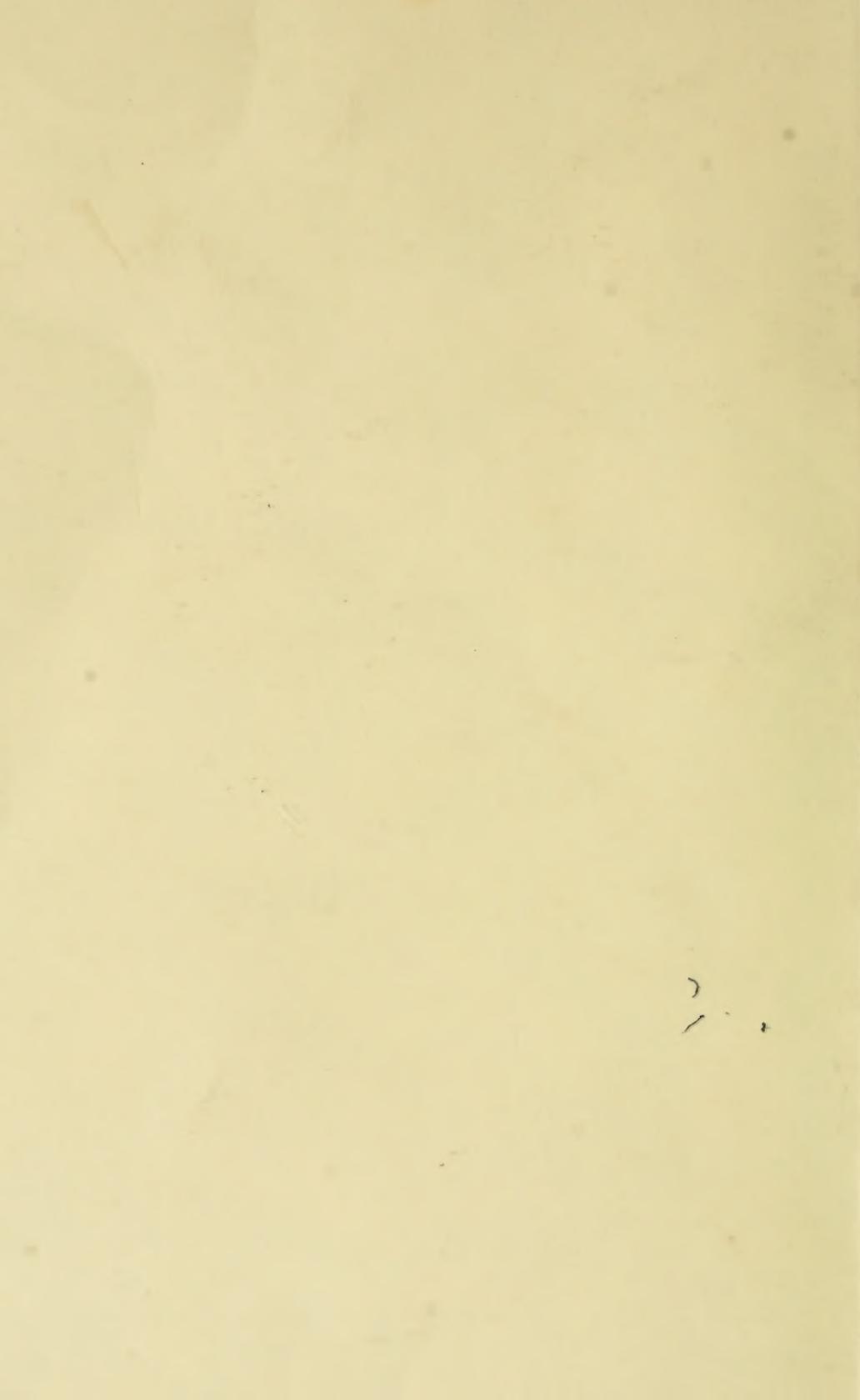


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REPORT

ON

METHODS FOR

ANALYSIS OF SOILS AND ASHES,

FOR THE AMERICAN ASSOCIATION OF OFFICIAL
AGRICULTURAL CHEMISTS.

BY R. C. KEDZIE, REPORTER.

LANSING:

D. D. THORP, PRINTER AND BINDER.

1891.

the soil distilled water (ammonia-free) sufficient to moisten all the soil, and let the whole stand undisturbed for half an hour, then add more pure distilled water, and if the filtration is too slow use the filter-pump till a liter of filtrate is secured. If the soil extract is cloudy, filter through a plain filter. Each cubic centimeter of filtrate contains the water-soluble materials of a gram of air-dry soil.

9. *Soluble solids*.—Evaporate 100 c. c. to dryness on the water-bath in a tared dish to determine the percentage of water-soluble materials in the soil; each gram of residue representing a per cent of such materials. Test this dry residue for nitrates by pouring over it 10 c. c. of C.P. H_2SO_4 holding in solution three or four milligrams of sulfate of brucia.

10. *Chlorides*.—Titrate 100 c. c. with standard decinormal argentic nitrate with two drops of solution of K_2CrO_4 as indicator. Titrate in white porcelain dish and view the reaction through a yellow glass plate of such tint as will eliminate the color of the chromic solution. The reaction will then be sharply defined. More than one part of soluble chlorides in one thousand of soil is injurious to agricultural plants.

11. *Sulfates*.—Precipitate the soluble sulfates in 100 c. c. with $BaCl_2$ in presence of a few drops of HCl and estimate the soluble sulfates.

Reserve the rest of the water solution (8) for the estimation of nitrates (26).

ACID-SOLUBLE MATERIALS.

In the following scheme for soil analysis it is recommended to use the air-dry soil from the sample bottle for each separate investigation. A determination made once for all of hygroscopic moisture and of water of combination on a separate specimen of air-dry soil will afford corrections for all the other samples used. It is not desirable to ignite the soil before analysis, or to heat it so as to change its chemical properties.

In an agricultural chemical analysis the object is to find the kind and quantity of soil materials available for the growing plant. The reserve or inactive materials are not objects of immediate concern. Prof. Hilgard takes C.P. HCl of specific gravity 1.115 as the solvent for soil materials, which may be supposed to fully represent the solvent action that may be secured by water and other solvents in the soil, and the action of the roots of growing

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FEB 4 1916

plants or other corroding agents. The same acid and of the same strength is here recommended, but with a modified form of using the same. Instead of digesting the soil with this acid in a covered beaker, with liability to continual variation of strength of the acid, it is proposed to use the acid with constant strength except so far as it may be neutralized by combination with the soil minerals.

Instead of a porcelain beaker covered with a watch glass I propose for the soil digestion a four-ounce vial of Bohemian glass, with a flat-topped ground glass stopper. The small steam bath is a copper vessel eight inches in diameter and five inches deep, with vertical sides; the cover has four openings through which the vials may readily pass down two and three-quarter inches to a perforated false bottom upon which the vials rest, and the space of two and a quarter inches below the false bottom serves for the hot water chamber of the steam bath. Through the center of the cover and of the false bottom a vertical tube, open at both ends, extends nearly to the bottom of the vessel, for pouring in water to replenish the waste; or a side tube near the bottom of the hot water chamber may be connected with a water reservoir to keep the water in the steam bath at a constant level. A Bunsen burner serves to heat up the steam bath and to keep the body of the vials at the constant heat of boiling water. When such a bath is set to work the digestion can go forward day and night with very little care and attention. If the vials charged for digestion are placed in the apparatus when cold and then heated up to steam heat, no trouble is found from the vials breaking. When the vials are properly charged and the escape of acid prevented, thirty-six to forty hours of continuous digestion will be as effective as five days of intermittent digestion in a covered beaker.

12. *Acid digestion of the soil.*—Weigh five grams of the air-dry soil into a four-ounce Bohemian vial, add 50 c. c. of C.P. HCl. sp. gr. 1.115, insert glass stopper, wire it securely, place in steam bath and digest for thirty-six to forty hours at the temperature of boiling water. Pour the contents of the vial into a small beaker, wash out the vial with distilled water, add the washings to the contents of the beaker, pour into this 2 c. c. of HNO₃ to peroxidize the iron and oxidize organic matter, and evaporate the contents of the beaker to complete dryness over the water bath. Cool the beaker, add 10 c. c. of C.P. HCl. sp. gr. 1.115 and 50 c. c. of distilled water and heat to near boiling. Filter from sand and silica,

wash the filter with distilled water till the filtrate shows no reaction with silver nitrate, and make the filtrate up to 500 c. c. (Solution A), 100 c. c. of which represents the soluble materials from one gram of air-dry soil.

13. *Sand and silica.*—Dry the filter and insoluble residue from A, transfer the residue to a tared platinum dish, burn the filter and add its ash to the dish, heat the dish and contents, at first gently to avoid spurting of silica, then intensely to destroy organic matter, cool in desiccator and weigh. The increase of weight—minus the filter ash—represents the sand and silica. Boil this residue for fifteen minutes in 50 c. c. of strong solution of sodic carbonate, add 100 c. c. of boiling water, filter while still hot, and wash the filter and contents with boiling water till the sodic salts are washed away. Dry the residue, burn the filter and add its ash to the insoluble residue, heat this to redness, cool and weigh. Deduct the ash of filter and enter the balance as SAND or INSOLUBLE SILICATES. The difference in weight between sand, and sand and silica, enter as SILICA. This sand and silica will respectively represent the amount of these materials in five grams of air-dry soil, and these weights multiplied by twenty will give the per cent respectively of sand and silica in such soil.

14. *Ferric oxide and alumina.*—To 200 c. c. of Solution A (in an Erlenmeyer flask) add NH_4OH to alkaline reaction (avoiding excess), to precipitate ferric and aluminic oxides and phosphates. Expel excess of ammonia by boiling, let it settle, decant the clear solution through a filter; add to the flask 50 c. c. of hot distilled water, boil, settle and decant as before. After pouring off all the clear solution possible, dissolve the residue with a few drops of HCl . with heat, add just enough NH_4OH to precipitate the oxides. Wash by decantation with 50 c. c. of distilled water, and then transfer all the precipitate to the filter, and wash with hot distilled water till the filtrate becomes free from chlorides. (Save the filtrate and washings, Solution B.) Dry the filter and precipitate in the air-bath at 110° , transfer the precipitate to a tared platinum crucible, burn the filter and add the ash to the precipitate, heat the whole red-hot, cool in desiccator and weigh. The increase of weight—minus the ash of filter and the phosphoric acid (found in a separate process)—represents the weight of the ferric and aluminic oxides.

15. *Ferric oxide.*—Place the whole of the ignited oxides in an

Erlenmeyer flask (200 c. c. capacity), add 10 c. c. of conc. H_2SO_4 and digest on steam bath till complete solution is effected; cool and add 100 c. c. of distilled water, a piece of amalgamated zinc and a slip of platinum foil, cover with a watch glass and allow to stand for twenty-four hours to reduce ferric to ferrous salt. When the reduction is complete, as tested by transferring on a glass rod a drop of the solution to a drop of ammonic-sulphocyanide on a white porcelain surface, pour the solution at once into a beaker, wash out the flask and transfer the washings to the beaker, taking special pains to exclude any zinc, mercury or other reducing agents, add 2 c. c. of H_2SO_4 , make up the solution to 250 c. c. with pure recently-boiled water and titrate with standard solution of permanganate for the ferric oxide present in two grams of air-dry soil.

Preparation of standard permanganate solution.—Dissolve 3.156 grams of pure crystallized permanganate of potassium in 1,000 c. c. of distilled water at 16° , and preserve this in ground-glass stoppered bottle, shielded from the light. Standardize this solution with pure ferrous sulphate or ammonic-ferrous sulphate, or oxalic acid, according to directions in Johnson's Fresenius, § 112, or Sutton's Volumetric Analysis, § 30, and determine the equivalent weight of Fe_2O_3 for each c. c. of the permanganate solution.

The weight of ferric oxide deducted from ferric oxide and alumina (14), with corrections for filter ash and phosphoric acid, will give the weight of alumina in two grams of air-dry soil.

16. *Manganese.*—Concentrate the filtrate and washings from B to 200 c. c. If a qualitative test of the soil shows the presence of manganese, add a few drops of bromine to the solution till the color becomes orange, and keep the solution at the temperature of 60° for twenty-four hours. The manganese will separate as a brownish hydrate, $\text{Mn}_2\text{O}_2(\text{OH})_2$. Filter, wash the precipitate, dry, and heat to redness, weigh and estimate as Mn_3O_4 .

17. *Lime.*—If no manganese is precipitated, add to solution B, or the filtrate and washings (from 16), 20 c. c. of a strong solution of NH_4Cl and 40 c. c. of saturated solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to completely precipitate all the lime as oxalate and convert the magnesia into soluble magnesian oxalate. Heat to boiling and let stand for six hours till the calcic oxalate settles clear, decant the clear solution onto a filter, pour 50 c. c. of hot distilled water on the precipitate and again decant the clear solution on the filter, trans-

fer the precipitate to the filter and wash it free from all traces of oxalates and chlorides. Place the funnel over the mouth of a 500 c. c. Erlenmeyer flask, puncture the apex of the filter with a glass rod, wash the oxalate into the flask with a jet of water, dissolve any adhering oxalate from the filter by dilute H_2SO_4 (ten per cent solution), wash the filter with a stream of distilled water, add to the flask 20 c. c. of H_2SO_4 , make the volume up to 300 c. c., heat to 70° and titrate with a standard solution of permanganate of such strength that one cubic centimeter will be decolorized by .0063 grams of crystallized oxalic acid. Each c. c. of permanganate solution will represent .0028 grams of Ca O.

18. *Alternate method.*—Transfer the washed and dried oxalate to a tared platinum crucible, burn the filter on the crucible cover, add the ash to the precipitate, cover this with conc. H_2SO_4 , heat gently to dryness, and then intensely to expel excess of H_2SO_4 , cool in desiccator, and weigh. Estimate the increase of weight, minus filter ash, as calcium sulfate. $CaSO_4 \times .41158 = CaO$.

19. *Second alternate method.*—Transfer the precipitate to a tared platinum crucible, burn the filter and add this to the precipitate, heat the crucible and contents to low red heat to burn the oxalate. Moisten the cooled mass with a saturated solution of ammonic carbonate, dry and heat cautiously to low red heat, cool and weigh. The increase of weight (minus filter ash) represents calcic carbonate, $CaCO_3 \times .56 = CaO$.

20. *Magnesia.*—Concentrate the filtrate and washings (from 17) to 200 c. c., place in half liter Erlenmeyer flask, add 30 c. c. of a saturated solution of Na_2HPO_4 , and 20 c. c. of conc. NH_4OH , cork the flask and shake violently at intervals of a few minutes till crystals form, then set the flask in a cool place for twelve hours. Filter off the clear liquid through a tared Gooch filter, transfer the precipitate to the filter and wash with dilute ammonic hydrate (1: 3) till the filtrate is free from phosphates; dry and ignite the crucible, at first gently and then intensely, to form magnesium pyrophosphate. The increase of weight $\times .36024 = MgO$. By using an Erlenmeyer flask free from scratches and marks, and shaking violently instead of stirring with a glass rod, the danger is almost entirely avoided of crystals adhering to the sides of the vessel. But if crystals do adhere they are as readily removed

by a rubber tipped glass rod from an Erlenmeyer flask as from a beaker.

21. *Sulfuric acid*.—Evaporate 200 c. c. of Solution A (12) nearly to dryness on a water bath to expel excess of acid, then add 100 c. c. of distilled water; heat to boiling and add 10 c. c. of solution of BaCl_2 , and continue the boiling for five minutes. When the precipitate has settled, pour the clear liquid on a tared Gooch filter, heat the precipitate with 50 c. c. of boiling water, and transfer the precipitate to the filter and wash with boiling water till the filtrate is free from chlorides. Dry the filter and ignite strongly. The increase in weight is barium sulfate, which $\times .34331 = \text{SO}_3$ in two grams of air-dry soil.

22. *Phosphoric acid*.—To the filtrate and washings from 21 add NH_4HO to alkaline reaction, then $(\text{NH}_4)_2\text{CO}_3$ and a few drops of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to complete precipitation; boil, settle and decant the clear solution on a filter, add boiling water to the precipitate and again decant; finally bring the precipitate on the filter and wash thoroughly. Dissolve the precipitate in HNO_3 , and add molybdate of ammonium in excess to the solution. Keep at temperature of 70° for six hours, and from the phosphomolybdate of ammonium, estimate the phosphoric acid in the usual way.

The material used in estimation of ferric oxide and alumina (14) may also serve for a separate estimation of P_2O_5 . After titration with permanganate, heat the solution to boiling and precipitate with NH_4HO . Wash the precipitate by decantation, dissolve in hot HNO_3 and precipitate by ammonic molybdate as before, and estimate as pyrophosphate of magnesia. The pyrophosphate $\times .6396 = \text{P}_2\text{O}_5$. In estimating the alumina in the mixed precipitate of ferric and aluminic oxides and phosphates, the P_2O_5 must be subtracted to obtain the final weight of alumina. Thus, from the final weight of the precipitate, by NH_4HO (14) subtract the filter ash, the ferric oxide as determined by titration, then the P_2O_5 , and the remainder will be Al_2O_3 .

The solubility of the phosphates in the soil is intimately related to their availability for growing crops. It has been assumed that phosphates soluble in acetic acid are active and immediately available for crops, and that soils containing acetic-soluble phosphates will not be benefited by the use of super-phosphates. To determine the solubility of soil phosphates, boil ten grams of soil

in 50 c. c. of strong acetic acid for fifteen minutes, filter, evaporate the filtrate to dryness, ignite, dissolve the residue in HNO_3 with heat, and test the solution with excess of molybdate of ammonium at 70° .

23. *Potash and soda*.—Evaporate the filtrate and washings (from 22) to dryness, heat to low red heat to decompose oxalates and expel ammonia salts, dissolve in 25 c. c. of distilled water, filter and wash the precipitate, add to the filtrate and washings 10 c. c. of baryta water, and digest for an hour. Filter and wash precipitate, add ammonic carbonate to the filtrate to complete precipitation of baryta, filter and wash this precipitate. Evaporate the filtrate and washings in a tared platinum dish, gently ignite the residue to expel ammonic salts, cool and weigh. The increase of weight represents the chlorides of potassium and sodium in two grams of air-dry soil.

Separate and estimate the potassium chloride by platinic chloride according to the official method of the Association of Agricultural Chemists.

Subtract the weight of potassium chloride as thus found from the weight of potassium chloride and sodium chloride. The difference represents sodium chloride.

Alternate method.—For alternate method for alkalies, use J. Lawrence Smith's method as given in Crook's Select Methods, second edition, pp. 28 to 40.

24. *Other alkali metals*.—The salts of lithium, cesium and rubidium are occasionally found in very small amounts in soils. The agricultural uses of these salts are still in question, and their amount is too small to admit of quantitative estimation. A qualitative examination may be made by the spectroscope with the water-soluble materials (8) evaporated to dryness and dissolved with two or three drops of HCl . Test by spectroscope with platinum wire in Bunsen flame.

25. *Nitrogen of the soil*.—The combined nitrogen in the soil and the state of combination in which it is held are subjects of great importance to the agricultural chemist. The nitrogen compounds in the soil are usually placed in three classes:

1. The nitrogen combined with oxygen as nitrates or nitrites, existing as soluble salts in the soil.

2. The nitrogen combined with hydrogen as ammonia, or organic nitrogen easily convertible into ammonia. The ammonia

may exist as salts or be occluded by hydrated ferric or aluminic oxides and organic matter in the soil.

3. The inert nitrogen of the soil or the humose nitrogen.

The nitrogen in the first and second classes is considered the active nitrogen of the soil so far as plant food is concerned, while the inert nitrogen is, for the time being, incapable of affording sustenance to agricultural plants, and hence is properly placed in a class by itself. But the exchanges between the first and second classes are well known to chemists; the reduction of nitrates to ammonia, and the oxidation of ammonia to nitrates are familiar to agricultural chemists. It has also been a matter of discussion which of these forms is best fitted to nourish plant life. They seem to have equal agricultural activity, and their exchanges are matters of almost daily occurrence. Why should they be separately estimated in an agricultural chemical analysis? Why not class them together as ACTIVE SOIL NITROGEN and estimate their amount in one operation?

26. *Active soil nitrogen.*—The material proposed for reducing the nitrates to ammonia, and at the same time to bring ammonia salts and organic nitrogen into condition for separation by distillation, is sodium amalgam. Liquid sodium amalgam may be readily prepared by placing 100 c. c. of mercury in a flask of half liter capacity, covering the warmed mercury with melted paraffine and dropping into the flask at short intervals metallic sodium the size of a large pea (taking care that the violence of the reaction does not project the contents from the flask), till 6.75 grams of sodium have combined with the mercury. This amalgam contains one-half of one per cent of sodium, and may be preserved indefinitely under the covering of paraffine. The mercury is easily recovered at the close of the operation, and nothing of value is wasted except the sodium.

To estimate the active soil nitrogen, weigh fifty grams of air-dry soil and place it in a clean mortar. Take 200 c. c. of ammonia-free distilled water, rub up the soil with a part of the water to a smooth paste, transfer this to a flask of one liter capacity, washing the last traces of the soil into the flask with the rest of the water. Add 25 c. c. of the liquid sodium amalgam, and shake the flask so as to break the sodium amalgam into small globules distributed through the soil. Insert a stopper with a Kroonig valve and set aside in a cool place for twenty-four hours. Pour into the flask 50 c. c. of milk of lime and distil on a sand bath 100 c. c.

into a flask containing 20 c. c. of decinormal sulfuric acid, and titrate with decinormal soda solution, using dimethyl orange as indicator. Estimate the nitrogen of the ammonia found as *active soil nitrogen*.

If the ammonia produced is too small in amount to be readily estimated volumetrically, determine the ammonia by Nesslerizing the distillate.

27. *Estimation of nitrates in the soil.*—When it is desired to estimate separately the nitrates in the soil the following modification of 26 may be used: Evaporate 100 c. c. of the soil extract (8) to dryness on the water bath; dissolve the soluble portion of the residue in 100 c. c. of ammonia-free distilled water, filtering out any insoluble residue, place the solution in a flask and add 10 c. c. of liquid sodium amalgam, insert stopper with Kroonig valve, set it aside to digest in a cool place for twenty-four hours, add 50 c. c. of milk of lime, distil and titrate as in 26, and estimate the nitrogen as $N_2 O_5$.

Nesslerizing may be substituted for titration when the amount of nitrates is small.

An approximate estimation of the amount of nitrates will be of value in determining which method of estimation to use. This may be done by evaporating a measured quantity of the soil extract (8) say 5 c. c., more or less, on a porcelain cover on a steam bath or radiator, having first dissolved a minute fragment of pure sulfate of brucia in the soil extract. When dry, pour over the residue concentrated sulfuric acid free from nitrates, and observe the color reactions produced.

If the nitrate (reckoned as KNO_3) left upon evaporating the quantity of water taken does not exceed the two thousandths part of a milligram, only a pink color will be developed by adding the sulfuric acid; with the three thousandths part of a milligram, a pink with faint reddish lines; with the four thousandths part, a reddish color; with the five thousandths part, a red color.

By increasing or diminishing the amount of soil extract evaporated to secure a color reaction of a certain intensity, an approximate estimate may be made of the amount of nitrates present.

Blank experiments to test the acid, and the brucine will be required before confidence can be placed in such estimation.

28. *Total nitrogen of soils.*—The total nitrogen of soils may be determined by the usual combustion with soda-lime, but this

process is often unsatisfactory, because of the large amount of material required when the organic matter or humus is in small amount.

A modification of the Kjeldahl method is more easy to carry out, and gives results equally satisfactory. Weigh out twenty grams of air-dry soil, place this in a Kjeldahl flask and pour in 20 c. c. of sulfuric acid (free from ammonia) holding in solution one gram of salicylic acid. (If the soil contains much lime or magnesia in the form of carbonate, enough more sulfuric acid must be added to secure a strongly acid condition of the contents of the flask.) Add gradually two grams of zinc dust, shaking the contents of the flask to secure intimate mixture. Place the flask in a sand bath and heat till the acid boils, and maintain the boiling for ten minutes. Add one gram of mercury and continue the boiling for one hour, adding 10 c. c. of sulfuric acid if the contents of the flask are likely to become solid. Cool the flask and wash out the soluble materials in the flask with 200 c. c. of pure water, leaving the heavy earthy materials in the Kjeldahl flask. Rinse the residue with 100 c. c. of water and add this to the first washings. Place this soluble acid extract in a liter digestion flask, add 35 c. c. of solution of potassium sulphide and shake the flask to secure intimate mixture of the contents. Introduce a few fragments of granulated zinc, pour in 75 c. c. of saturated solution of caustic soda, connect the flask with a condenser and distil 150 c. c. into a flask containing 20 c. c. of decinormal sulfuric acid, and titrate with decinormal soda solution, using cochineal or dimethyl orange as indicator.

Enter the nitrogen found in this operation as *total soil nitrogen*.

The difference between the total soil nitrogen and the active soil nitrogen will express the inert nitrogen of the soil.

29. *Acid soils*.—Soils of good agricultural quality are usually neutral or slightly alkaline, but soils are found which give a decidedly acid reaction when blue litmus paper is pressed upon the moist surface. Swamp muck is often acid from the presence of humic acid. Drying the muck removes the acid quality by rendering the muck insoluble in water. If an acid soil becomes neutral by drying, and the water filtered through the dried soil is free from acidity, it is probable that the acid condition was caused by an organic acid of the humus class. But if the acid condition persists after drying the soil, the cause is to be sought in sulfates of some heavy metal, e. g., iron or copper, whose sulfates have an acid reaction.

METHOD FOR ANALYSIS OF ASHES.

PREPARATION OF ASH.

The material before combustion must be thoroughly cleaned from all foreign matters, especially from adhering soil: woods, barks, roots, etc., by brushing and dusting, wiping with a moist sponge, and finally by rubbing gently with a soft cotton cloth; seeds by placing on a fine sieve and drenching them with distilled water with constant shaking till the water runs off clear, and finally rubbing the seeds between a soft cotton cloth. The material should then be dried to constant weight at the temperature of boiling water.

COMBUSTION OF ORGANIC SUBSTANCES.

The combustion should be carried on at a comparatively low temperature, never reaching a full red heat, because of danger of volatilizing alkaline chlorides, etc., nor in a strong draught of air lest the lighter parts of the ash, e. g., silica, be carried away.

Combustion is best carried on in a flat platinum dish in a cast-iron muffle, eighteen inches long, three and a half inches high, and five inches wide at the bottom, the muffle resting on a fire-brick inside the furnace to moderate the bottom heat, and the fuel piled upon the top and sides of the muffle to burn the material by surface heat.

When this "Lawes & Gilbert muffle" is not at command the ordinary assay furnace may be used by placing a fire-brick under the muffle, placing the platinum dish and material for combustion near the middle of the muffle, feeding the furnace with fuel on the top and sides of the muffle so as to maintain it at a low red heat, and leaving the plug of the muffle so as to allow a very slow draught of air.

When no muffle of any kind is available the substance may be burned to ash in a platinum dish properly guarded. In place of a muffle use the sheet-iron dish commonly employed for a four-inch sand-bath. Place the empty sheet-iron dish on an iron tripod or other support, so that the gas flame from a Bunsen

burner may cover the whole bottom of the dish. On this dish place a sheet-iron cone (of Russia iron), six inches high, three and a half inches in diameter at the bottom, and one inch at the top. Such dish-and-cone-cover approximates the condition of a muffle for materials placed inside the cone.

For the incineration use a flat-bottomed platinum dish, three inches in diameter and one inch deep. Place the material for combustion in the platinum dish, put this in the empty sheet-iron dish, place over the platinum dish and inside the sheet-iron dish the sheet-iron cone, and heat the sheet-iron dish to low red heat by gas flame. The cone should be made of Russia sheet-iron to avoid the danger of scales of iron rust falling into the ash during combustion.

The cost of such combustion apparatus is small and the manipulation simple, the platinum dish and contents will not be heated to volatilizing alkaline chlorides, there will not be sufficient draught of air to carry away any ash, yet the heat within the cone will slowly and securely incinerate the contents of the dish.

With substances rich in silica and alkalies it is better to first char the substance. Wash with distilled water to remove soluble salts, then dry and incinerate the residue. Evaporate the watery extract and add this to the rest of the ash.

With substances rich in phosphates, e. g., seeds and animal substances, char the material and remove salts by acetic acid, decant the acetic solution, wash with distilled water, and then complete the combustion. Add the acetic solution and washings to the final ash, evaporate to dryness, and gently ignite the whole to decompose the acetates. By this method seeds, etc., may be incinerated in eight to ten hours.

In whatever way obtained the whole of the ash should be pulverized and intimately mixed before analysis:

ANALYSIS OF WOOD ASHES.

Weigh out one hundred grams of air-dry ashes, and pass them through a ~~fine~~ sieve (~~twenty meshes to the inch~~) to separate materials manifestly foreign, e. g., nails, broken glass and pottery, pebbles, etc., and estimate the per cent of such accidental materials. Pulverize any charcoal and semi-fused portions of ash remaining on the sieve, sift them and mix intimately with the sifted ashes, and preserve in stoppered bottles for analysis.

1^o *Moisture*.—Weigh out five grams of these ashes in a tared

with round holes of 1 millimeter in diameter

platinum dish and heat to 110° C., in air bath to constant weight. Cool in desiccator, and weigh. The loss of weight $\times 20 =$ per cent of moisture in the ash.

2° *Carbon*.—Heat this dried ash in platinum dish in the sheet-iron and cone apparatus described for incinerating organic substances till the ash is uniformly grayish-white and there is no further loss of weight; weigh and determine this loss of weight, which $\times 20 =$ per cent of charcoal in original ash.

3° *Sand and silica*.—Place this ignited ash in a four-ounce glass-stoppered vial; measure out 50 c. c. of HCl (sp. gr. 1.115) and pour on the ash cautiously to prevent loss of ash by spurting, and when all effervescence has ceased, add the balance of the acid, insert glass stopper, wire it securely, and place in steam bath (described under soil analysis) for two hours; empty the vial into a platinum dish, wash the vial with distilled water, adding the washings to the ash solution, and evaporate the whole to dryness on water bath. Add 10 c. c., dilute HCl and 50 c. c. of distilled water to the contents of the platinum dish, transfer the contents to a Schleicher & Schuell filter, wash with distilled water till the last drops of filtrate are free from chlorides (when tested by solution of AgNO_3), dry and ignite the precipitate and filter. If there are no grains of sand (revealed by grittiness when stirred with a glass rod), subtract the ash of the filter from the weight of this residue and estimate the balance as silica. If sand is present, boil the ignited and weighed residue in strong solution of Na_2CO_3 to dissolve silica, wash by decantation to remove all soda salts, dry and weigh the sand, the difference between the weight of sand and silica + sand, will give the weight of silica, and this $\times 20 =$ per cent of silica in the ash.

4° *Phosphoric acid*.—Evaporate the acid, filtrate and washings from silica to 100 c. c., place this in an Erlenmeyer flask of 250 c. c. capacity, add NH_4HO till nearly neutralized, then add 30 c. c. of citro-magnesian* mixture, then 30 c. c. of conc. NH_4HO , cork

* The citro-magnesian mixture is prepared by dissolving two hundred and seventy grams of citric acid in 350 c. c. of warm water and adding, by degrees, twenty-seven grams of MgCO_3 . When effervescence ceases and the liquid is cool add 400 c. c. of dilute (1 to 10) ammoniac hydrate, and dilute the whole to a liter. Preserve in a well-stoppered bottle. In the presence of a large excess, of NH_3 , 20 c. c. of this mixture will insure the precipitation of a decigram of P_2O_5 even in the presence of ferric and aluminic salts, unless their quantity is excessive.

See Sutton's Volumetric Analysis, 5th edition, page 239.

the flask and shake the flask and contents violently at intervals of a few minutes till crystallization is well established. Set the flask in a cool place for four hours, then filter out $MgNH_4PO_4$ on a tared Gooch filter, wash the precipitate with dilute ammonia (1 to 3), dry the Gooch filter, ignite, at first gently and then intensely, to form pyrophosphate of magnesia. The increase of weight of the Gooch filter equals the pyrophosphate of magnesia from five grams of ash. This multiplied by $\frac{12.792}{5.168} \times 8 = 12.792$, will give the percentage of $P_2 O_5$ in the ashes.

In this method it is important to remove all the silica before precipitating the phosphoric acid. It is also essential to use so much of the citro-magnesian mixture as to prevent the precipitation of phosphate of iron or alumina. If the addition of the citro-magnesian mixture causes an *immediate* precipitation, the precipitate is ferric or aluminic phosphate, and not enough of the citro-magnesian mixture was used. In this case the process must be renewed from the separation of silica, and the amount of citro-magnesian mixture increased till no precipitate forms *immediately* after its addition. In this case the addition of NH_4HO in excess will cause the complete precipitation of phosphate of magnesia and ammonia after a time, while ferric and aluminic salts will be held in solution.

Alternate method.—Molybdate of ammonia. The official method for analysis of insoluble phosphates as prescribed for determination of total phosphoric acid is recommended as the alternate method.

5° Carbonic acid.—Heat four or five grams of ash in the sheet-iron and cone muffle till all charcoal is consumed; cool in a desiccator, weigh out two grams of ash and transfer to a Schroetter alkalimeter. Fill one chamber of the alkalimeter with HNO_3 (sp. gr. 1.2) and the other with conc. H_2SO_4 to dry the escaping CO_2 . Wipe the outside of the alkalimeter from every trace of dust and moisture, and weigh the apparatus. Open the stop-cock of the HNO_3 chamber and permit the acid to flow so as to decompose the ash slowly, the CO_2 bubbling up, a bubble at a time, through the H_2SO_4 . When effervescence ceases let the whole of HNO_3 flow into the reservoir below, attach a $CaCl_2$ tube to the top of HNO_3 chamber, heat the alkalimeter on sand bath to gentle ebullition and suck dry air through the apparatus till

CO₂ is removed. Set aside the alkalimeter till it becomes cold, and then weigh the apparatus. The loss of weight will represent the weight of CO₂ in two grams of ash.

Alternate method.—By Liebig's potash bulbs. The usual process of absorption by solution of KHO, weighing, etc.

6° Chlorine.—Pour out the nitric solution from the alkalimeter upon a filter, wash out the last traces of the solution, pass the soluble matters through the filter and wash the insoluble residue with the water acidulated with HNO₃. To this filtrate add solution of AgNO₃ to complete precipitation of the chlorides, boil and stir with a glass rod till the silver chloride separates in flocks, let it settle, decant the clear liquid upon a filter, add 100 c. c. of water acidulated with HNO₃ and heat to boiling, again decant the clear liquid upon the filter and wash the precipitate with boiling distilled water; finally bring the precipitate upon the filter and wash with distilled water till the filtrate gives no reaction with dilute HCl. Dry the precipitate thoroughly and transfer to a tared porcelain crucible with cover, ignite the filter on the crucible cover, moisten the ash with a drop of HCl, evaporate the excess of acid, place the lid on the crucible and heat the crucible till the silver chloride begins to melt around the edges. Cool the crucible and weigh. The increase of weight (minus the filter ash) multiplied by .1236 (i. e. $\frac{35.46}{143.43} \times 50$) will give the per cent of chlorine in the ash.

This process should be carried on in the absence of direct sunlight.

Alternate method.—Boil ten grams of ash in 400 c. c. of pure water for half an hour; transfer all to a measuring flask of 500 c. c. capacity, wash the beaker and add the washings to the flask, cool, make up the volume to 500 c. c. and mix intimately. Filter off through a dry filter 100 c. c., add a drop of solution of phenolphthalein, and neutralize with dilute HNO₃ till only a faint pink color remains, add two drops of strong solution of K₂CrO₄ and titrate with standard decinormal solution of AgNO₃ (16.956 grams AgNO₃ @ 1000 c. c.). Every c. c. of the standard silver solution equals .003546 grams of chlorine in two grams of ash, or c. c. $\times .1773 =$ per cent of chlorine in ash.

In performing this titration, watch the reaction through a plate of amber colored glass of such tint as will neutralize the

color of potassic chromate. The reaction to form silver chromate then becomes sharply defined.

The reliability of this method will depend upon the accuracy with which neutralization by nitric acid has been made. The least trace of free acid or alkaline carbonate will vitiate the results.

Second alternate method.—To 100 c. c. of the solution in the foregoing method add HNO_3 to strong acid reaction, then solution of AgNO_3 to complete precipitation, and then proceed as in the first method for estimating chlorine.

These alternate methods are based on the assumption that boiling water will dissolve all the chlorides present in wood ashes.

7° Sulfuric acid.—Place five grams of ash in a digestion vial. Measure out 50 c. c. of HCl . (sp. gr. 1.115) and cautiously pour the acid on the ash till effervescence ceases, then pour in the rest of the acid, place the glass stopper in place and wire it securely, and place the vial in the digestion steam bath for two hours. Pour the contents of the vial into a 250 c. c. measuring flask, wash out the vial and add the washings to the flask, cool, make up to 250 c. c. with distilled water and mix intimately. Filter through a dry filter 100 c. c. into a beaker, and evaporate on water bath till excess of acid is expelled; add 100 c. c. of distilled water, heat to boiling temperature and precipitate with BaCl_2 in excess. Let it stand for twelve hours in a warm place, then decant the clear liquid through a filter, add 100 c. c. of boiling water to the precipitate, let it settle and then pour off the clear liquid through the filter, repeating the process till the filtrate is free from chlorides; finally transfer the precipitate to the filter, wash this with distilled water, dry the precipitate and transfer it to a tared crucible, separating the precipitate from the filter as completely as possible, burn the filter separately, letting the ash fall into the crucible, heat this to low redness, cool and weigh. Subtract the filter ash from the increase in weight and multiply the remainder by .34335 for SO_3 in two grams of ash. (Preserve the filtrate and washings for 11°, *Estimation of alkalies.*)

8° Oxide of iron.—Filter 100 c. c. of the original acid solution (for 7°) through a dry filter, nearly neutralize with ammonia water, then add a gram of sodic acetate and acetic acid till the odor of acetic acid is perceptible, boil to precipitate ferric phosphate, filter while hot and wash precipitate with boiling distilled water till the filtrate is free from chlorides. Dissolve the ferric

precipitate on the filter with dilute H_2SO_4 into a small Erlenmeyer flask, wash the filtrate, dry and ignite the same and add the ashes to the acid solution in the flask, reduce the ferric to ferrous salt by amalgamated zinc or by a coil of magnesium wire, till a drop of the solution gives no color, with $\text{NH}_4\text{C}_2\text{S}_4$. Pour off the solution of ferrous salt into a beaker, rinse the flask and add the rinsings to the beaker, add freshly-boiled distilled water to make 200 c. c. of the solution, add 2 c. c. of sulfuric acid, heat to 70° , and titrate with standard solution of permanganate, and estimate the iron as ferric oxide.

2^d Lime.—Evaporate the filtrate and washings from ferric phosphate (8°) to 100 c. c. To the hot solution add 20 c. c. of concentrated solution of ammoniac chloride, and 40 c. c. of saturated solution of ammoniac oxalate; boil the whole for ten minutes, and then let it stand in a warm place for six hours; decant the clear liquid upon a filter, wash the precipitate twice by decantation, then bring the precipitate upon the filter and wash it free from chlorides and oxalates, testing the washings by argentic nitrate. Puncture the point of the filter with a glass rod, wash the calcic oxalate into a 500 c. c. flask by a stream by the wash bottle, dissolve any oxalate adhering to the filter by dilute H_2SO_4 (1:10), add 20 c. c. of H_2SO_4 to the flask and make the volume to 300 c. c. with pure water, heat to 70° and titrate with standard solution of permanganate in which each cubic centimeter of permanganate is equivalent to .0063 grams of crystallized oxalic acid. Each cubic centimeter of the permanganate solution used will be equivalent to .0028 grams of Ca O .

Alternate method for lime.—Dry the washed precipitate of calcic oxalate; transfer the oxalate to a tared crucible, burn the filter on a platinum wire, letting the ashes fall into the crucible, heat the crucible to low red heat, cool and moisten the contents with a saturated solution of ammoniac carbonate, dry and heat carefully to low red heat to expel ammoniac salt, cool and weigh. Subtract the weight of filter ash, and estimate the increased weight as Ca CO_3 .

Second alternate method for lime.—Dry the washed precipitate of calcic oxalate, transfer to a tared platinum crucible, burn the filter and add the ash to the contents of the crucible. Overflow the calcic oxalate with conc. H_2SO_4 , heat gently to dryness, and then intensely to expel excess of H_2SO_4 , cool in desiccator and

weigh. The increase of weight, minus filter ash, estimate as calcic sulfate, $\text{Ca SO}_4 \times .41158 = \text{Ca O}$.

10° *Magnesia*.—Evaporate the filtrate and washings from calcic oxalate to 200 c. c., pour into a clean and unscratched Erlenmeyer flask of 500 c. c. capacity, add 30 c. c. of strong solution of $(\text{NH}_4)_2\text{HPO}_4$ and 50 c. c. of conc. ammonia hydrate, cork the flask and shake violently at intervals of a few minutes till crystallization is established, and then set aside for twelve hours in a cold place. When precipitated in this way crystals will seldom adhere to the sides of the flask, yet more perfect crystallization than when stirred with a glass rod. If crystals should form on the sides of the flask they are as readily detached by a rubber-tipped rod as in a beaker. Filter through a tared Gooch filter, wash the precipitate with ammonic hydrate, diluted with distilled water (1 to 3), till filtrate is free from phosphates (acidify a few drops of filtrate with nitric acid and test with molybdate of ammonia). Dry the precipitate, ignite, at first very gently and then intensely, with blast lamp, to convert $2 \text{ Mg NH}_4 \text{ PO}_4$ into $\text{Mg}_2 \text{ P}_2 \text{ O}_7$. Cool in desiccator and weigh. The increase of weight $\times .36024 = \text{Mg O}$, in two grams of air-dry soil.

11° *Estimation of alkalis*.*—Concentrate the filtrate and washings from (7°) to 100 c. c., add $\text{NH}_4 \text{ HO}$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to complete precipitation of barium and calcium, filter, wash the precipitate, evaporate the filtrate and washings to dryness in platinum dish and ignite gently. Add to the residue concentrated solution of oxalate of ammonia, evaporate to dryness and ignite gently. Dissolve residue in distilled water, filter from insoluble Mg O , acidify the filtrate with HCl , and evaporate to dryness in a tared platinum dish and ignite gently. The increase of weight represents the chlorides of potassium and sodium in two grams of ash. Separate and estimate potassium by PtCl_4 , in the usual way, and the sodium by difference.

* Test the filtrate from (7°) for lithia by the spectroscope with a loop of platinum wire moistened with the filtrate, held in a colorless Bunsen flame. The quantity of lithia is usually too small to be determined gravimetrically, but it may be estimated by diluting the solution with distilled water till the lithia line is on the point of disappearing from the spectrum when a loop of clean platinum wire moistened with the solution is placed in the Bunsen flame. The wire must be clean for each trial, and no concentration of the salt by repeatedly evaporating the solution on the loop of wire without cleaning it. One part of Li Cl in 450,000 parts of water will show the lithia line in the spectrum.



12³ *Manganese*.—Manganese is not a usual constituent of wood ashes. Test the ashes for manganese by heating on platinum foil over a colorless Bunsen flame half a gram of ashes with a gram of sodic carbonate and a few grains of nitrate of potash. The green manganate of soda in the fused portion as it cools will show the presence of manganese.

To estimate manganese, dissolve two grams of ash in HCl. Evaporate excess of acid over the water bath, pour the whole on a filter and wash with distilled water to make 100 c. c., nearly neutralize with sodic carbonate, and then add half a gram of sodic acetate and 20 c. c. of strong bromine water and set the flask aside in a warm place for twenty-four hours, or until the bromine has nearly disappeared. Filter out the manganese oxide, wash thoroughly, transfer to tared crucible, heat gently, and then intensely, and estimate the residue as Mn_2O_4 . $Mn_2O_4 \times .93013 = MnO$.

The manganese may be precipitated by passing a stream of chlorine through the solution till fully saturated, instead of using bromine water.

The ashes of mineral coal contain only a small amount of alkalis and phosphates, but a large amount of insoluble material, clay, etc. Their value depends mostly upon the sulfate of lime and phosphate present. They are often decomposed with difficulty. They should be ground to a fine powder, and five grams placed in the digestion vial, with 50 c. c. of HCl (specific gravity 1.115) and digested in the steam bath for six hours, and the soluble portion analyzed in the usual way.

The aluminic material is in so large proportion that it is better to use the molybdic method for estimating phosphoric acid, after eliminating soluble silica.

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