter and use 50 cubic centimeter portions for analysis. Conduct the analysis from this point as when standardizing the iodine solution.

*Total Arsenious Oxid. Method II.*⁹⁸—*Solutions Required.*—(a) *Standard iodine solution.*—Prepare an iodine solution as in Method I. To standardize this solution place one gram of dry, chemically pure arsenious oxid in a 250 cubic centimeter flask, and dissolve by boiling about 20 minutes with five grams of sodium bi-

⁹⁸ Haywood, Bureau of Chemistry, Bulletin 81, 1904 : 195.

Journal of the American Chemical Society, 1903, 25 : 963.

Bureau of Chemistry, Bulletin 107, 1907 : 26.

carbonate and approximately 100 cubic centimeters of water; cool, add hydrochloric acid until acid, and then sodium bicarbonate until alkaline; make up to the mark and titrate aliquots of 50 cubic centimeters with iodine solution as in Method I.

(b) *Sodium acetate solution*.—Dissolve 12.5 grams of the crystallized salt in each 25 cubic centimeters.

(c) *Sodium potassium tartrate solution*.—Dissolve from two to three grams of sodium potassium tartrate in each 50 cubic centimeters.

(d) *Starch solution*.—Prepare a starch solution as in Method I.

Determination.—Place one gram of paris green in a 100 cubic centimeter flask and boil for five minutes with 25 cubic centimeters of the sodium acetate solution. Make to the mark, shake, and pass through a dry asbestos gooch filter. Use an aliquot of this filtrate for the determination of the soluble arsenious oxide by means of the iodine solution. Transfer the residue on the filter to a beaker, beat up with a little water, dissolve in concentrated hydrochloric acid adding a drop at a time, then add three or four drops in excess. Transfer the whole to the 100 cubic centimeter flask originally employed and analyze aliquots of from 20 to 40 cubic centimeters. Add concentrated sodium carbonate solution, a drop at a time, to each of these aliquots until a slight permanent precipitate is formed. Dissolve this precipitate by adding 50 cubic centimeters of the sodium potassium tartrate. Dilute to about 200 cubic centimeters, add solid sodium bicarbonate and starch water, and titrate with standard iodine.

*Total Arsenious Oxide. Method III.*⁹⁹—*Solutions Required*.—Prepare the same solutions as were required for Method II.

Determination.—Boil 0.4 gram of the finely ground paris green with 25 cubic centimeters of the sodium acetate solution for from five to 10 minutes. Add concentrated hydrochloric acid, a drop at a time, until solution is effected (about 10 cubic centimeters of the acid is usually necessary). Add concentrated sodium carbonate solution, a drop at a time, until a slight

⁹⁹ Haywood, Bureau of Chemistry, Bulletin 81, 1904 : 197.

Journal of the American Chemical Society, 1903, 25 : 963.

Bureau of Chemistry, Bulletin 107, 1907 : 26.

precipitate appears, then proceed as directed in the last two sentences of Method II.

*Sodium-Acetate-Soluble Arsenious Oxid.*¹—*Solutions Required.*—Prepare the same solutions as are used in Method II for total arsenious oxid, with the exception of the sodium potassium tartrate solution.

Determination.—Proceed as described in the first three sentences of Method II for total arsenious oxid, except that a paper filter is used, instead of asbestos.

*Water-Soluble Arsenious Oxid. Method I.*²—*Solutions Required.*—Prepare starch and standard iodine solutions as described under Method II for total arsenious oxid.

Determination.—Treat one gram of paris green in a large flask with 1,000 cubic centimeters of water previously boiled to expel carbon dioxide and then cooled to room temperature. Stopper the flask and shake eight times each day for ten days. At the end of this time filter the solution through a dry filter. Treat 200 cubic centimeters of this filtrate with sodium bicarbonate and titrate with the iodine solution.

*Water-Soluble Arsenious Oxid. Method II.*³—*Solutions Required.*—The same solutions are required as are used in Method I for water-soluble arsenious oxid.

Determination.—Digest one part of paris green in 1,000 parts of water for twenty-four hours with occasional shaking. At the end of this time filter through a dry filter, treat an aliquot with sodium bicarbonate and titrate with iodine solution.

*Water-Soluble Arsenious Oxid. Method III.*⁴—*Solutions Required.*—The same solutions are required as are used in Method I for water-soluble arsenious oxid.

¹ Avery and Beans, Journal of the American Chemical Society, 1901, 23 : 111.

Bureau of Chemistry, Bulletin 107, 1907 : 27.

² Haywood, Journal of the American Chemical Society, 1900, 22 : 568, 705 ; 1901, 23 : 111.

Bureau of Chemistry, Bulletin 67, 1902 : 98.

³ Cathcart, New Jersey Agricultural Experiment Station, Bulletin 205, 1905 : 9.

⁴ Colby, California Agricultural Experiment Station, Bulletin 151, 1903 : 18.

Determination.—Place half a gram of paris green in a 250 cubic centimeter erlenmeyer flask, add 100 cubic centimeters of distilled water and agitate by shaking every few minutes throughout a working period (eight hours) of a day, keeping the liquid at only 25° to 30°. The next day after pouring off the clear liquid, add a fresh 100 cubic centimeter portion of water and repeat the treatment mentioned above. Repeat the same treatment on a third day, in all 24 hours. Finally, combine the three 100 cubic centimeter leachings, filter through a double filter and determine arsenious oxid by means of standard iodine in the filtrate.

*Total Copper Oxid. Method I.*⁵—Pour the cuprous oxid (obtained in Method I, for total arsenious oxid by boiling the paris green with sodium hydroxid) on the filter and wash well with hot water, after an aliquot of the filtrate has been used for the determination of arsenious oxid. Then dissolve in hot dilute nitric acid and make up to a volume of 250 cubic centimeters. Use 50 to 100 cubic centimeters of this solution for the electrolytic determination of copper, as described on page 52, paragraph (2), under "VII General Methods for the Analysis of Foods and Feeding Stuffs." Bulletin 107, Bureau of Chemistry.

*Total Copper Oxid. Method II.*⁶—*Solutions Required.*—*Standard thiosulfate solution.* Dissolve 24.8 grams of the crystallized salt and make up to two liters. Standardize this solution against chemically pure copper foil dissolved in nitric acid by the method of analysis given in the following paragraph.

Determination.—Use an aliquot portion of the nitric-acid solution of copper oxid, employed in Method I for total copper oxid. Make it alkaline with sodium carbonate, then make slightly acid with acetic acid, dilute with water, and add about three or four grams of solid potassium iodid. When the potassium iodid is all dissolved by shaking, titrate the free iodine with thiosulfate, using starch as indicator toward the end of the reaction.

*Total Copper Oxid. Method III.*⁷—*Solutions Required.*—A

⁵ Bureau of Chemistry, Bulletin 73, 1903 : 158; Bulletin 81, 1904 : 195; Bulletin 90, 1905 : 95.

⁶ Journal of the American Chemical Society, 1900, 22 : 568.

⁷ Bureau of Chemistry, Circular 10, 1905, Revised.

fifth-normal solution of potassium cyanid which is prepared by standardizing against a known weight of copper dissolved in nitric acid, the method being the same as that described in the following paragraph.

Determination.—Neutralize an aliquot portion of the nitric acid solution used in Method I for total copper oxid with sodium carbonate and add a trifling excess of the carbonate; add one cubic centimeter of 0.960 specific gravity ammonia and titrate the dark blue solution to the disappearance of the blue color with standard potassium cyanid.

Sand.—Dissolve the sample used for moisture determination in hydrochloric acid, filter, wash, dry and finally burn the filter and calculating the residue as sand.⁸

Sodium Sulfate.—Treat the boiling filtrate from the determination of sand with a boiling solution of barium chlorid, allow to stand until the precipitate settles, leaving a clear solution; filter, wash, dry and burn with the usual precaution used in determining barium sulfate. Calculate the barium sulfate found to sodium sulfate, since it is in this form that sulfuric acid is supposed to be present.

Acetic Acid.—This figure is obtained by subtracting the sum of the other constituents from 100.

530. Discussion of Methods of Analysis of Paris Green.—Haywood has very carefully tested all three of the methods given above for total arsenious oxid and has found that all of them give excellent results. The methods have also been tested by the Association of Official Agricultural Chemists with like results.

The electrolytic method for total copper is of course a standard method, the accuracy of which has long since been determined. The thiosulfate method for total copper gives most excellent results when precautions are taken, but is a failure unless certain precautionary details are followed to the letter. It is absolutely necessary that there be only a very slight excess of acetic acid present when the potassium iodid is added, otherwise iodine is continuously set free and an end point can not be obtained. It is also necessary that the chemist be very careful

⁸ Bureau of Chemistry, Bulletin 68, 1902 : 13.

about reading the end point when the standard thiosulfate solution is added to use up the iodine set free. The end point is not reached when the solution is a dirty white, but only when the white is entirely unsoiled by any darker coloring. The potassium cyanid method gives very fair results when carefully carried out, but there is a tendency to get figures slightly above the truth.

A full discussion of the method of determining sodium-acetate-soluble arsenious oxid and Method I of determining water-soluble arsenious oxid will be found in the Proceedings of the 18th Annual Convention of the Association of Official Agricultural Chemists.⁹ To what is said there of water-soluble arsenious oxid, it is only necessary to add that future work will probably show that the time of extraction with water, *i. e.*, ten days, can probably be considerably reduced, say to about five days, without in any way decreasing the value of the method. From the work performed by Colby it would appear that Method II gives results considerably below the truth, in that all free arsenious oxid is not dissolved in 24 hours.¹⁰ Haywood has never tested Method III for soluble arsenious oxid, nor has he seen it used by any one but Colby, its originator. It would appear that this last method would give just about the same results as would be obtained by extracting one part of paris green with 1000 parts of water for three to five days. If such is the case, it would be simpler to extract all at once instead of by three operations.

531. Green Arsenoid.—The same methods of analysis are used in examining this compound as are used for paris green, except that the sum of moisture, sand, sodium sulfate, total arsenious oxid and total copper subtracted from 100 represents coloring matter instead of acetic acid.

532. London Purple.—London purple is a by-product obtained in the manufacture of certain of the anilin dyes. It is composed principally of calcium arsenate and calcium arsenite together with an organic dye residue. Both the calcium arsenate and arsenite are soluble in water to a limited extent, but in addition to this london purple may contain a certain amount of

⁹ Bureau of Chemistry, Bulletin 67, 1902 : 98.

¹⁰ California Agricultural Experiment Station, Bulletin 151, 1903 : 18.

"ic" and "ous" arsenic in the form of the uncombined oxids. Dirt in the form of sand may also be present in the mixture to a limited extent. It will thus be seen that the analysis of london purple should include determinations of moisture, total arsenic oxid, total arsenious oxid, soluble arsenic oxid, soluble arsenious oxid, calcium oxid, sand and the dye by difference.

Following are the methods of analysis commonly used in determining the above constituents.

Moisture.—Dry from one to two grams for from 10 to 12 hours at a temperature of 105° to 110° .¹¹

Total Arsenious Oxid. Method I.—*Solutions Required.*—Prepare starch and iodine solutions by either of the methods given under paris green.

Determination.—Dissolve two grams of london purple in a mixture of about 80 cubic centimeters of water and 20 cubic centimeters of concentrated hydrochloric acid at a temperature of from 60° to 70° ; filter and wash to a volume of 300 cubic centimeters. Treat 100 cubic centimeters of this solution with sodium bicarbonate in excess and make up to the mark in a 500 cubic centimeter flask, using a few drops of ether to destroy the bubbles. Pass a portion through a dry filter, and to 250 cubic centimeters, add starch water, and titrate the solution with standard iodine to the appearance of a blue color. The result is the arsenious oxid, as such, in 50 cubic centimeters of the original solution, or in 0.3333 gram of the original london purple.

*Total Arsenious Oxid. Method II.*¹²—The method is designed to eliminate part of the coloring matter. The solutions required are as in Method I for total arsenious oxid.

Determination.—Place two grams of london purple in a beaker and dissolve in about 80 cubic centimeters of water and 20 cubic centimeters of concentrated hydrochloric acid at a temperature of 60° to 70° , cool and add sodium carbonate in slight excess, transfer to a 250 cubic centimeter flask, bring to the mark, shake, and filter through a dry filter. Acidify 50 cubic centimeters of the filtrate with hydrochloric acid and make al-

¹¹ Haywood, *Journal of the American Chemical Society*, 1900, **22** : 800. Bureau of Chemistry, Bulletin 107, 1907 : 28.

¹² Bureau of Chemistry, Bulletin 81, 1904 : 199; Bulletin 107, 1907 : 29.

kaline with sodium bicarbonate. Titrate the amount of arsenious oxid present with the standard iodine solution.

*Total Arsenic Oxid. Method I.*¹³—*Solutions Required.*—Use the same solutions as described above for total arsenious oxid.

Determination.—Heat 50 cubic centimeters of the hydrochloric acid solution of London Purple prepared by the preceding method, to 80° on the water bath, remove and add 50 cubic centimeters of concentrated hydrochloric acid and three grams of potassium iodide. Allow the mixture to stand for at least 15 minutes, the arsenic acid thus being reduced to the arsenious condition and the iodine, set free.

Then rinse the solution into a large beaker, dilute well, and add twentieth-normal sodium thiosulfate, drop by drop, to eliminate the free iodine. The end point here is rather difficult to read on account of the very dark color of the solution, but with a little practice the chemist can determine it by proceeding as follows:

Run in the sodium thiosulfate a little at a time, occasionally withdrawing a drop of the solution and adding it to a drop of starch paste. This will give a blue color of varying intensity, which becomes fainter as the iodine is used up. Finally when a drop of the solution gives only the slightest blue color with the starch, add a little starch paste directly to the whole solution and dissipate the blue color with a few drops of thiosulfate. With a little practice the chemist can in this way get the exact end point. Immediately make the solution alkaline with solid sodium carbonate. Again make it slightly acid with hydrochloric acid, taking care that all of the solid particles of the sodium carbonate on the bottom are neutralized by the acid, and finally make alkaline with sodium bicarbonate. Add starch paste and titrate with the standard iodine solution. The end point is easily read if the beaker is placed on a white surface between the eye and the light and the iodine solution run in until a distinct purple color appears. The figure thus obtained gives the number of cubic centimeters of iodine corresponding to the total amount of arsenic in the solution expressed as arsenious oxid. Subtracting from this the number of cubic cen-

¹³ Haywood, Journal of the American Chemical Society, 1900, 22 : 800.

timeters of iodine corresponding to the arsenious oxide in the previous method gives the number of cubic centimeters of iodine corresponding to the arsenic oxide in 0.3333 gram of the sample.

Total Arsenic Oxide. Method II.—The method is designed to eliminate part of coloring matter. The solutions required are the same as in Method I for total arsenious oxide.

Determination.—Acidify 50 cubic centimeters of the solution, prepared as directed in the preceding paragraph, with concentrated hydrochloric acid, heat to 80°, add 50 cubic centimeters more of hydrochloric acid and three grams of potassium iodide, and proceed as described in Method I for total arsenic oxide in London Purple beginning with the second sentence.

*Water-Soluble Arsenious Oxide.*¹⁴—Use the same solutions as in Method I for total arsenious oxide.

Determination.—Extract one gram of London Purple in a stoppered flask with 500 cubic centimeters of cold carbon dioxide free water for seven days, shaking eight times each day. Filter through a dry filter; to 100 cubic centimeters of filtrate, add sodium bicarbonate, and titrate with standard iodine, using starch as indicator.

Water-Soluble Arsenic Oxide.—Use the same solutions as in Method I for total arsenious oxide.

Determination.—Transfer an aliquot (about 200 cubic centimeters) of the water extract from the determination of soluble arsenious oxide to a flask, make slightly alkaline with sodium hydroxide, and concentrate to about 25 cubic centimeters. Remove the flask and allow it to cool to about 80°, and add an equal volume of concentrated hydrochloric acid and three grams of potassium iodide. Allow it to stand 15 minutes, dilute, exactly use up the iodine set free with twentieth-normal thiosulfate (using starch if necessary), and neutralize the solution with sodium carbonate. Again make slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate are acted on, then make alkaline with an excess of sodium bicarbonate, and titrate with iodine, using starch as indicator. From this figure subtract

¹⁴ Haywood, *Journal of the American Chemical Society*, 1900, 22 : 800. Bureau of Chemistry, Bulletin 107, 1907 : 29.

the figure representing the amount of soluble arsenious oxid, and calculate the remainder as arsenic oxid.

Calcium Oxid.—Dissolve a portion of london purple in hydrochloric acid by the aid of heat, filter, wash the residue with hot water, and pass hydrogen sulfid through the filtrate. Wash the precipitate so obtained in the filter with hot water till clean. Evaporate the filtrate to a small bulk, transfer to a 200 cubic centimeter flask, treat with ammonium hydroxid to precipitate iron and make to the mark. Filter the solution through a dry paper and determine the calcium in an aliquot portion of the filtrate by means of ammonium oxalate.

*Sand.*¹⁵—Dry the residue remaining from the hydrochloric acid extraction in the previous method, transfer to a crucible, burn paper and contents, and finally weigh as sand.

533. Discussion of Methods of Analysis of London Purple.—Method I for total arsenious and arsenic oxid have been carefully tested by Haywood and excellent results have been obtained. The Association of Official Agricultural Chemists has also tested Method I, sometimes obtaining good results and sometimes obtaining widely divergent results. It is undoubtedly true that it is extremely difficult to read the two end points in Method I for total arsenic oxid, *i. e.*, the point where the thiosulfate uses up all the iodine and the point where all arsenious oxid is oxidized to arsenic oxid by standard iodine, however by closely following the directions it is easy to obtain closely agreeing results.

Method II for total arsenious and arsenic oxid have also been tested by Haywood and results were obtained that closely agreed with the results obtained by Method I. The Association of Official Agricultural Chemists has also tested Method II, but with unsatisfactory results up to the present time, the tendency being to obtain low results on arsenious oxid and high results on arsenic oxid. Method II is a decided improvement on Method I, as it greatly lessens the difficulty of reading the two end points mentioned above and gives equally good results.

The methods for determining soluble arsenious and arsenic

¹⁵ Bureau of Chemistry, Bulletin 68, 1902 : 20.

oxids have been carefully tested by the Association of Official Agricultural Chemists and have usually given good results.

534. Lead Arsenate.¹⁶—Lead arsenate is usually prepared by the action of either lead acetate, or lead nitrate on crystallized disodium hydrogen arsenate and usually comes on the market in the form of a thick paste. In making an analysis of this compound, the following determinations are usually made: Moisture, total arsenic oxid, soluble arsenic oxid, total lead oxid, soluble lead oxid, and soluble impurities (exclusive of soluble lead oxid and arsenic oxid).

General Direction.—In case the sample is in the form of a paste, as it usually is, dry the whole of it to constant weight at the temperature of boiling water and calculate the results as total moisture. Grind the dry sample (which will gain a small amount of moisture by so doing) to a fine powder and determine the various constituents as follows:

Moisture.—Heat two grams of the sample in the water bath for eight hours or in the hot air bath at 110° for five to six hours or till constant weight is obtained.

Total lead oxid.—Dissolve two grams of the sample in about 80 cubic centimeters of water and 15 cubic centimeters of concentrated nitric acid on the steam bath; transfer the solution to a 250 cubic centimeter flask and make up to the mark. To 50 cubic centimeters of the solution add three cubic centimeters of concentrated sulfuric acid, evaporate on the steam bath to a sirupy consistency and then on a hot plate till white fumes appear and all nitric acid has been given off. Add 50 cubic centimeters of water and 100 cubic centimeters of 95 per cent. alcohol, let stand for several hours and filter off the supernatant liquid, wash about ten times with acidified alcohol (water 100 parts, 95 per cent. alcohol 200 parts, and concentrated sulfuric acid three parts) and then with 95 per cent. alcohol till free of sulfuric acid. Dry, remove as much as possible of the precipitate from the paper into a weighed crucible, and ignite at a low red heat. Burn the paper in a separate porcelain crucible and treat the residue first with a little nitric acid, which is afterwards evaporated off, and

¹⁶ Haywood, Bureau of Chemistry, Bulletin 105, 1907 : 165.

then with a drop or two of sulfuric acid. Ignite, weigh, and add this weight to the weight of the precipitate previously removed from the paper for amount of the lead sulfate.

Water-soluble lead oxid.—Place two grams of lead arsenate in a flask with 2,000 cubic centimeters of carbon dioxid free water and let stand ten days, shaking eight times a day. Filter through a dry filter and use aliquots of this for determining soluble lead and arsenic oxids and soluble solids; determine lead as described above for total lead oxid, using the same relative proportions of sulfuric acid, water, and alcohol, but keeping the volume as small as possible.

Total arsenic oxid.—Transfer 100 cubic centimeters of the nitric acid solution of the sample, prepared as in the above determination of lead, to a porcelain dish, add six cubic centimeters of concentrated sulfuric acid, evaporate to a sirupy consistency on the water bath and then on a hot plate to the appearance of white fumes of sulfuric acid. Wash into a 100 cubic centimeter flask with water, make up to mark, filter through dry filters, and use 50 cubic centimeter aliquot parts for further work. Transfer this to an erlenmeyer flask of 400 cubic centimeters capacity, add four cubic centimeters of concentrated sulfuric acid and one gram of potassium iodid, dilute to about 100 cubic centimeters and boil until the volume is reduced to about 40 cubic centimeters. Cool the solution under running water, dilute to about 300 cubic centimeters, and exactly use up the iodine set free and still remaining in solution with a few drops of approximately tenth-normal sodium thiosulfate solution. Wash the mixture into a large beaker, make alkaline with sodium carbonate, and slightly acidify with dilute sulfuric acid; then make alkaline again with an excess of sodium bicarbonate. Titrate the solution with a twentieth-normal iodine solution to the appearance of a blue color, using starch as indicator.

Water-soluble arsenic oxid.—For this determination use 200 to 400 cubic centimeters of the water extract obtained under the determination of soluble lead oxid. Add 0.5 cubic centimeter of sulfuric acid and evaporate it to a sirupy consistency, then heat on a hot plate to appearance of white fumes. Add a very

small amount of water and filter the lead through the very smallest filter paper, using as little wash-water as possible. Place this filtrate in an erlenmeyer flask, and determine arsenic as described above for total arsenic oxid, using the same amount of reagents and the same dilutions.

Soluble solids or impurities.—Evaporate 200 cubic centimeters of the water extract obtained above to dryness in a weighed platinum dish, dry to constant weight at the temperature of the boiling water bath and weigh. The soluble solids so obtained represent principally any sodium acetate or sodium nitrate present, with a very small quantity, perhaps, of lead acetate or nitrate and some soluble arsenic, probably in the form of lead arsenate.

The above methods for determining the constituents of commercial lead arsenate have been carefully tested by Haywood, as well as by several other chemists all of whom have reported that exceptionally good results were obtained.

535. Insecticides for External Sucking Insects.—This group of insecticides includes soaps, caustic soda and potash, lime-sulfur-salt mixtures, kerosene emulsions, dilute nicotine solutions, hydrocyanic acid gas, vapors of carbon bisulfid, etc.

536. Soaps.—Soap may be used to destroy soft bodied insects, such as plant lice, and in strong solutions, as a winter wash to destroy scale insects. Fish oil soap, prepared by the action of caustic potash or soda on fish oil is one of the most effective soaps, and is the one which the chemist is most often called upon to examine. The potash soap is the better of the two, as it does not clog the spraying machine when the solution becomes cold.

It is usually necessary to know only three constituents of a soap in order to judge of its value for spraying purposes, namely: moisture, total fatty matter, and total soda or potash. The moisture and alkali are usually determined and the total fatty matter approximately estimated by difference.

Following are the methods of analysis usually employed:¹⁷

Moisture.—Tare accurately a 100 cubic centimeter beaker, the

¹⁷ Bureau of Chemistry, Bulletin 107, 1907 : 31.

bottom of which is covered about one-half inch deep with recently ignited, perfectly dry sand, and in which is a small glass rod. Place in the beaker about five grams of the sample; add 25 cubic centimeters of alcohol or more if necessary, and dissolve the soap in the alcohol by constant stirring on the water bath. Evaporate the alcohol and finally dry in an oven at 110° until the weight is constant. A few precautions should be taken which are not mentioned in the above method, namely: If the soap is hard the five grams should be cut off in very thin strips so that it will dissolve more readily in the alcohol; also most samples of soap never come to a constant weight on drying, but gain or lose nearly indefinitely. It is, therefore, best to heat the soap at 110° until it is nearly dry and weigh, then return the soap to the oven and dry another half hour. Continue this alternate drying and weighing until the weight changes only a few milligrams during the course of a half hour's drying.

*Total Alkali.*¹⁸—Dissolve a weighed quantity of the soap in water; decompose with hydrochloric acid, filter off the water from the fat, and wash with cold water. Determine both potassium and sodium in the filtrate first as mixed chlorids in the ordinary manner and then determine the potassium by means of platinum chlorid.

A rapid but only approximate determination of the alkali in soap is made in the following manner: Weigh a small quantity of the soap, treat with concentrated sulfuric acid, burn, repeat treatment with sulfuric acid, and burn again. Add a small amount of ammonium carbonate to the dish, cover; and heat. Repeat this a number of times till all bisulfates have changed to sulfates. Test the residue qualitatively to determine whether it is sodium or potassium sulfate, and calculate the residue to soda or potash, as the case may be.

537. Caustic Soda and Potash.—These two substances are sometimes used in water solutions as winter washes. They are more often used by the entomologist, however, in preparing resin and fish oil soaps, lye-sulfur mixtures, etc. To judge of their value for any of the above purposes and to calculate how much of

¹⁸ Bureau of Chemistry, Bulletin 107, 1907 : 31.

the caustic soda or potash should be used, it is necessary to know the carbonate and hydroxid content.

Following are the methods usually employed in examining this class of goods:

*Carbonate and Hydroxid. Method I.*¹⁹—*Solutions Required.*—A half-normal solution of hydrochloric acid; methyl orange and phenolphthalein indicators.

Determination.—Weigh a large quantity of the sample from a weighing bottle, dissolve in carbon dioxid-free water, and make up to a definite volume. Analyze aliquots of this solution. Titrate one portion with half-normal acid, using methyl orange as indicator, and note the total alkalinity thus found. Transfer another aliquot of the same size to a measuring flask and add enough barium chlorid to precipitate all carbonate, avoiding any unnecessary excess. Make the volume up to the mark with carbon dioxid-free water, stopper, shake, and set aside to allow the precipitate to settle. When the liquid becomes clear, draw off one-half by means of a pipette and titrate with half-normal hydrochloric acid, using phenolphthalein as indicator. This number of cubic centimeters of half-normal acid multiplied by two gives the number of cubic centimeters of half-normal acid corresponding to the original amount taken. The last figure obtained represents sodium or potassium hydroxid and the difference between the first and last figures represents the sodium or potassium carbonate.

*Carbonate and Hydroxid. Method II.*²⁰—*Solutions Required.*—A fifth-normal solution of potassium acid sulfate; methyl orange and phenolphthalein indicators.

Determination.—Dilute with carbon dioxid-free water an aliquot of the solution as prepared in Method I and add a few drops of phenolphthalein. Add a fifth-normal solution of potassium acid sulfate at the rate of about one drop per second, with constant stirring, until the pink color fades out and the solution becomes colorless. The reading thus obtained (n) represents the sodium or potassium hydroxid and one-half of the sodium or potassium carbonate present, since the sodium or potassium car-

¹⁹ Bureau of Chemistry, Bulletin 107, 1907 : 31.

²⁰ Bureau of Chemistry, Bulletin 107, 1907 : 32.

bonate is changed to sodium or potassium bicarbonate. Add methyl orange and continue the titration to the appearance of a pink color. This reading (m) represents the sodium or potassium bicarbonate present or one-half of the sodium or potassium carbonate; $2m$ represents all the sodium or potassium carbonate present, and $n-m$ the sodium or potassium hydroxid.

538. Discussion of Methods of Analysis of Caustic Soda and Potash.—By Method I higher results are always obtained for sodium hydroxid than by Method II, while by Method I lower results are always obtained for sodium carbonate than by Method II. Although Method II is somewhat more difficult than Method I because of the great care necessary in reading the two end points, Haywood is inclined to think that it is somewhat more accurate for the following reasons: In Method I after the carbonates are precipitated out by barium chlorid, the supernatant liquid is titrated for the hydroxid present. Since barium carbonate is soluble to quite an extent in water that portion which is soluble is also titrated as hydroxid, thus increasing the hydroxid figure. In Method II all the hydroxid and one-half the carbonate are first titrated, then the other half of the sodium carbonate, so there does not seem to be the same chance of error.

539. Lime-Sulfur-Salt Mixture.—The lime-sulfur-salt mixture or simply the lime-sulfur mixture without the salt is very largely used in this country against the San José scale. On account of the trouble incident to its home preparation it has of late years appeared on the American market in a concentrated form. The chemist is often called upon to examine this concentrated mixture in order that the entomologist may calculate the proper dilution.

It has been shown by Haywood that the liquid portion of the lime-sulfur-salt wash, which is the portion sold on the market, when prepared by any of the formulas ordinarily employed, consists principally of sulfids and polysulfids together with a moderately large quantity of thiosulfates and very small quantities of sulfates and sulfites.²¹ It is therefore necessary to make the following determinations on a commercial sample of the lime-sul-

²¹ Bureau of Chemistry, Bulletin 101, 1907.

fur-salt wash: Total sulfur, sulfur as sulfids and polysulfids, sulfur as thiosulfates, sulfur as combined sulfates and sulfites, and calcium oxid. Following are methods of analysis which give good results:

*Total Sulfur.*²²—*Solutions Required.*—(a) A saturated potassium hydroxid solution or a solution of sodium hydroxid containing 100 grams to 100 cubic centimeters of water; (b) A 10 per cent. barium chlorid solution; (c) An approximately three per cent. solution, of hydrogen peroxid free from sulfates. If the solution contains sulfates add freshly precipitated barium carbonate and shake occasionally for several hours, then filter and use the clear solution.

Determination.—Place 10 cubic centimeters of the clear sample in a 100 cubic centimeter measuring flask and fill to the mark. Analyze 10 cubic centimeter aliquots of this solution. Treat with three cubic centimeters of the caustic potash or soda solution, following by 50 cubic centimeters of hydrogen peroxid free from sulfates. Heat on the steam bath for one-half hour exactly and then acidify with hydrochloric acid, precipitate with barium chlorid in the usual way in boiling solution, and finally weigh as barium sulfate.

*Sulfur as Sulfids and Polysulfids.*²³—*Solutions Required.*—The same solutions are required as are used in the above determinations with the following addition:

Ammoniacal zinc chlorid solution.—Dissolve 3.253 grams of pure zinc in hydrochloric acid, supersaturate with ammonia and make up to a liter.

Determination.—Pipette 10 to 25 cubic centimeters of the liquid portion of the wash into a 100 cubic centimeter flask and make up to the mark. Use 10 cubic centimeters of this representing one to 2.5 cubic centimeters of the original solution, for analysis. Add the ammoniacal zinc chlorid solution until slightly in excess, as shown by the reaction of a drop of the solution with nickel sulfate. Place on the steam bath and heat until the odor of ammonia becomes faint, filter; and wash. Transfer filter and contents to a beaker, add about 10 to 15 cubic centimeters of a saturated

²² Avery, Bureau of Chemistry, Bulletin 90, 1905 : 105.

²³ Haywood, Bureau of Chemistry, Bulletin 101, 1907 : 9.

solution of potassium hydroxid, and heat for some time. Add 50 cubic centimeters of hydrogen dioxid, free of sulfates, and heat on the steam bath exactly 30 minutes. Acidify with hydrochloric acid and precipitate with barium chlorid in the usual way.

Sulfur as Thiosulfates.—*Solutions Required.*—Ammoniacal zinc chlorid prepared as in the previous method, tenth-normal hydrochloric acid, and tenth-normal iodine prepared in the usual way.

Determination.—Pipette five cubic centimeters of the original solution into a 50 cubic centimeter flask and add ammoniacal zinc chlorid until it is slightly in excess, as shown by nickel sulfate. Make this mixture up to the mark, shake, and filter off through a dry filter. To a 25 cubic centimeter aliquot of the filtrate add methyl orange and titrate with tenth-normal hydrochloric acid to exact neutrality. Next titrate the liquid with a tenth-normal iodine solution. The reading thus obtained gives the total thiosulfates and sulfites; since, however, the sulfites are present in such small amounts as to be negligible the number of cubic centimeters of iodine solution used may be considered to represent only the thiosulfates.

*Sulfur as combined sulfates and sulfites.*²⁴—*Solutions Required.*—The same solutions are used as are described in the preceding method with the addition of 10 per cent. barium chlorid.

Determination.—Follow the preceding method to the point where the thiosulfates have been changed to tetrathionates, and sulfites to sulfates by the addition of tenth-normal iodine. Make slightly acid with hydrochloric acid and precipitate the combined sulfates and sulfites (now sulfates) with barium chlorid in the usual way.

*Lime.*²⁵—*Solutions Required.*—Alkali and hydrogen peroxid solutions prepared as described under total sulfur. Also a solution of ammonium oxalate.

Determination.—Proceed as in the method for determining total sulfur to the point where all sulfur has been oxidized and

²⁴ Haywood, Bureau of Chemistry, Bulletin 101, 1905 : 9.

²⁵ Avery, Bureau of Chemistry, Bulletin 90, 1905 : 105.

the solution is acid. Then add ammonia in slight excess and filter if a precipitate appears. Determine the lime in the filtrate by precipitating with ammonium oxalate and finally weighing as calcium oxid.

540. Kerosene Emulsion.—In kerosene emulsions as usually prepared the emulsifying agent is soap. On account of the trouble of preparing these mixtures at home, various kerosene emulsions in a concentrated form have appeared upon the market in late years. In determining the value of an emulsion of this kind it is usually only necessary to determine the amount of kerosene present. A centrifugal method has been worked out by Colby which seems to give very excellent results.²⁶

Kerosene.—Weigh six, nine, or even 18 grams according to the strength of the kerosene emulsion, and measure in cubic centimeters at 15.5° into a babcock cream bottle, graduated to 35 or 50 per cent. To this add three or four cubic centimeters of strong sulfuric acid and twirl one minute in a babcock machine; then add cold water and twirl again one minute; finally add water sufficiently to bring the water to or above the zero mark in the neck of the babcock bottle; read the cubic centimeters of kerosene at 15.5°. Calculate the volume percentage of kerosene on the number of cubic centimeters of emulsion used in the test.

541. Tobacco and Tobacco Extract.—Decoctions of tobacco and diluted tobacco extracts are often used against external sucking insects. They are valued by the entomologist for the amount of nicotin which they contain, hence this is the only determination necessary in analyses of such articles. The Association of Official Agricultural Chemists has made careful studies of the Lloyd and Winton methods of determining nicotin, but unsatisfactory results were obtained.²⁷ The only method that has given satisfactory results, is that of Kissling. The Emery method, tested by the association in 1904, appeared to lead to fairly satisfactory results.

²⁶ Bureau of Chemistry, Bulletin 105, 1907 : 165.

²⁷ Bureau of Chemistry, Bulletin 56, 1899 : 114, 125 ; Bulletin 73, 1903 : 165 ; Bulletin 81, 1904 : 203.

*Nicotin. Method I.*²⁸—*Solutions Required.*—(a) *Alcoholic soda.*—Dissolve six grams of sodium hydroxid in 40 cubic centimeters of water and 60 cubic centimeters of 90 per cent. alcohol.

(b) *Sodium hydroxid.*—Dissolve four grams of sodium hydroxid in 1,000 cubic centimeters of water.

(c) *Sulfuric acid.*—A standard solution.

Determination.—Place from five to six grams of tobacco extract or 20 grams of finely powdered tobacco, which has been previously dried at 60° so as to allow it to be powdered, in a small beaker. Add 10 cubic centimeters of the alcohol-soda solution and follow, in the case of the tobacco extract, with enough chemically pure powdered calcium carbonate to form a moist but not lumpy mass. Mix the whole thoroughly. Transfer this to a soxhlet extractor and exhaust for about five hours with ether. Evaporate the ether at a low temperature by holding over the steam bath, and take up the residue with 50 cubic centimeters of the dilute sodium hydroxid solution. Transfer this residue by means of water to a kjeldahl flask, capable of holding about 500 cubic centimeters and distil in a current of steam, using a condenser through which water is flowing rapidly. Use a three-bend outflow tube, a few pieces of pumice, and a small piece of paraffin, to prevent bumping and frothing. Continue the distillation till all the nicotin has passed over, the distillate usually varying from 400 to 500 cubic centimeters. When the distillation is complete only about 15 cubic centimeters of the liquid should remain in the distillation flask. Titrate the distillate with standard sulfuric acid, using phenacetolin or cochineal as indicator. One molecule of sulfuric acid is equivalent to two molecules of nicotin.

*Nicotin. Method II.*²⁹—Render a weighed amount of the sample alkaline with 50 cubic centimeters of approximately tenth-normal soda and transfer to a round bottom flask of about 300 cubic centimeters capacity with 150 cubic centimeters of distilled water. Subject the whole to distillation in a current of steam in the usual way and make the distillate to a volume of 500 cubic cen-

²⁸ Bureau of Chemistry, Bulletin 107, 1907 : 32.

²⁹ Emery, Journal of the American Chemical Society, 1904, 26 : 1113.

timeters. Place a portion of the distillate in a 40 centimeter tube and take a polariscopic reading, calculate the result on the value of one degree on the sugar scale as previously established from chemically pure nicotin. From this calculate the percentage of nicotin in the weight of sample originally taken.

Method II for nicotin can only be used by those who have had long enough experience with the polariscope to make an exceedingly close reading.

542. Potassium Cyanid.—Potassium cyanid is not used by itself, nor in solution in water for spraying purposes. It is used however as a reagent in preparing hydrocyanic acid gas, which in its turn is of value in destroying scale insects, controlling insect pests in green houses and cold frames, destroying insects and vermin in homes, etc. In examining this compound chemically it is the amount of cyanogen present that is of interest to the entomologist. A very accurate method of determining this constituent is given below.

*Cyanogen.*³⁰—*Solutions Required.*—Prepare a twentieth-normal solution of silver nitrate.

Determination.—Weigh a large quantity of the sample from a weighing bottle, dissolve in water and make up to a definite volume. To an aliquot add twentieth-normal silver nitrate, a drop at a time, with constant stirring, until one drop produces a permanent turbidity. In calculating the results, one equivalent of silver is equal to two equivalents of cyanogen, according to the following equation:



543. Carbon Disulfid.—The vapors of carbon disulfid are often used to destroy such insects as plant lice on melons and squash vines, insects in granaries, and insects and vermin in homes. Special chemical methods for examining the purity of this compound have not been approved.

544. Insecticides for Subterranean Insects.—Insecticides for this purpose must either be of such a character that they will dissolve in water and be carried down to the insects beneath the ground, or must be volatile, so that they will smother the insects.

³⁰ Bureau of Chemistry, Bulletin 107, 1907 : 30.

Among the insecticides that are used for this purpose are kerosene emulsions, potash fertilizers, strong soap, or tobacco washes, tobacco dust, carbon disulfid, etc. Methods for examining these materials, except carbon disulfid, have been given in the previous parts of this article. The potash fertilizers are examined for potash by the usual fertilizer methods.

545. Insecticides for Insects Affecting Stored Grains and Other Stored Products.—While there are a number of important remedial measures against insects in stored products, such as agitation of the grain, heating, etc., the only important insecticide that is necessary to consider in this connection, is carbon disulfid. As has previously been mentioned, special chemical methods for testing the purity of this compound have not been proposed.

546. Insecticides for Animal Parasites.—Among the most important insecticides of this class are tobacco extracts, lime-sulfur mixtures and creosote dips. There are of course other remedies, but not any that the chemist will be called upon to examine with anything like the frequency that he is called on to examine the three classes of insecticides mentioned above. Methods for examining tobacco extracts and lime-sulfur mixtures have already been given. For examining creosote dips, the method given by Allen is usually followed. This method is far from perfect and gives only approximate results.³¹

547. Fungicides.—Among substances that are used as fungicides, or as ingredients in making insecticides, the chemist is most often called upon to examine the following: Bordeaux mixture, copper sulfate, copper carbonate, lime-ferrous sulfate, sulfur and formaldehyde solutions. Methods for examining the first six of these are based on general principles and are so self-evident that it does not seem necessary to mention them. It may be said, however, in passing, that the Association of Official Agricultural Chemists has adopted official methods for determining copper in copper carbonate.³²

³¹ Allen, *Commercial Organic Analysis*, 3rd Edition, 1907, 2, Part 2 : 262. Bureau of Chemistry, Bulletin 90, 1905 : 103.

³² Bureau of Chemistry, Bulletin 107, 1907 : 30.

For determining formaldehyde in solutions of this substance the following methods are commonly used:

*Formaldehyde. Method I.*³³—*Solutions Required.*—A normal solution of sulfuric acid, a normal solution of sodium hydroxid and a solution of purified litmus.

Determination.—Place 50 cubic centimeters of normal sodium hydroxid in a 500 cubic centimeter erlenmeyer flask and add 50 cubic centimeters of hydrogen dioxid. Then add three cubic centimeters of the formaldehyde solution under examination (the specific gravity of which has been previously determined), allowing the point of the pipette to almost reach the liquid in the flask. Place a funnel in the neck of the flask and put on the steam bath for five minutes, shaking occasionally during this time. Remove from the steam bath, wash the funnel with distilled water, cool the flask to about room temperature, and titrate the excess of sodium hydroxid with normal acid, using litmus as indicator. This cooling of the flask before titration with acid is necessary in order to get a sharp end reading with the litmus. From the volume of formaldehyde used and the specific gravity determine the per cent. of formaldehyde.

*Formaldehyde. Method II.*³⁴—*Solutions Required.*—Double normal sodium hydroxid and double normal sulfuric acid.

Determination.—Place three grams of the solution in a tall erlenmeyer flask containing 25 to 30 cubic centimeters of double normal sodium hydroxid. Then gradually add 50 cubic centimeters of pure 2.5 to three per cent. hydrogen peroxid during a space of three minutes through a funnel placed in the neck of the flask to prevent spurting. After standing two or three minutes, wash the funnel with water and titrate the unused sodium hydroxid with double normal sulfuric acid, using litmus as indicator.

When analyzing solutions containing less than 30 per cent. of formaldehyde, the mixture must be allowed to stand 10 minutes after adding the hydrogen peroxid to complete the reaction.

³³ Haywood and Smith, *Journal of the American Chemical Society*, 1905, 27 : 1183.

³⁴ Bureau of Chemistry, *Bulletin* 107, 1907 : 33.

Find the percentage of formaldehyde by multiplying by two the number of cubic centimeters of soda solution used, when three grams of substance are examined.

Acetaldehyde reacts much more slowly with the reagent than formaldehyde, and it is doubtful whether the reaction is quantitative.

Paraldehyde reacts still more slowly with hydrogen peroxid, even in the presence of a trace of ferrous salt. Benzaldehyde is acted upon more quickly, particularly in presence of ferrous sulfate, and a considerable evolution of gas takes place, but a long time is needed to complete reaction.

*Formaldehyde. Method III.*³⁵—This method is to be used especially in solutions containing a small amount of formaldehyde.

Solutions Required.—(a) *Silver nitrate.*—A tenth-normal solution.

(b) *Ammonium sulfocyanate.*—A tenth-normal solution.

(c) *Potassium cyanid.*—A solution containing 3.1 grams to 500 cubic centimeters of water.

(d) *Nitric acid.*—A 50 per cent. solution.

Determination.—Treat 15 cubic centimeters of the silver nitrate with six drops of 50 per cent. nitric acid in a 50 cubic centimeter flask; add 10 cubic centimeters of the solution of potassium cyanid and shake well. Then make the solution up to the mark and titrate an aliquot of the filtrate (say 25 cubic centimeters) with tenth-normal solution of ammonium sulfocyanate for the excess of silver. Acidify another 15 cubic centimeter portion of tenth-normal silver nitrate with six drops of 50 per cent. nitric acid and treat with 10 cubic centimeters of the potassium cyanid solution to which has been added a weighed quantity of the dilute formaldehyde solution. Make up the whole to 50 cubic centimeters and titrate a 25 cubic centimeter filtrate from it with tenth-normal ammonium sulfocyanate for the excess of silver as before. The difference between these results multiplied by two gives the amount of potassium cyanid that has been used by the formaldehyde in terms of tenth-normal ammonium sulfocyanate. Each cubic centimeter of this is equivalent to three milligrams of formaldehyde.

³⁵ Romijn, *Zeitschrift für analytische Chemie*, 1897, **36** : 18.

548. Discussion of Methods of Analysis of Formaldehyde Solutions.—Method I has been carefully tested and has been found to give excellent results on strong solutions of formaldehyde. Method II, the original hydrogen peroxid method, gives results that are slightly below the truth. The reasons for the superiority of Method I over Method II has been explained by Haywood and Smith.³⁶ Method III has been carefully tested and has been found to give good results. It can, however, only be used on dilute solutions of formaldehyde, or on concentrated solutions, which are diluted to a large extent. Since the error of analysis would be greatly multiplied by examining concentrated solutions of formaldehyde by this method it seems best to restrict it to solutions that are dilute in the beginning.

549. Statement of Insecticide Analyses.—Two typical insecticides may be considered in presenting a scheme for expressing the results of analyses, namely, paris green and london purple. In making complete analyses of paris green the following constituents should be determined, namely, moisture, sand, sulfur trioxid, copper, total arsenic, soluble arsenic, and acetic acid.

It is best to report the sulfur trioxid in the form of sodium sulfate, since from the method of manufacture of paris green it is almost certain that the sulfur trioxid present exists in this form in the green. The copper should be reported as cupric oxid (CuO), and the total arsenic as arsenic trioxid or arsenious oxid. The acetic acid present should not be reported as acetic acid as is usually done, but as acetic anhydrid, since the reporting of the copper as CuO has left the acetic acid as acetic anhydrid.

In reporting soluble arsenic it should be given as arsenious oxid or arsenic trioxid and should be determined in two ways; (1) by the Avery-Beans method to approximately determine the actual free arsenious oxid present, and (2) by the prolonged water soluble method to determine to some extent the stability of the green.

In examining samples of london purple the following determinations should be made, moisture, insoluble in hydrochloric

³⁶ Journal of the American Chemical Society, 1905, 27 : 1183.

acid, total and soluble *ic* arsenic, total and soluble *ous* arsenic, calcium and dye by difference. The *ic* arsenic in both cases should be reported as arsenic pentoxid and the *ous* arsenic as an arsenic trioxid. The calcium should be reported as calcium oxid. The words "by difference" should always follow the dye figure.

SCHEME FOR REPORTING RESULTS OF ANALYSES

PARIS GREEN

Moisture	%
Sand.....	
Sodium sulfate	
Total arsenious oxid	
Total copper oxid.....	
Acetic anhydrid	
Total.....	
Soluble arsenious oxid by Avery-Beans Method.....	%
Soluble arsenious oxid by water extraction method	

LONDON PURPLE

Moisture	%
Insoluble in hydrochloric acid.....	
Total arsenic oxid	
Total arsenious	
Calcium oxid	
Dye (by difference).....	
Total.....	
Soluble arsenic oxid	
Soluble arsenious oxid	
Soluble calcium oxid.....	

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