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Henry P. Slade
1902.

A. C. Crawford
1905

PROXIMATE ANALYSIS

OF

PLANTS AND VEGETABLE SUBSTANCES

BY

FREDERICK ROCHLEDER, M. D.

PROFESSOR OF ORGANIC CHEMISTRY IN THE UNIVERSITY OF PRAGUE.

[Intended as instructions to beginners, and students in chemistry in the prosecution of the qualitative proximate analysis of plants, etc.]

Reprinted from the American Journal of Pharmacy.

PHILADELPHIA:
MERRIHEW & THOMPSON, PRINTERS,
Lodge St., corner of Kenton Place.
1862.

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NOTE.

The following work of Dr. Rochleder was originally published in Germany, at Wurzburg, by Stahel, in 1858.

In 1859, Mr. JOHN M. MAISCH, now Professor of Materia Medica and Pharmacy in the New York College of Pharmacy, made a translation, and offered it for publication in this city, but it was declined by the Publisher, owing to the limited number of persons by whom such a work is sought.

In May, 1860, the Editors of the *Pharmaceutical Journal*, of London, commenced the publication of a translation by Mr. William Bastick, Pharmaceutical Chemist of that city, in parts of a few pages, which continued with occasional interruption until March, 1861. Notwithstanding this translation had several defects, it was determined to adopt it as the basis of a reprint, in parts, in the American Journal of Pharmacy, Mr. Maisch having, very liberally, agreed to carefully revise the pages, before they were submitted to the printer, by a comparison with the original text. Its publication commenced in that Journal in January, 1860, and was continued until September, 1862, with but one interruption. The work as here presented will be found to vary somewhat from the translation of Mr. Bastick, and it is believed has been rendered clearer.

The subject is exceedingly difficult to convey in the abstract way in which the Author has seen fit to present it, and involves a constant repetition of terms that might perhaps have been partially avoided, and rendered more interesting to the student, if he had adopted the plan of giving actual examples of proximate analysis.

Believing that the printing of a small separate edition of the work would prove a useful aid to American pharmaceutical students, especially in the preparation of their theses, it has been accomplished and is here presented.

WILLIAM PROCTER, JR.

Philadelphia, August, 1862.

PROXIMATE ANALYSIS
OF
PLANTS AND VEGETABLE SUBSTANCES.

INTRODUCTION.

The medicinal action which many plants, or parts of plants, possess, may have been principally the earliest occasion of the examination of plants. It is probable that the analysis of plants, and particularly of their sap, was the first original labor in relation to analytical chemistry, when the term analysis could be scarcely employed in the sense which we attach to this word at the present time. Indeed, some derive the word "Chemistry" from χυμος (the sap), because the sap of plants had been the object of the earliest chemical research. The applicability of many plants to technical purposes was the later and profitable occasion for the analysis of plants and their parts. It is, therefore, evident why the earliest labors were not directed to discover all the constituents of a plant or of its parts, but had for their object the isolation of one or the other of its constituents. Chemists endeavored to isolate the medicinally active substance, or the poison of medicinal or poisonous plants, and the substances, as coloring matters, tannin, &c., of plants, used for industrial purposes, and on these accounts employed. Nevertheless, we very seldom find analyses of all parts of a plant; mostly, analyses were preferred of those parts of plants which were employed in medicine or in the arts. All analyses were undertaken from views which must remain foreign to chemistry as a science, which proceeds without regard to medical or technical objects. Another period commenced first in more recent times in the investigation of plants, in which the former predominating views were more and more thrown into the background; chemists became sensible that one constituent of a plant possessed for the plant the same degree of importance as any other, quite independently of its applicability to different objects. They perceived that all the constituents of a plant must stand in the closest relations to one another; that one is formed from the other, that the existence of one constituent could not be regarded independently of the existence of the others, and that all constituents are links of one chain. The principal result of these new views was an alteration in the method of investigating plants; it could no longer be said to be a one-sided endeavor for the isolation of a substance with a disregard to all other simultaneously existing constituents. It became necessary to search for all the constituents of a vegetable substance by analysis, and to study them closely. The inquiries concerning the process by which one constituent is formed from others, and, according to the nature of the affinities, is converted into other substances, have rendered requisite more correct analyses with reference to all the constituents.

The first efforts of chemists in the analysis of plants and their parts were limited to the separation of their constituents from one another, as far as it was possible, by their different behaviour to solvents. The substances thus separated, often still a mixture of several bodies, had a peculiar name conferred on them, but their composition, their relation to other bodies, with the exception of some observations concerning their color, or the precipitates produced by the addition of reagents, were not further investigated. From a resemblance in the properties of individual constituents with bodies already known, their identity with the same was decided upon. While some chemists rather predicted than were able to detect an unlimited quantity of different bodies in various plants by a great number of analyses in the highest degree imperfect, others proceeded to examine more closely the detected constituents individually. It was quite in the nature of things to be expected that for the investigation of the composition and constitution of their individual constituents, those bodies in particular should be selected which from their properties appeared to give a guarantee of their purity by reason of the facility with which they could be isolated and purified. For example; volatile oils, by the facility with which they are volatilized undecomposed, and are separated at certain boiling points from other volatile substances with some precision; also crystallizable bodies of some permanence which may be easily separated from other amorphous substances by their disposition to assume the crystalline form. These were the objects of attention to those men of science who expected more benefit to chemistry from a fundamental study of some substances than by the discovery of many. Thus, then, it happens that besides some few well-conducted analyses of vegetable substances, we possess a great mass of imperfect analyses, and sometimes an exact chemical investigation of one or the other constituent of a vegetable substance, in which the remaining constituents have received no consideration. There exists, at the present day, no investigation of the various parts of a plant which has been completed so that, uniting the details of each investigation of all the constituents to a whole, it could give us a representation of the constitution of the plant.

The investigation of an individual constituent of a vegetable often requires a long time, and a great expenditure of patience and sagacity, not to speak of the pecuniary sacrifice combined with it. For these reasons few of the substances have been at present examined in comparison with the number whose existence is already known. But an exact and complete analysis is endlessly troublesome when the nature of the constituents are not known. To this is to be ascribed the few analyses we possess which correspond to the acquirements of science. For an analysis which informs us what constituents a plant contains in its various parts, and in what quantity they are present therein, we seek in vain in chemical works.

As we find only some analyses of plants which possess a value, when we examine the long series of such analyses, so also we search vainly for a definite method according to which they could be arranged. There is no difficulty in explaining why no method is given for the analysis of plants such as we possess in mineral chemistry. Inorganic analysis is, in general, the analysis of defined compounds, the properties of whose elements are, for the most part, correctly known, and likewise the properties of their most important combinations with one another. When the analysis of plants treats of the analysis of mixtures which cannot be separated mechanically, then terminates the precision and certainty of inorganic chemistry, which we only can boast of in its relation to elementary analysis. The investigations of the various minerals, as phonolithe, &c., show how little we know of the means of separating the individual constituents. Every part of a plant is a mixture of many constituents not mechanically separable, the number of contemporaneously existing constituents of such a mixture being infinitely greater than in the most complex fossils. If it be difficult in this case to find out a method of separation, how much more difficult will it be with plants, whose principal constituents are so readily decomposable and changeable that they may be altered not only by the reagents employed for their separation, but act reciprocally on one another, producing bodies which were not originally present.

When we have to deal, in the analysis of plants, with known compounds, as is mostly the case in mineral chemistry, still the investigation is not easy. In the analysis of a vegetable substance heretofore unexamined, we can reckon almost with certainty on meeting with one or more quite unknown bodies. The intimation which has been already often expressed, that a rational method for the analysis of plants is quite impossible until at least we are correctly acquainted with the majority of vegetable bodies, is, consequently, not without some foundation, for only when we know the properties of the constituents of plants and their combinations, can a method be established which will be available for all time. Consequently, both for the present and the next century we must renounce the hope of a permanent and rational method of vegetable analysis, as it is scarcely possible, in a shorter space of time for chemists to study correctly and copiously enough the majority of the constituents of plants. The number of plants is great, and increases yearly by fresh discoveries, and with the number of plants the number of peculiar vegetable substances also increases. Therefore, if we would wait for the establishment of a method of vegetable analysis until we are acquainted with the majority of all vegetable bodies, we should never arrive at one, because we can only learn the properties of these bodies by organic analysis, and to investigate plants without some such method of analysis tends to aimless researches. However, this is clear, that every method of vegetable analysis which is arranged for the present, must be only a provisional one, to be made more comprehensive as soon as the knowledge of the constituents of plants has been extended by its aid—in other words, the provisional method is the means to arrive at better methods.

With the majority of the older analyses of vegetables the foundation of the process was the application of different solvents in succession. Ether, alcohol and water were the solvents most commonly employed. In many cases, the residues were brought into contact with dilute acids and alkalies, generally with the assistance of heat, after having been more or less exhausted with the three fluids mentioned. In consequence of the facility with which many substances are transformed into others by the action of acids and alkalies in the heat, these latter methods of treatment often gave rise to incorrect views of the composition of the plants, or those parts under examination. The treatment of the substance to be examined in succession with ether, alcohol, and water, would have afforded much better results, as in fact was mostly the case when two conditions which did not prevent a complete separation in this way, were not sufficiently attended to and calculated upon. These conditions are the following: the exhaustion of the substance under examination with one fluid must always be imperfectly effected before the second is allowed to act thereon. We cannot so prepare the material that each individual cell and its contents are exposed to the action of the solvent, because the material reduced to an impalpably fine powder, and exhausted with a solvent, affords again to the same solvent substances after it has been freshly triturated. Thus it happens that there are always bodies retained in the substance under examination after its treatment with a solvent which are soluble therein. If we now bring the substance in contact with the second solvent, the bodies not only will dissolve that we intend therewith to extract, but often also the remainder of the bodies which the first solvent left behind. The same holds good with regard to the third solvent. A solution of certain bodies by a solvent will afford thereby no means in many cases for the separation of other bodies which are insoluble in this solvent, because frequently substances which are *per se* insoluble in a liquid, are not insoluble in a solution of other substances in the same liquid. In this way we obtain, in a watery or alcoholic extract of a vegetable substance, bodies which *per se* are insoluble in water or alcohol, but which, by the agency of other bodies, are dissolved therein. Independently of these detrimental circumstances, which are produced by an incomplete exhaustion with one liquid before the application of a second solvent, there is associated the condition that the exhaustion with a liquid, at the same time, produces a solution of bodies which should not dissolve, because they are held to be insoluble therein. But what is termed insoluble are, in the majority of cases, only very difficultly soluble substances, that is, such substances as require a large quantity of the liquid when a little shall be dissolved therein. However, when it is desired to exhaust as much as possible a substance by means of a liquid, it is necessary to employ a large quantity of the liquid, as it is essential to effect the extraction with renewed portions of the solvent. In so great a quantity of liquid, a quantity not inconsiderable of the very difficultly soluble bodies dissolve, which, by the concentration of the liquid, are often prevented from being separated by other constituents, thus rendering impure, in a serious degree, the substance which we wish to extract free from the other constituents.

The method for the analysis of plants, given in the following pages, depends on the treatment of materials with various solvents. Every resulting solution then undergoes a further appropriate treatment therein. It must be here mentioned that the preparation of some of these solutions, and their further investigation, promise no certainty, and that only by a comparison of the results which are obtained by the investigation of all the individual constituents, separately and collectively, can we deduce a correct conclusion on the constitution of a vegetable product.

It would have been, as every competent judge will concede, a perfectly unfruitful, useless labor, to publish, as far as it is known, the behaviour of all known constituents of plants with reagents; and more so, because we would but deceive ourselves or others if from the apparently identical behaviour of two analogous bodies with some reagents a conclusion with regard to their identity should be drawn. Only by identical composition, surely established by elementary analysis, the identity of reactions proves something; through the attempts at recognizing and detecting in a mixture of bodies the individual constituents by their behaviour with reagents without further corroboration, have arisen numberless false statements. Malic acid, gum, &c., are stated to have been found as constituents in numerous plants. Whoever has carefully tested these statements will find, by a repetition of the analysis, no malic acid, and convince himself that the supposed gum is a salt of an organic acid with an inorganic base, which possesses no remarkable taste, dries to a gum-like mass, dissolves in water, and is precipitated by alcohol therefrom in white flocks, &c. To prove that a body, which has been obtained by analysis, is identical with an already known substance, the elementary analysis of this body, or one of its suitable combinations, must be undertaken. Only the reactions of substances rendered pure, deserve in this respect consideration, not the reactions of mixtures. Without elementary analysis, in regard to identity, only a high degree of probability can be arrived at, but no certainty. But an error, in a high degree probable, is more dangerous than a palpable mistake. Elementary analyses, which alone bestow a value on the identity of reactions, are, besides, the least difficult and tedious part of the labor. They require no great amount of ability. This is only necessary for the preparation of the substance to be analyzed.

SECTION 1.—*Mechanical treatment of the material preliminary to its investigation.*

When we desire to be able to learn the composition of a vegetable substance, the first requisite is to simplify and facilitate the subsequent chemical operations by a suitable mechanical preparation of the substance to be examined.

If we were in a position so to dismember a plant that only its equally similar cells were separated and subjected to a chemical investigation, not only would the analysis be thereby greatly simplified, but a source of error would be quite removed—the formation of bodies not originally present, by the action of the constituents of dissimilar cells on one another. But such an anatomical preparation of the material for the subsequent chemical investigation is an impossibility. Now, as the separation of the individual tissues of a plant, at least of such a large quantity of the material as we require for a chemical investigation, belongs to the limits of the impossible, we must accomplish at least the possible in this respect by the mechanical separation of the parts as completely as practicable. How far this can be effected in certain cases depends on the structure and anatomical relations of the substance to be examined.

To render the substance intended for examination suitable for treatment with liquids, it must be comminuted. The more points of contact presented by the material to the liquid, the better it is. The comminution cannot easily be carried too far with materials which cannot be penetrated with the liquid which is intended for their extraction. In this case merely moistening of the surface of the smallest portions takes place. The smaller these portions, the greater the surface, the more completely the extraction with the solvent is accomplished. With a material which is readily penetrated with the solvent employed, a careful comminution is superfluous. In so far as a substance swells up by means of the fluid used for its extraction, its minute division is objectionable. Under such circumstances a gelatinous mass results, which absorbs and retains much fluid, the solvent cannot be separated, and when pressure is employed for this purpose, the pasty mass escapes through all the pores of the press-cloth.

Frequently a very fine powder of the substance cannot be prepared on account of the peculiar tenacious property of the material. Nevertheless, if it be desirable to divide such a substance as much as possible, it may be often readily effected after the removal of the greatest part of several constituents.

Often a certain degree of moisture, the presence of water, renders the substance tenacious and elastic, so that it is difficult to pulverize it. A careful drying suffices in such cases to deprive the material of its tenacity, and to render it pulverizable. For example, it is extremely difficult to beat to a fine powder coffee beans in the condition in which they exist in commerce. However, this is easily effected when they are exposed for several days to a temperature between 140° and 150° Fahr., and thereby rendered free from a portion of their hygroscopic water. The presence of a fatty oil oftentimes makes the substance to be examined tenacious; after the expression of the oil from the coarsely powdered material, the residue can then be finely divided.

When resins or fats in smaller quantities are the cause of the tenacity and elasticity, the comminution of substance may be effected by first removing, by a suitable solvent, the objectionable portion of the constituents from the coarsely powdered substance, then drying it, when it can be finely divided.

The pulverization is always facilitated when it is accomplished by stamping or rubbing, by separating the coarser from the finer particles by means of a sieve, and repeating the operation on the coarser portion.

Whether a substance is to be reduced to a fine state of division by stamping, rubbing, rasping, cutting, or crushing between rollers, depends on its properties, and no instructions can be previously given here in this respect. The apparatus required for these operations are so well described in various works, and rendered intelligible by the aid of engravings that it appears superfluous to enter more closely into this matter.

Before the pulverized material is treated with appropriate solvents, it is advisable in all cases to observe whether it is not possible by expression to completely separate certain constituents. In the investigation of vegetable substances which contain liquid fats, or fats fusible at a moderate temperature, a great portion of the fat may be separated by cold expression, or by plates heated to 212° Fahr. In the investigation, the advantage is not only thereby gained that a considerable quantity of fat is separated from the other constituents, but many other advantages are thus attained in the further treatment of the substance—for example, in its extraction with water as well as with alcohol, as the presence of a large quantity of fat occasions many inconveniences. The watery decoction, as well as the watery residue, which remains behind after the expulsion of the alcohol from the extract prepared with spirit, is rendered, with materials rich in fat, often turbid, and cannot be obtained clear by filtration. With such liquids the filtration proceeds with extreme slowness. This disadvantage is everywhere evident when saponin or analogous bodies are present in solutions, which divide the fat so finely and suspend it in the liquid, that it passes through a moist filter simultaneously with the liquid. Even when the liquid can be obtained clear by filtration, its filtration is very much retarded thereby, and the opportunity to decompose is afforded to the dissolved substances. When a turbid fluid, containing fat, is mixed with a saline solution to produce a precipitate, the precipitate mechanically throws down the fat, becomes so pasty in consequence, and difficultly divisible in water, that its solution in acids, its decomposition by a current of gas, and by other agents, are very difficult to be accomplished. There often remains no other means for the separation of the fat than to precipitate a portion of the constituents, which are dissolved in the fatty liquid by a reagent, and then to filter the liquid. It is evident that by this method of separating the fat a portion of the other constituents are sacrificed. It is advisable to avoid such loss when it can be prevented.

SECTION 2.—*On the nature of the substance to be examined, and on the quantity required for its investigation.*

If we desire the investigation of one, several, or all the constituents of a plant, by means of analysis, we should endeavor to obtain the material for the investigation in the freshest condition possible. I have had occasion to convince myself that some fresh vegetable substances, even when most carefully dried and preserved, did not, after some months, contain even a trace of several bodies which were easily detected in their recent state. It is often impossible to use the material in a fresh state for investigation. When plants or their constituents have to be examined, which are brought from distant countries, we must be contented to obtain them in the best possible state of preservation, as it is not possible to draw with full certainty a correct conclusion from the composition of such dried materials as to their composition when in a fresh condition. Indeed, such investigations are calculated to afford very useful results in pharmacological, dietetic, or industrial relations, because the materials are employed in the same condition in which they are investigated; but they are not suitable for giving a representation of the true composition of the living plant. Chemical changes often proceed on keeping the plants without observable external alterations, and the composition resulting from these changes is then often regarded as the original one. Consequently, when we are in a position to select the material for the analysis of a plant, and are not compelled to employ for the investigation vegetable substances which we cannot procure in a fresh state, it is always most convenient to select such plants or their parts as can be obtained in a fresh condition, which enable us to undertake the investigation at places not far distant from where they grow. Only in these cases are we sure to obtain a correct result from a correct analysis; that is, to be able to learn the true composition of the living plant. Results are only obtained in this way, which, in vegetable physiology or botany, are truly trustworthy. It would appear, from what has been stated, that the field of activity is a circumscribed one; but this is not so. We know the composition of plants which grow in our immediate neighborhood, less than that of many others. The tree under whose shadow we walk, as well as the vegetable we tread upon in our path, are chemically unknown things. We know the salicin of the willow and the populin of the poplar, we know the amygdalin of the almond and the volatile oils of the chamomile and the sage, but a representation of the composition of those plants we have not. He who knows the composition of oil of valerian, knows nothing of the composition of the plant which produces it. We know infinitely more of the cinchona-tree and other exotic plants than of the lime and nut trees of our own woods. If all chemists were to occupy themselves with the analyses of plants, after several centuries there would be still materials enough growing before their eyes to employ hundreds of hands with their chemical investigation.

The investigations which spread the most light are those which enable us to learn the composition of the individual parts of a plant at different periods of its growth, and at different epochs of its development. The material for such investigations can scarcely be procured at a distance, so we are constrained to examine that which lies near us, and not to seek afar off that which is better and easier obtained at home.

With regard to the quantity of material required for the investigation, no certain weight or measure as a minimum can be fixed. But it is better in all cases to employ too much, rather than too little, material. With materials which cannot be procured in any required or unlimited quantity, it is better to commence no analysis. Through a scarcity of material the operator is constrained to terminate the research, unable to complete it, and has time and money uselessly spent, or he arrives at incorrect results, when, from a failure of the material, he is unable to undertake a number of control experiments. It is on that account that the results of analyses which, as frequently happens, were undertaken with a few ounces of the material, seldom possess any value. In the best instances of such analyses some constituents were overlooked which were present in small quantities in the material. Many incorrect statements are made in such analyses because an insufficient number of methods of separation were employed. Mixtures of bodies are regarded as new substances, and are long carried on as the ballast of science, until later analyses prove their non-existence. Substances which are widely different from one another are confounded with each other, because an insufficiency of material was employed to prepare enough of the constituent to establish its composition in the pure state. Thus, one chemist finds tartaric acid, when another is stated to have found oxalic acid, and a third seeks unsuccessfully for tartaric acid, and finds instead citric acid. If we could previously determine the quantity of material, it would often be useful, but such a previous determination is impossible. The operator can easily ascertain how much water or dry substance a material contains; and when it is very rich in water, concludes therefrom that he will require proportionately more of it than from one poor in water under other similar conditions. But from the abundance of dry substance, no conclusion can be drawn as to the quantity which will be required for the investigation. Many parts of plants contain large quantities of cellulose, starch, and other ordinary constituents, which may be readily detected, but little of the remaining constituents. Frequently all the constituents are present in rather considerable quantities, so that the investigation can be terminated with a little material, unless one constituent is present in very small quantity. In such a case a very great mass of material must be operated upon to obtain the constituent which is present in small quantity, because from a smaller quantity of the material we cannot obtain enough to arrive at a conclusion upon its nature by a suitable research. If we abstract from the weight of a substance under examination the weight of water which it contains, also that of the inorganic constituents and the weight of cellulose which remains after the material has been treated with ether, alcohol, water, diluted acids, and alkalies, we obtain an inconsiderable residue, which represents all the other bodies together present, except the cellulose, water, and inorganic constituents. As a general rule, we seldom find more than 300 grains of these bodies in from 3 lbs. to 5 lbs. of the crude material, which must be subjected to a close investigation if we would arrive at a correct view of their true nature. From this general estimate, it will be seen that 5 lbs. of crude material is a quantity that scarcely is sufficient at any time for the completion of an analysis. The least quantity of material is required in those cases where the known, easily recognized constituents are in the smaller quantity, and the unknown ones, on the contrary, are in the greater quantity.

SECTION 3.—*Treatment of materials with various solvents.*

The material mechanically prepared for the investigation should be divided into several parts, and each part treated with a solvent to obtain a number of extracts, which are to be submitted to a further examination.

The fluids most frequently used for a long time for this purpose are ether, alcohol, and water; the latter is often mixed with acids or alkalies. The ether is generally used in a perfectly pure condition, the alcohol mixed with more or less water, according to the strength of the spirit required. Experience has shown that water, after it has extracted bodies from a material which are quite soluble in water, also possesses the power of dissolving substances, as already mentioned, which are either insoluble, or difficultly soluble *per se* therein. This disadvantageous circumstance occurs less with alcohol, and still less with ether. In consequence, it has become a general rule to treat the material first with ether, then with alcohol, and lastly with water, when it is intended to treat it with these three solvents. I have found it the most convenient to extract a portion of the material with hot water, another portion with cold water, a third portion with acidulated water, a fourth portion with ammoniacal water, a fifth portion with alcohol, and to treat a sixth portion with ether. In peculiar cases, a treatment with alcohol containing ammonia or potash is suitable. The preparation of these solutions, as well as the precautions to be therein observed, will here be more minutely discussed.

I.—*Treatment of the substance under examination with boiling water.*

The treatment with boiling water, as previously stated, should afford us a decoction and a distillate, of which the former will contain the non-volatile constituents and the non-volatile compounds of the volatile bodies in so far as they are soluble in water, the latter the volatile, or rather the constituents, distillable with water, of the material. For the treatment of the material under examination with water, an ordinary still is required. The still, which must be sufficiently capacious, is filled with the water intended for the extraction of the material, and this is heated to the boiling point. When the water boils, the material suitably divided, is thrown into the water, the receiver adjusted, and proper care taken for its refrigeration. To introduce the divided material, carefully into the boiling water, and to prevent burning as much as possible, I employ an apparatus which I will in a few words here describe. This consists of a cylinder, open at the top and closed at the bottom, made of tinned iron plate. The sides and the bottom of the cylinder are perforated with holes, so that the cylinder represents a coarse sieve. Externally, at the bottom, three short feet are attached, and a cover of tinned iron plate, likewise perforated, closes the cylinder in which it is inserted, being in diameter about two lines less than the cylinder. The material is introduced into this cylinder without being pressed, and the cover is laid on. By means of twine the cover is fastened to the place where it lays. The size of the cylinder depends upon the capacity of the still. In filling the cylinder, care must be taken that the material is only in such quantity that it is covered at least three inches high by the water in the stlll when the cylinder is inserted in the boiler, which is dóne while the water boils.

When the material is thus introduced into the already boiling water, the decomposing action of ferments contained therein on the other constituents is prevented, from which decomposition products would be produced whose formation must not be permitted. We know by the treatment described that bitter almonds afford no bitter almond oil, and mustard no mustard oil. It is of importance in the investigation of the distillate to prevent the formation of volatile products from the non-volatile constituents of the material. But independently of the volatile decomposition products which could be formed when the directions mentioned are not observed, decomposition might occur which would give rise to erroneous ideas of the composition of the substance under examination in the investigation, of its watery decoction, because there are in many plants bodies, besides ferments, which are broken up into two or more non-volatile products when they are long in contact with water and ferments. This is the case when the material is placed in cold water and then heated to the boiling point, which occupies a longer time the greater the quantities of material and water that are to be raised to the boiling point. The root of the rubia tinctorum is an example of this kind, which contains a peculiar ferment by which ruberythric acid in the presence of a ferment is decomposed into alizarine and sugar, when the comminuted root is placed in cold water and then heated to the boiling point. On the contrary, when the divided root is introduced into boiling water, the ruberythric acid remains unchanged and dissolves in the water, while the ferment is converted into an inactive condition.

With materials which contain easily oxidizable constituents it may be readily perceived that by the introduction of the substances into boiling water their oxidation takes place in a much smaller degree than by being immersed in cold water and subsequently heated. The decoctions which are obtained according to the method here recommended are on that account generally much paler than those produced by gradual heating.

When the substance to be extracted has been sufficiently long in contact with the boiling water, and no more volatile products can be detected in the distillate, in case such have been formed therein at the commencement of distillation, the operator, after the neck has been removed, withdraws the cylinder and its contents, places it on a capacious dish or basin to catch the droppings, and presses the material in a press between two vertical plates. The decoction is filtered, whilst hot, through paper. To prevent it cooling while being filtered, as large a number of funnels as are necessary should be employed. If, in consequence of the liquid cooling, anything should be separated by the filter which had been previously dissolved, the filtration must be performed by means of a hot water funnel. From a watery decoction of the flower-buds of capparis spinosa, the quercitrine, or the so-called rutinic acid, is precipitated by cooling in voluminous flocks. The distillate thus obtained is either pure water, in those cases where the substance under examination did not contain bodies distillable with the vapor of water, or such as are not in a free condition, but in the form of non-volatile compounds, or there are volatile bodies dissolved therein or suspended with others. The distillate is then either clear when the volatile substances are readily soluble in the water distilled over with them, or are present in very small quantity, or it is turbid from suspended undissolved substances which exist in the fluid either in the form of oily globules, or crystals, but seldom in the form of flocks. More frequently, when the material contains a considerable quantity of volatile substances which are not readily soluble in water, an oily film swims on the surface of the distillate, or collects at the bottom of the liquid. The volatile bodies which may be dissolved or suspended in the distillate belong often to the most different classes of bodies. Volatile bases, volatile acids, hydrocarbons, indifferent volatile oils containing oxygen, aldehydes, compound ethers, may be contained in such a distillate. It is a rare case for only one volatile substance to be found by a close examination of the distillate. If the substance under examination contains only small quantities of volatile substances, recourse must be had to cohobation. When a portion of the material has been treated in the manner directed, and a sufficient quantity of the distillate has been obtained to point out by means of a preliminary examination to what classes of bodies the volatile substances found therein belong, it may be easily determined whether cohobation is necessary or not. Assuming there were only volatile acids or volatile bases contained in the distillate, a cohobation would be superfluous even when their quantity was very small.

The treatment of the watery decoction and the watery distillate for the purpose of ascertaining their constituents, the next section will describe.

II.—*Treatment of the material to be examined with cold water.*

A portion of the material, as finely divided as possible, is treated with cold water. As much water is employed as will thoroughly saturate the material, and cover it about a couple of lines. After a short time, the saturated mass is placed upon a fine strong piece of linen, and the liquid pressed off by a gradually increased force. The liquid thereby obtained is filtered through moist paper, in as many small filters as possible. In most cases the liquid passes slowly through the filters. By this method of treatment it is not possible to prevent the formation of decomposition products by the action of the ferment on the other constituents. As all these decompositions proceed with more difficulty in proportion to the lowness of the temperature, this disadvantage may be considerably removed by employing ice-cold water for the extraction, and by preventing the heating of the filtering liquid by surrounding the funnels with such water. The filtrates should be collected in vessels surrounded with cold water.

The further investigation of this filtered liquid will be described in the next section. It serves principally for the detection of those substances which remain undissolved by the treatment of the material with boiling water, because they become by elevated temperatures insoluble in water, that is coagulated, as is the case with bodies analogous to albumen, emulsin, &c.

III.—*Treatment of the substance to be examined with acidulated water.*

A portion of the material is treated with water, to which a little sulphuric acid has been added, and heated in a water-bath, or by a current of steam. The boiling hot fluid, together with the material previously placed therein, is allowed to cool, and the fluid is separated from the undissolved material, which is then gently expressed. This fluid serves chiefly to detect some few organic acids which are contained in the material, in the form of salts insoluble in water and alcohol, but which are set free by the sulphuric acid, and thereby become soluble in water; and also to show the presence of organic bases, which are contained in the form of sulphates in this extract.

IV.—*Treatment of the material to be examined with ammonical water.*

For the preparation of the extract with water to which a little caustic ammonia has been added, a small quantity of the residue is taken which is obtained after boiling the material with water and expressing it. This residue is introduced into water containing ammonia, and the whole allowed to stand quietly some time, until the liquid has properly saturated the substance. After passing the liquid through linen and expressing the substance, the liquid is filtered through paper. This fluid is suitable for the detection therein of some bodies which are soluble in alkaline liquids, but not in water or dilute acids. Only when the addition of dilute hydrochloric acid produces a precipitate in this fluid is it prepared on a larger scale for the further examination of the precipitate. When no precipitate results, it is no longer employed for the investigation.

V.—*Treatment of the material to be examined with alcohol.*

Whether alcohol containing more or less water is employed for the extraction of the material, whether the extraction should be conducted at an ordinary temperature or at a boiling heat, depends on the properties of the material to be extracted. The operator must first convince himself whether a considerable quantity of fat is present or not. It is easy to ascertain this with certainty. The extraction of a small quantity of the material with ether, and the evaporation of the ether, proves this. It may be readily observed whether the residue, after the evaporation of the ether, contains much fat or not. When the material contains only a very little fat, the alcohol should be applied boiling hot for the extraction. In this case a spirit of .825 sp. gr. should be employed. If a great quantity of the fat is present in the material, which is the case when by expression between cold or heated plates the chief bulk of the fat is separated, weaker spirit of specific gravity, between .850 and .855, must be employed, and the extraction performed at an ordinary temperature.

Should the material be treated with hot alcohol, and a large quantity be operated upon, a still is the best for this purpose which is provided with an inner receptacle for the material and the alcohol. The heat employed is that of a water-bath. When the head of the still is affixed, and proper care taken for cooling the distillate, but little alcohol is lost, because its vapor is condensed. If volatile substances exist in the material, they pass over simultaneously with the spirit. Easy as it is to separate volatile acids or bases from the spirit, it is equally difficult to remove volatile oils therefrom. Such alcohol is constantly again and again used for the extraction of a fresh quantity of the same material; in the worst cases it can be employed for combustion, &c. When the spirit has acted sufficiently long on the material to be extracted, the head of the still is removed, and the receptacle and its contents together withdrawn from the still, then the liquid is strained through linen, and the material is expressed by slowly increased pressure. The alcoholic decoction is filtered while hot through paper, and placed aside to cool, whereby frequently bodies separate which are more difficultly soluble in cold than in hot spirit. The extraction of the material with cold alcohol is conveniently performed in a bottle with a very wide mouth, which is furnished with a glass stopper well ground in. It should be of such dimensions that materials to be introduced should almost fill it when loosely inserted therein. It is better to employ several small bottles instead of one large one. Into these bottles the quantity of material is introduced necessary to fill them, the material is covered with spirit, and the completely filled bottles closed with glass stoppers. After standing 24 or 36 hours in a moderately warm place, the spirit is poured off. As far as possible this filtered extract is preserved in a stoppered bottle quite full, and the material is treated with a fresh quantity of spirit, which is allowed to remain on the material for examination 24 hours. The extract thus obtained is employed for the extraction of a second quantity of material instead of fresh spirit. The extracted material is taken from the extracting vessel and expressed; the expressed fluid is treated in the same way as that obtained by pouring off. In this manner suitably concentrated extracts are obtained. As in Robiquet's glass apparatus for extraction a little material can only be introduced at once, and on account of the danger of its breakage when operating with hot alcohol, I use an extraction apparatus of tinned iron plate for the extraction of large quantities of the substance for examination with cold alcohol, or the extraction of smaller quantities with hot alcohol, with which it is not worth the trouble to employ a still. This apparatus is so arranged, that it permits the employment of hot or cold alcohol with equal facility. The apparatus consists of two concentric cylinders joined together, which are about eighteen inches high. The diameter of the inner cylinder is from four to five inches, and the diameter of the outer one double that size. Both cylinders are fastened together below by an horizontal ring of tinned iron plate. The inner cylinder projects about an inch below. This projection passes through a ring which is fixed to a funnel. When the funnel is fastened by its spout to a filter stand, it is only necessary to fix the funnel to the apparatus for extraction firmly in a vertical position. The inner cylinder is closed at the bottom with a finely perforated plate. The space between the two cylinders can be filled with water at any required temperature. From a flask closed with a perforated cork, through which passes a glass tube twice bent at right angles, steam is conducted into the water between the cylinders. Any required temperature can be obtained during the time of extraction by regulating the heat under the flask, and thus regulating the current of steam. To prevent the evaporation of the alcohol added to the material which fills the inner cylinder, into the hole at the bottom of which has been inserted a loose layer of cotton wool, the cylinder is closed with a tin cover, but not hermetically tight. When the space between the two cylinders has been filled with hot water, it is closed with a circular cover, which has a perforation to admit the steam tube to the water. It is evident that this tube must reach nearly to the bottom of the vessel. To be able to empty the water conveniently which is placed between the cylinders, a small cork is attached to the external cylinder at the bottom of its outer edge. When the extraction is conducted in this apparatus, the alcoholic extract passing through the material is poured back several times on the mass undergoing extraction, to increase the period of contact. When the extract appears sufficiently concentrated, it is placed aside, and a fresh quantity of alcohol employed for the further extraction. The latter weak tincture is used instead of pure spirit for the extraction of a fresh portion of the material, so as to render the extract as strong as possible.

The further treatment of the alcoholic extract, whether prepared at ordinary temperatures or by heat, will be described in the next section.

VI.—*Treatment of the material to be examined with ether.*

The treatment of the material with ether is effected at ordinary temperatures in Robiquet's glass apparatus for extraction, or with large quantities in such an apparatus made of larger dimensions of tinned iron plate. In many cases it is necessary to treat the material to be extracted with ether previously to macerating it in alcohol. This is the case when free fatty acids are contained in the substance under examination. These acids are even dissolved out with other bodies by the exhaustion of the material with cold alcohol containing water. To surmount this disadvantage, these fatty acids must be removed by treatment with ether. In fresh materials, the presence of free fatty acids can seldom be detected. On the contrary, in substances which have been kept a long time, they can be frequently recognized. In these cases the fatty acids result from the decomposition of the fats contained in the fresh material.

VII.—*Treatment of the material to be examined with alcohol containing a small quantity of ammonia or potash.*

For this purpose a small quantity of the material is taken, and one portion is macerated with alcohol containing potash, and another with alcohol containing ammonia. The alcohol contains sufficient alkali when to an ounce of the spirit six or eight drops of a concentrated aqueous solution of potash or ammonia have been added. This operation must be performed in well stoppered bottles, which must be quite full of the material, but lightly packed. The alkaline spirit is poured in until the bottle is full up to the stopper, which is then closed. By the admission of the air an oxidation of the dissolved bodies would easily result. After standing several hours undisturbed, the contents of the bottle are placed on a linen filter and gently pressed. The fluid is mixed at once with as much hydrochloric acid as will render it slightly acid, and it should be observed whether a precipitate is produced in consequence or not. When no precipitate results, no further proceedings are taken; on the contrary, should there be a precipitate, a larger quantity of the material must be treated in the manner described. The method of further examining these solutions will be given in the next section.

FURTHER INVESTIGATION OF THE SEVEN DIFFERENT SOLUTIONS, AND THE DISTILLATE OBTAINED FROM THE AQUEOUS DECOCTION.

SECTION I.—*Examination of the aqueous decoction and the distillate therewith obtained.*

A.—Examination of the distillate.

The watery distillate, which is obtained by the decoction of the material with water according to the previous directions, is either a clear or a turbid fluid. It has either a film of oil floating on the surface, or precipitated at the bottom, or not. If the distillate is a clear fluid, it contains either only a very little quantity of substances sparingly soluble in water, or none of these substances. If the water is turbid from the separated oil globules, or solid particles, it contains little of substances difficultly soluble in water or much of readily soluble ones. The water at first, when a layer of oil has collected at the top or bottom, mechanically separates from the oil. After the principal bulk of the water has been removed by a syphon, its complete removal is effected by means of a separatory funnel or a pipette. The water is then treated precisely as when no layer has been separated on the surface or at the bottom. This method of treatment is described at length further on.

a.—Examination of the separated oil.

It is first ascertained whether the separated oil reacts on litmus paper or not. If the blue litmus paper is reddened thereby, the oil is either a volatile acid or a mixture of several volatile acids, or lastly a mixture of one or several volatile acids with other volatile bodies. It is scarcely necessary to remark that, besides the peculiar volatile acids, some aldehydes also may be present; for example, salicylous acid as well as the acid ethers of bibasic acids—as, for instance, the acid salicylate of methyloxide, which is obtained by the distillation of Gaultheria procumbens, and which behave in this and other respects as volatile acids.

If the oil has an acid reaction, the oil is introduced into a flask, and baryta water added thereto with agitation. This addition is continued until it has no longer an acid reaction; afterwards it is allowed to precipitate quietly. Either the oil has quite disappeared by this treatment with baryta water—if so it was a volatile acid, or a mixture of several such acids, or an acid aldehyde resembling the salicylous acid, or an acid ether, possibly a mixture of several aldehydes or ethers, or a mixture of several members of these two classes of bodies, or of all three.

The oil which remains, after the treatment with baryta water, is neutral or *alkaline.* In the latter case it is treated with dilute sulphuric acid.

When a volatile base is present therein, it dissolves in the dilute sulphuric acid. If absent, as much oil is dissolved as would be dissolved in an equal quantity of pure water. If the first separated oil has exhibited an alkaline reaction instead of an acid one, it is at once treated with dilute sulphuric acid. Either a complete solution of the oil takes place, in this case an organic volatile base, or a mixture of several such bases is present, or a partial solution is effected when it is a mixture of one or more volatile bases with non-basic bodies.

As we learn by these experiments whether bases or acids are at the same time present, or bodies which behave as acids towards bases, and in case such bodies were found they have been removed by the treatment with sulphuric acid and baryta water, we now proceed to detect the presence of the aldehydes. If neither an acid nor a base is present, the oil can at once be used for testing for aldehydes. With this object, a portion of the oil is mixed with a solution of the bisulphite of potash as concentrated as possible. When an aldehyde is present, it is generally taken up by the solution of bisulphite of potash. Either a portion of the oil, or the whole of it, is dissolved, depending on the presence of indifferent bodies, besides one or more aldehydes. It should be observed, by the solution, when it takes place, whether a more or less elevation of temperature results, caused by heat becoming free, in consequence of the combination of the aldehyde or aldehydes with the bisulphite of potash. When no reaction is produced at ordinary temperatures, this may be promoted by heat. Sometimes after the solution of the oil, or a portion of it, in the concentrated aqueous solution of the bisulphite of potash, by long standing and cooling, a separation of crystals results. If no such separation is observed, the undissolved portion of the oil can be removed mechanically, and alcohol carefully added to the solution, by which the separation of the aldehydes, or aldehyde in combination with the bisulphite of potash, is facilitated. Sometimes the addition of bisulphite of potash quite or partly congeals the oil, in consequence of the formation of a compound of the aldehyde with bisulphite of potash. In this case the solid or semi-solid mass should be washed with alcohol, and the washed product pressed between bibulous paper. If neither before nor after the addition of alcohol a solid compound of one or more aldehydes with bisulphite of potash results, the action of the corresponding soda-salt is tried, and when this affords no solid product, the corresponding ammoniacal bisulphite should be employed. If an aldehyde, or several of them together, are present, we obtain with the bisulphites of potash, soda, or ammonia, a compound or a mixture of them, from which, by the addition of dilute sulphuric or hydrochloric acid, or a solution of caustic potash or soda, the aldehyde or aldehydes can be again separated.

In the same way here described, the oil, freed from acids by baryta water, and from bases by dilute sulphuric acid, is treated to remove the aldehyde or aldehydes present.* If, after the separation of the bases and acids or aldehydes present, any oil remains, this portion may either be a hydrocarbon or a mixture of several such bodies, or an oxygenated indifferent oil, or a neutral compound ether, or a mixture of several of these bodies.

To ascertain whether we have to do with a *hydrocarbon or a mixture of several hydrocarbons*, or whether *an oxygenated volatile substance* is also present, a fragment of sodium or potassium is introduced into the oil, previously dried by means of chloride of calcium. If the metallic fragment remains unacted upon in the fluid even after the application of a gentle heat, no oxygenated body exists in the oil; consequently the oil must be a hydrocarbon, or a mixture of several hydrocarbons. On the contrary, if that oil reacts on the potassium or sodium, an oxygenated body, or a mixture of several such bodies, is present.

To prove whether or not the oxygenated body present is *a compound ether*, the oil under examination is divided into two parts. One portion is treated with caustic ammonia in a small flask, by which, in many cases, an amide of the acid of the ether separates, while the alcohol corresponding to the ether becomes free. The second portion of the oil is introduced with baryta water into a small retort, a little of the crystals of hydrate of baryta thrown in, and the retort so connected with a small Liebig's refrigeratory apparatus that the condensed vapors are compelled to flow back again into the retort, when the contents of the retort are heated to the boiling point. When the ebullition has been continued for some time, the refrigeratory apparatus is brought into its ordinary position, and the distillation proceeded with. The hydrocarbons present, as well as the indifferent oxygenated oils, pass over with the aqueous vapor; likewise the alcohols derived from the ethers. The acids of the ethers remain behind, combined with the baryta. The residue of the retort is, when cold, removed, and the baryta separated from the liquid, which, when necessary, should previously be filtered, by means of dilute sulphuric acid. After separating the sulphate of baryta by a filter, the liquid is again distilled, whereby the acid contained either in the distillate in which

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* I found, by the examination of oil of origanum, that it consisted of two volatile oils, which afforded, when heated with an aqueous solution of bisulphite of soda or ammonia, a solid body, but which contained no sulphur, soda, or ammonia. I have deemed it necessary to call attention to this circumstance, as it is highly probable that there are many other volatile oils which behave like oil of origanum. Consequently, if we would decide with certainty on the presence of an aldehyde, we must ascertain whether the product obtained by the action of alkaline bisulphites contains sulphurous acid, or the alkali employed in its preparation. If sulphurous acid and alkali cannot be detected, no aldehyde is present.

its presence may be easily detected, or when it is not distillable with water, its concentrated solution remains behind in the retort. From this fluid the acid, under proper conditions, may be crystallized out. The existence of compound ethers in the oil, separated from the distillate, is not very frequent, as the majority of ethers, being readily soluble in water, are found dissolved in the aqueous distillate.

If no compound ether is present, it is still to be determined whether *an oxygenated indifferent volatile oil* is admixed with hydrocarbons or not, which was partly discoverable from the treatment of the oil with potassium or sodium. To detect such body, the oil to be examined is introduced into a small retort, which is half filled with coarsely powdered soda-lime.* The oil is absorbed by the soda-lime. After a flask, as a receiver, has been adjusted, the retort is carefully heated. The hydrocarbons will be distilled over, unchanged in their composition, while the oxygenated oils will be decomposed by the action of the alkaline compound. Generally, non-volatile compounds result therefrom, which only are decomposed by higher temperatures, under the formation of volatile compounds. Gerhardt and Cahours, in this way, have separated the hydrocarbons from the oxygenated oils, in many mixed oils. Frequently the oxygenated oils afford, by this treatment, colored decomposition products. Thus the distillate of the oil of calamus over soda-lime is at first colorless, so long as the lighter volatile oils distil over unaltered. Later, a blue distillate appears, arising from the decomposition of the less volatile oxygenated portion of the oil of calamus, by the alkali at a higher temperature.

We turn back to the aqueous solution of the baryta salt or salts, which was obtained by agitating the oil with baryta water, which oil had collected on the surface, or at the bottom of the watery distillate. The solution is divided into two parts. The first is introduced into a retort, into which a little hydrate of baryta is placed. The retort is connected with a refrigerator, and the greater part of the water is distilled off. If an acid ether was present, this is decomposed. The corresponding alcohol is separated, and is found in the distillate, and the acid in combination with the baryta is in the residue of the distillation. The second part of the solution is mixed with dilute sulphuric acid, as long as a precipitate of sulphate of baryta is formed. The sulphate of baryta is separated by filtration, and the filtrate distilled off until a small residue remains. As the fluid must contain a tolerably large quantity of volatile acid compounds, it may be ascertained whether an aldehyde of an acid character is present or not, by the addition of a highly concentrated solution of alkaline bisulphites,

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* Soda-lime is made by mixing lime with a solution of caustic soda, in such proportion that, upon evaporation, the mixture, when heated to redness, shall be equivalent to one part of the hydrate of soda, with two parts of anhydrous lime.—EDITOR PHARM. JOUR.

and a sufficiently large quantity of anhydrous alcohol. If this is not the case, then only a volatile acid, or a mixture of several such acids, is present.

It was previously mentioned that the oil separated from the distillate, when before or after treatment with baryta it reacted alkaline, should be shaken with dilute sulphuric acid, that the base or bases present may be obtained dissolved as sulphates. The solution of sulphates is then mixed with baryta water as long as a precipitate of sulphate of baryta ensues; for certainty, one or two drops of baryta water is added in excess, and the liquid distilled from a retort which is connected with a refrigeratory apparatus, as long as the distillate has an alkaline reaction. The distillate is now exactly neutralized with dilute sulphuric acid and evaporated to dryness. The residue is treated with alcohol, which dissolves the sulphates of the bases. If a residue remains, either ammonia or methylamine is present, or a mixture of both, in the form of sulphates. After the expulsion of the alcohol from the alcholic extract in the water-bath, the salts of the other bases perchance present remain behind. They may be easily obtained therefrom, by distillation with a solution of caustic potash, in an isolated form, or by mixing the salts with a solution of caustic potash and agitating with ether, by which an ethereal solution of the bases is obtained, from which the ether can be distilled off. If by the examination of the separated oil no bases, acids, or aldehydes have been found; if no compound ethers are present, or if these bodies have been removed; further, if the oxygenated indifferent volatile oils sometimes present have been separated from the hydrocarbons by distillation over soda-lime, in so far as it is possible, by this method, we have still to ascertain *whether only a hydrocarbon, or a mixture of several hydrocarbons, is present.* To arrive at a conclusion on this point, the oil in question is distilled in a small retort in which a thermometer is inserted. A rapid continued rising of the boiling point proves that the oil is a mixture of several volatile substances.

It should be always observed whether a portion of the original oil, as it floats on the watery distillate, or falls to the bottom of the same as a layer, cannot be congealed by exposure to very low temperatures, independently of its reactions and other properties. Frequently *a partial separation, simply by exposure to cold,* may be effected in substances of that kind, more readily in this than in any other way.

In winter, the most convenient method is to stick a test tube containing the oil in a beaker glass filled with snow, and to stand the whole in a wooden vessel. The space between the glass and the wood vessel is filled with sawdust; the glass should stand on a layer of sawdust several inches high; into the glass, alcohol is poured carefully, when the snow melts, and the mixture cools down to 13° Fahr. below zero. The whole is covered with a quire of filtering paper. As paper and sawdust are bad conductors of heat, the depressed temperature continues sufficiently long to congeal the oil or to cause the separation of solid substances from it when this can be accomplished by cold.

Besides the volatile bodies just under consideration, which in the form of oils can be separated on the surface or at the bottom of the distillate, there exists still a class of bodies which in their composition are readily distinguished from those spoken of. These are the *essential oils containing sulphur,* as they are generally termed ; for example, oil of mustard, oil of onion, oil of assafetida, oil of garlic, &c. The presence of these oils is generally rendered evident by their odor. But to be certain as regards their absence or presence, a portion of the oil is oxidized with nitric acid, and then tested for sulphuric acid. If sulphur is contained in the oil, it is converted into sulphuric acid by treatment with nitric acid, which can be detected by nitrate of baryta. The majority of these oils afford precipitates when dissolved in alcohol and mixed with a solution of bichloride of platina or bichloride of mercury. By the application of bichloride of platina the precipitates are either pure red, reddish-yellow, brownish yellow or reddish brown ; and by the use of bichloride of mercury, on the contrary, white, sometimes with a shade of yellow.

It still remains to be stated *how the alcoholic solutions of ethereal oils* must be treated, as obtained when an oil is treated with alkaline bisulphites, and thereby partly congealed, and the fluid portion remaining removed from the solid compound by washing with alcohol.

Such a spirituous solution is shaken with milk of lime, and in a closed vessel allowed to remain undisturbed until the insoluble portion is deposited at the bottom. The clear fluid is taken off and distilled, to the distillate is added a piece of anhydrous, but not fused, chloride of calcium, after it has been placed in a stopped bottle surrounded with cold water. The chloride of calcium dissolves in the alcohol and water present, and the volatile oil which *was* dissolved separates on the saline solution as a slight film, which can be removed by a pipette, washed with a little water, and obtained pure by rectification with water. As a strong bumping is unavoidable by boiling with a little water in the retort, I employ for this purpose a flask, and introduce with the water and the ethereal oil some large pieces of clean linen. This plan also prevents the spirting over in rapid distillation.

b.—Examination of the watery distillate.

If the watery distillate has a layer of oil on the surface or at the bottom which has been examined in the manner described, this distillate is a concentrated watery solution of the bodies contained in the layer of oil. The method of investigation, when the bodies are known, can be previously determined with exactness. As the bulk of these volatile substances which are readily soluble in water, must be contained in the distillate, a sufficient quantity of these bodies can be obtained from this watery solution when only a little was present in the separated oil. The *volatile acids*, in particular, which almost all are, tolerably soluble in water, can be obtained in large quantity from this fluid; likewise *the volatile bases*, when present. To obtain the volatile bases therefrom, the distillate is mixed with a few drops of sulphuric acid, and subjected to distillation. The bases remain as sulphates dissolved in the residue of the distillation. To separate the acids, they must be combined with a base, and the liquid removed by distillation.

Although potash or soda, as the strongest bases, have the preference before all other bases, as by boiling they do not permit the volatile acids to become free, with which they have been once combined, their employment is still limited, when, besides the volatile acids, other volatile substances exist in the distillate which by alkalies undergo a change in the heat if a small excess of such alkalies is present, or when they are rapidly decomposed by the oxygen of the air when in contact with alkalies. If soda or potash is employed, care must therefore be taken that no excess of alkali is present, but rather that a small quantity of free acid remains, which then clearly will not be retained, but be distilled off with the water and the other volatile bodies. The potash or soda can be replaced, often with advantage, by freely precipitated carbonate of copper, or the hydrated oxide of copper, by magnesia as well as by white lead, which has been specially prepared by passing carbonic acid through subacetate of lead, and should be applied in a fresh, moist condition, particularly when compound ethers are contained in the solution. When the distillate has deposited no layer of oil, but is clear or only slightly turbid, recourse must be had, as already mentioned, to *cohobation*. But as with cohobation a tedious heating of the fluid with the substance under examination is unavoidable, and the possibility of forming decomposition products is thereby afforded, I prefer the direct concentration of a distillate, which contains little volatile ingredients, to cohobation. The concentration is accomplished in the following manner:—The distillate poor in volatile substances is mixed with so much dry common salt as it will dissolve, and the resulting fluid is subjected to distillation. Generally, after half the water has distilled off, only pure water passes over. The distillation is then interrupted, the distillate is again saturated with common salt, and re-distilled. By the repetition of the distillation as often as it appears requisite, a concentration can be effected which affords a highly concentrated solution of the substances under examination soluble in water, and accomplishes a separation of the greatest part of the substances difficultly soluble in water. If the concentration is not accompanied by the separation of oily bodies by this treatment with common salt, then only bodies are present which are very soluble in water. To obtain these, two methods are proposed ; either the fluid is saturated with common salt and agitated with ether, which, when it separates, is removed, and may be evaporated, or the distillate is treated with chloride of calcium. When ethereal oils with high boiling points are present, the treatment with ether is to be preferred. The ether evaporates quickly when exposed in a dish to the air ; and to prevent the evaporation of the volatile oil with it, care must be taken that the dish which contains the ethereal solution of the volatile oil is set in a place where a good current of air rapidly conducts away the ethereal vapor. On the contrary, when volatile oils with rather low boiling points are present, the treatment with chloride of calcium has the advantage. Into the fluid concentrated by distillation with common salt, chloride of calcium in fragments is thrown in until the fluid appears as thick as syrup ; it is then subjected to distillation. The distillate is again treated with chloride of calcium, and re-distilled. By three or four repetitions of these operations either a separation of the dissolved substances ensues (sometimes only a partial one,) or the concentration has so far progressed that the substance can be freed from water by the addition of a large quantity of fused chloride of calcium, and distillation, and may be obtained as a distillate, which certainly will be the case when the body possesses a boiling point not much above 212° Fahr. It is clear that a concentration of this kind is quite as little necessary as cohobation, when only acid or basic bodies are contained in the distillate.

Before I conclude the examination of the distillate, or rather the volatile bodies present in it, I must here make some observations on the so-called fractional distillation.

Fractional distillation is recommended for the separation of mixed volatile substances. As this operation is generally performed, it is certainly suitable for the preparation in a pure state of the least volatile bodies in a mixture of that kind, but is not adapted for obtaining the more volatile constituents, because at the temperature by which the mixture boils, many of the constituents are evaporated which do not boil at that temperature. The vapors of the boiling constituents do not pass over alone, but also the vapors of the less volatile substances are carried over with them. Instead of heating the mixture to the boiling point, it is more advantageous to heat it near to the boiling point. *A slow evaporation* then takes place, which proceeds, indeed, rather slowly, but by adopting suitable precautions, the lighter volatile constituents of a mixture are to be obtained approximately pure, if not absolutely free from all admixture of the other bodies. To guard against the oxidation of substances which so long exposed to the air at elevated temperatures, have opportunities enough to combine with the oxygen, the distillatory apparatus as well as the receiver should be filled with carbonic acid gas during the evaporation.

While fractional distillation, or an evaporation undertaken at somewhat lower temperatures in a similar manner, is often the only means of separating volatile bodies which are neutral or indifferent, *the method of partial combination is a method of separating volatile bases or volatile acids from one another* when several bases or acids are present at the same time. How the volatile acids are to be separated from other volatile bodies, and likewise the bases from other volatile compounds, has been above set forth.

The method of partial combination was first used by Liebig in separating volatile acids. When we have prepared a fluid which contains the volatile acids separated from the other volatile constituents, and after it has been measured off in a graduated glass, it is divided into ten equal parts, one part of which is accurately saturated with a solution of soda or potash, and after the nine remaining parts have been added, the fluid is distilled. The distillate is thereon divided into nine equal parts, one part saturated with alkali, and the other eight parts added, and the whole again subjected to distillation. The distillate is now divided into eight parts, one part neutralized with alkali, the remaining seven parts mixed with this, and the fluid again distilled. In a similar way this proceeding is continued until only a tenth part of the original solution of acids remains in a free condition; consequently in this we have the weakest acid in a condition approximately pure; in the rest of the liquids the potash or soda salts of the other acids, in the first residue of the distillation the strongest acid either pure or contaminated with a little of the next weakest acid, and so forth. It is clear that, in a similar way, many volatile bases could be separated from one another. The only alteration required in the method given for acids would be that the neutralization of the parts of the fluid must be effected with dilute sulphuric acid or phosphoric acid instead of soda or potash. If in this way we have obtained ten parts of the soda or potash compounds of the acids, or even as many portions of the sulphuric acid or phosphoric acid compounds with the bases, we can procure, by the decomposition of the alkaline compounds with acids, or the salts of the bases with alkalies and distillation, the corresponding acids and bases in a free condition, and then be convinced whether we have had to do with two or more bases or acids. Of course there still remains the determination of the atomic weight and elementary analysis to afford a guide whether the individual acid portions or base portions require or not a further separation by the same method. On this subject I shall speak later in the treatise.

B.—Examination of the aqueous decoction.

We turn back to a closer examination of the watery decoction which was obtained by the treatment of the material under investigation with boiling water in the still at the same time with the watery distillate. It has been already mentioned that *by cooling of the hot fluid a separation often* takes place of one or other substance. If such a separation is observed, the separated body is removed by filtration for a closer examination, and it is noticed whether a small portion of the fluid which has been filtered, by further evaporation and cooling throws out more of the bodies which were separated by the cooling of the original decoction. When this is the ease, the filtered decoction is concentrated by evaporation, to obtain the principal bulk of such substances difficultly soluble in water. After collecting the substances on a filter, the filtrate is treated as the decoction would have been treated if nothing had separated by cooling.

Frequently the watery decoction contains a proportionately *large quantity of slimy substances*, which belong either to the group of *indifferent carbo-hydrates* or to the class of *pectine compounds*. By the presence of a great quantity of these bodies, the watery decoction is often so dense that, when cold, it is quite stringy. These substances, without exception, are insoluble in alcohol. But even when the decoction is not so dense, the precipitates obtained therefrom are mostly so voluminous and gelatinous that the fluid cannot be completely filtered from them, but is retained in the voluminous gelatinous flocks. In such cases these substances must be removed. For this purpose the decoction is concentrated by evaporation, and anhydrous alcohol is added to the still hot fluid as long as a bulky flocculent precipitate is thrown down. By filtration the fluid is separated from the precipitate. In many instances alcohol does not produce a flocculent precipitate, but it causes a considerable turbidity, and the precipitate deposits itself as a tenacious mass at the bottom, which is particularly the case when gum or an analogous body is precipitated by alcohol simultaneously with various salts of organic acids.

The spirituous fluid separated from the precipitate is subjected to distillation, which is stopped as soon as all the alcohol has passed over, and the liquid is free from it. This watery residue of the distillation is treated precisely as the original watery decoction, when no such gelatinous substances, or those rendering the fluid dense and tenacious, were precipitated by alcohol therefrom.

This treatment is as follows:—The watery decoction is divided into several parts. *To one part of the watery decoction is added* a concentrated cold aqueous solution of *acetate of lead*, as long as a precipitate is thereby produced. The precipitate is brought on a filter and washed well with water. The liquid filtered from the precipitate is mixed with subacetate of lead as long as anything is thrown down. This precipitate is likewise collected on a filter and washed with water. The filtrate is freed from the lead contained therein by a stream of sulphuretted hydrogen, separated from the sulphuret of lead by a filter, and the sulphuretted hydrogen expelled by heating the filtrate. The sulphuret of lead is exhausted with hot water, and when this takes nothing up it is treated with hot alchhol, and the hot filtered solution is concentrated in a water-bath. Frequently bodies which are retained by the sulphuret of lead crystallize out after long standing from the concentrated aqueous or alcoholic extract. *The fluid precipitated with acetate of lead and subacetate of lead, freed from lead* *by sulphuretted hydrogen, and filtered from sulphuret of lead,* is, after the expulsion of the sulphuretted hydrogen, concentrated by evaporation until the residue has a thin syrupy consistence. A small portion of this residue is examined, to learn whether the addition of alcohol precipitates substances or not. If by *the addition of alcohol* at ordinary temperatures, or after heating in a water-bath, a precipitate is developed, the whole residue is treated with alcohol, and the alcoholic liquid filtered from the precipitate. It is then ascertained whether the *alcoholic fluid* from the precipitate when such was obtained gives or not a precipitate on *the addition of ether.* In this case frequently a precipitate results of a semi-fluid character. Sugar, which often exists in parts of plants, is separated by treatment with ether. The precipitate sometimes formed by alcohol is dissolved in the smallest possible quantity of water, and it is observed whether by long standing crystals separate or not. Exactly in the same manner, the precipitate caused by ether is treated. From the fluid containing ether and alcohol by a gentle heat the ether as well as the alcohol is expelled, and the watery residue reserved to observe if crystals form therein or not.

These are the examinations which are performed with a portion of the fluid which has been obtained by the treatment of the watery decoction with sugar of lead, subacetate of lead, and sulphuretted hydrogen.

Another portion of this fluid, after a suitable concentration, is allowed to stand for a long time, to ascertain whether crystals will form ornot therein. Frequently *a separation of crystals* takes place in greater or less quantity. If such crystals form, they are separated from the dense mother liquor by a moist linen filter on a glass funnel. The upper part of the filter is afterwards closed by means of a thread, and laid between bibulous paper, and pressed upon by a small board with weights, which are gradually increased to increase the pressure. *The mother liquid separated from the crystals* contains, besides other bodies, always a greater or less quantity of the crystalline substance, according to its degree of solubility, which, upon a closer examination of the mother liquid, must be taken into account. This closer examination will be spoken of further on.

A second portion of the watery decoction is treated with *animal charcoal.* A glass tube, about half an inch wide and eight or ten inches long, is taken, which should be drawn to a point at one end. The mouth of the point must be about the size of a hempseed. Into the wide end of the tube a piece of loose cotton wool is introduced and pushed into the pointed end of the tube, which is fastened vertically in a clamp, with the narrow mouth downwards. The tube is filled six or seven inches high with pure animal charcoal, and the watery decoction is poured in by the aid of a small funnel inserted in the upper mouth of the tube. The fluid, as it passes through the tube into a glass flask, is replaced in the same manner by a fresh portion. *Coloring and bitter principles* are taken up frequently by the animal charcoal from the watery decoction, so that the color and the taste of the escaping fluid are often very different from the color and the taste of the original liquid. When the quantity of fluid set apart for the experiment has run through the charcoal, and this fluid has been removed, the charcoal is washed with cold water, to completely separate the bodies which are not retained by the charcoal. The charcoal is transferred to a vessel suitable for boiling, and boiled with *strong alcohol.* The spirit is filtered hot from the charcoal by means of a hot-water funnel, and the decoction with alcohol repeated as long as this takes up anything. The spirituous solutions are concentrated by distilling off the greatest part of the alcohol, and the concentrated extract (the residue of the distillation) is allowed to stand, to ascertain whether crystals form or not therein. Should crystals not separate by long standing, the residue is dissolved in water and further examined. On the contrary, should crystals form, they are first separated from the mother liquor, and these, as well as the mother liquor, subjected to a closer examination. *The liquid treated with animal charcoal* is treated precisely as the first portion of watery decoction.

A third portion of the watery decoction is mixed with *a solution of alum,* and then *ammonia* is added to the fluid. If a *precipitate* results thereby, the alumina exists therein, partly as a hydrate, partly combined with one or more organic substances. The precipitate is removed by filtration, and washed on the filter with water. To the *filtrate* so much dilute sulphuric acid is added as will almost neutralize the whole quantity of free ammonia which has been added in excess. The residue of ammonia is satuurated with a few drops of acetic acid, the neutralized fluid is evaporated to a small volume, and the residue mixed with anhydrous alcohol. This precipitates a considerable quantity of sulphates of potash and ammonia, which should be removed from the alcoholic solution by filtration. From this solution the alcohol is distilled off, and the syrupy residue again treated with hot anhydrous alcohol, which separates the rest of the sulphates, sometimes mixed with more or less organic matter insoluble in alcohol. This alcoholic solution is likewise freed from the greatest part of its alcohol by distillation, and the residue set aside, by which crystals are frequently separated; the crystals and the mother liquor are separated, and submitted to a closer investigation. When no crystals are formed, the whole residue is subjected to investigation.

We return now to both *the precipitates* which were produced by *sugar of lead and subacetate of lead in the first part of the aqueous decoction.* As before remarked, the second part of the watery decoction, after treatment with animal charcoal, is precipitated with sugar of lead and subacetate of lead exactly in the same way as the first part of the watery decoction not treated with animal charcoal. If the animal charcoal has not taken up and retained any substances from the watery solution, it is self-evident that the precipitates obtained by sugar of lead and subacetate of lead in the portion of the watery decoction treated with animal charcoal, have quite the same composition as the corresponding precipitates from the first part of the decoction which was not treated with animal charcoal. In this case, the corresponding precipitates can be united with one another, and, as a whole, be employed for examination, which must not be done when the animal charcoal has separated any substances. In the latter instance the precipitates are separately examined with regard to their composition, and in the same way.

The precipitate produced by sugar of lead is extracted with alcohol when a small portion has shown that it is partially soluble in alcohol. If the alcohol dissolves nothing, a small portion is tried with spirit of specific gravity ·825, to ascertain whether that effects a partial solution. If the *alcohol or spirit* has partially dissolved the precipitate, the *insoluble* is separated from the *dissolved part* by a filter. The lead compounds of sulphuric and phosphoric acids, as well as those of oxalic acid and many other organic acids frequently present, do not dissolve in alcohol or spirit. On the contrary, there is a great number of substances which form compounds with lead insoluble in water, but soluble in alcohol and weaker spirit. The *alcoholic* solution is decomposed by a stream of sulphuretted hydrogen, and then filtered; the sulphuret of lead is washed on the filter with anhydrous alcohol as long as anything is taken up, afterwards the sulphuret of lead is treated with water on the filter, as it often happens that a substance quite or almost insoluble in anhydrous spirit is contained in the sulphuret of lead which dissolves in water, and can be thus extracted. By evaporation the filtrate spirituous as well as aqueous is reduced to a small volume, and this residue set aside to afford an opportunity for crystals to form; which sometimes happens when crystallizable substances are present.

The part of the precipitate thrown down by sugar of lead from the watery decoction, and insoluble in alcohol or spirit, is, after having been washed with alcohol or weaker spirit, formed with water into a thick smooth paste, and a small portion of this paste is mixed with a great excess of *acetic acid.* It is observed whether the whole or a part of the precipitate disappears. Sometimes very little or nothing dissolves in the acetic acid. When a partial or complete solution is noticed, the whole quantity of the precipitate, mixed with water, is treated with acetic acid as long as a decrease of the precipitate results. Now, either a complete solution is obtained, or in the resulting solution an insoluble portion is suspended. In the latter case the solution is filtered from the undissolved portion. Either this filtered solution, or the entire liquid when all the precipitate dissolves in the acetic acid, is mixed with subacetate of lead in a very concentrated condition. With continued agitation small quantities of the subacetate of lead are added. It often happens that a precipitate forms after a very small quantity of the subacetate of lead has been added, although the fluid is still strongly acid. After this precipitate has been removed by a filter, much subacetate of lead can be added before a fresh precipitate forms, which first appears when the free acetic acid has been neutralized by the subacetate of lead. If a second precipitate ensues by the addition of much subacetate of lead, this is collected on a filter by itself. Both precipitates which are thrown down from the acetic acid solution, or the precipitate when only one results, must be purified by washing with water on the filter, then distributed in water to be decomposed with sulphuretted hydrogen. The fluid is separated from the sulphuret of lead by filtration, and the excess of sulphuretted hydrogen expelled. This expulsion is most conveniently effected in a glass flask, or in a tubulated retort, in a water or chloride of calcium bath. Carbonic acid gas should be driven through the fluid to displace the air in the retort or flask, and prevent the decomposition of the sulphuretted hydrogen accompanied by the separation of sulphur. Heat must not be applied to the apparatus until all the air is displaced by carbonic acid gas. *The precipitate* which is produced by *subacetate of lead* in the fluid which was filtered from the precipitate which sugar of lead occasioned in the *watery decoction*, is likewise examined with reference to its solubility in alcohol and in weaker spirit, wherein it may be partially or quite soluble, or quite insoluble. *The precipitates soluble in alcohol or spirit, and those insoluble therein,* are treated in precisely the same manner as directed for the precipitates derived by sugar of lead from the watery decoction. The precipitate resulting from sugar of lead is manifestly always completely soluble in acetic acid. In many cases, indeed, a number of substances are entirely thrown down from the watery decoction by sugar of lead, so that the precipitate formed by subacetate of lead contains none of the substances which are contained in the precipitate produced by sugar of lead. But these favorable instances of complete separation are only exceptions to the rule. Mostly the precipitate obtained by subacetate of lead contains substances which were contained in the first precipitate—namely, in that part of the first precipitate by sugar of lead which dissolved in acetic acid, and was again thrown down by subacetate of lead from this acid solution.

It is here particularly necessary to draw attention to a circumstance, namely, to *the presence of bodies in the precipitates produced by subacetate of lead,* which are not contained *in these precipitates* in the form of lead compounds, but are in *a free condition.* Let it be assumed that the watery decoction contains an organic base very difficultly soluble in water in the form of a salt soluble in water, whose acid produces with oxide of lead a compound insoluble in water, it will be evident that the acid of this salt will be contained in the precipitate resulting from sugar of lead, and the base of this salt will be found as an acetate in the filtered watery solution. If this fluid is neutralized with subacetate of lead, a weak base can be thereby separated from the acetic acid, and is precipitated in water on account of its insolubility in conjunction with the different lead compounds formed. Bodies admixed with precipitates of that kind which are produced by subacetate of lead, generally dissolve in alcohol, especially when heated. They are in this way often easily obtained pure when the lead compounds in these precipitates are insoluble in alcohol, or possess a very slight solubility in that menstruum. What has been stated explains the peculiarity sometimes existing of a precipitate resulting from subacetate of lead dissolving partially in alcohol or spirit, without more than a trace of lead being detectable in the solution.

If acetate and subacetate of lead have produced two precipitates, if these have been divided into two parts by strong or weaker alcohol, if that portion of the sugar of lead precipitate, which is insoluble in alcohol, has again been divided into a portion soluble and another one insoluble in water containing acetic acid, and if all these portions have been freed from lead by sulphuretted hydrogen; then these substances thus freed from lead, as well as the different portions of sulphuret of lead, must be further examined.

For this purpose, the *various portions of the sulphuret of lead* are treated immediately, after being washed, first with *boiling water* and then with *boiling spirit*, to ascertain whether these fluids extract anything from the sulphuret of lead. After the sulphuret of lead has been exhausted with water and spirit, it is exhausted with *dilute aqueous ammonia*, and the filtered ammoniacal solution is completely neutralized with acetic acid. The oxidation products of tannin and analogous colored substances are often in this way extracted by the water containing ammonia from the sulphuret of lead, and precipitated from their solutions by acetic acid.

It is self-evident that the various (portions of) substances free from lead, which are obtained from those portions of the precipitates by acetate and subacetate of lead insoluble and soluble in strong or weaker alcohol, and from these portions of the sugar of lead precipitate insoluble in alcohol, which are soluble and insoluble in acetic acid, may still be a mixture of several bodies. To ascertain this, the individual parts, separated according to the directions above given, are further investigated by *fractional precipitation* with regard to their homogeneousness. It is scarcely necessary to mention that bodies which have been separated in a crystalline form by the standing of the fluids, properly evaporated in the air or in exsiccator, must be previously removed from the mother liquors, and that in an such cases the diluted mother liquors must be submitted to examination by fractional precipitation.

For *fractional precipitation*, the two lead salts, *sugar of lead* and *subacetate of lead* are employed, which served for separating up to a certain point, as previously described. The fluids which afford no precipitate with sugar of lead are treated with subacetate of lead. *Fractional precipitation* is conducted in the following way:—The whole quantity of the fluid to be examined is measured in a graduated glass to estimate its volume, and then it is ascertained how much of a certain solution of sugar of lead or subacetate of lead is required by volume to completely precipitate the fluid. With this object, a small portion of the fluid to be examined is taken before it is measured off, and exactly neutralized with ammonia. If the quantity of solution of sugar of lead or of subacetate of lead is known which is required to precipitate the whole quantity of the fluid, the whole quantity, after exact neutralization with ammonia, is mixed with a tenth part of the quantity of solution of sugar of lead or subacetate of lead which would be required for its entire precipitation. The precipitate is filtered off, and the second tenth of the solution of sugar of lead or subacetate of lead is added to the filtrate, whereon the precipitate is again collected on a filter. This process is continued until ten precipitates are obtained from the fluid, all of which are washed with water, diffused in the same medium, and decomposed with sulphuretted hydrogen, whereby ten parts result from the fluid, which are subjected to a more minute examination when the sulphuretted hydrogen has been driven off.

I have convinced myself that this fractional precipitation is not so suitable to effect the separation of various substances as another method, which I will call *fractional solution.* This is executed thus:—It is determined how much acetic acid is required to dissolve the whole quantity of a precipitate which has been diffused through water to a smooth paste. Now, if a tenth part of the acetic is added, a tenth part of the precipitate is dissolved. This solution is filtered off, the precipitate found on the filter is transferred to a beaker glass by means of a stream from a washing bottle, and then treated with the second tenth of the acetic acid, &c. The ten solutions are precipitated with subacetate of lead, the ten precipitates collected, each washed on a filter with water, diffused in water, and decomposed with sulphuretted hydrogen. The sulphuret of lead is separated by a filter, the excess of sulphuretted hydrogen expelled, and each of the ten fluids tested with reagents. It is evident that only lead compounds soluble in acetic acid can be in this manner treated, and not the parts of precipitates insoluble in that menstruum which are produced by sugar of lead in the watery decoctions, and remain undissolved by treatment with alcohol.

Before I pass to the examination of the precipitates which are produced in a portion of the watery decoction by alum and ammonia, I have still to mention the means by which a separation of the substances in some cases is effected, which are obtained from the precipitates developed by acetate and subacetate of lead, in a condition free from lead, according to the method previously given.

There are substances which, *per se*, or by the agency of other bodies with which they are mixed, are soluble in water in rather considerable quantity. *Many of the bodies lose their solubility* in considerable degree *when they are completely dried*, or then dissolve only very slowly in water; while drying, on many other bodies, exercises no influence of that kind on their solubility. Consequently it is often a good method, to obtain the greatest part of a substance in a state of separation from the other bodies accompanying it, to allow the mixture to thoroughly dry *in vacuo*; and best over sulphuric acid, to treat the dried mass with a little cold water, and then by stirring and trituration to bring the dried mass into close contact with the water. One of the constituents often then remains in the form of microscopic crystals or as an amorphous powder, at least for a short time, undissolved, and can be separated from the other bodies easily and quickly soluble in water by a rapid filtration.

We will now apply our attention to the *precipitates* which are thrown down by *a solution of alum and ammonia from a portion of the watery decoction.*

The *precipitate* washed on the filter with water is treated with *dilute sulphuric acid,* and allowed to remain some time in contact with the same, accompanied with frequent stirring. For this purpose, the precipitate on the filter is introduced into a capacious glass vessel. The solution is filtered from the portion remaining undissolved, and this is washed on a filter with water. The residue washed with water is treated with *hot alcohol,* wherein such substances dissolve. These can be precipitated from the alcoholic solution by *water,* and after being washed with water, may be preserved for a closer examination by being dried *in vacuo* over sulphuric acid.

The solution obtained by the application of dilute sulphuric acid is mixed with a saturated solution of *sulphate of potassa,* whereby the alum is reformed, and at the same time is partially precipitated. The fluid is mixed with *anhydrous alcohol* as long as an addition of the same produces a precipitate of alum and sulphate of potash, and the spirituous liquid is filtered from the precipitate. The quantity of sulphuric acid which is still present in the fluid in a free condition is separated by the introduction of moist *white lead,* prepared by passing carbonic acid into subacetate of lead. The sulphate of lead is separated by a filter, and the small quantity of lead dissolved removed from the liquid by sulphuretted hydrogen. After filtering off the sulphuret of lead and expelling the sulphuretted hydrogen, the alcohol is distilled off and the watery residue employed for further investigation. It is self evident that the greatest portion of the substances contained in this fluid are those which were precipitated by sugar of lead and subacetate lead from a portion of the watery decoction, with the exception of those which are not precipitated with alum, or remain undissolved by the treatment of the aluminous precipitate with dilute sulphuric acid. This fluid is therefore treated exactly as is above described with the first portion of the watery decoction—namely, with sugar of lead and subacetate of lead, and the resulting precipitates are examined in precisely the same manner.

It was mentioned before that a part of the watery decoction was to be treated with animal charcoal, and the charcoal washed with water and extracted with boiling alcohol. This alcoholic extract may contain coloring matters, indifferent bitter principles, organic bases, &c. After its evaporation, either *crystals* are separated which can be removed from the mother liquor, or no crystals are formed. The whole residue, where no crystals have separated, or the mother liquors from which the crystals have been removed, must now be subjected to a more minute investigation. The examination of the mixtures of substances which are contained in the fluids which are filtered from the precipitates produced by acetate and subacetate of lead in one portion of the watery decoction, and from the precipitates caused by alum in a second portion of the same, is facilitated when the former are freed from lead by sulphuretted hydrogen, and the latter from sulphate of potassa and ammonia by alcohol, and then distilling off the alcohol. Organic bases, many bitter bodies, and other substances, will likewise be contained in those fluids, as well as in the alcoholic extract of the animal charcoal. *The concentrated residue of this alcoholic extract is diluted with water.* Should a body difficultly soluble in water be thereby thrown down, it should be collected on a filter. A small portion of the watery fluid is now mixed with a *solution of sugar of lead* by which a precipitate often results, because coloring matters and other bodies possessing the character of weak acids, afford, with lead, insoluble compounds. The *fluid filtered* from the precipitate resulting from sugar of lead is mixed with *subacetate of lead,* to observe whether a precipitate thereby ensues or not. If a precipitate results, it is separated by a filter from the fluid, and this is freed from lead by sulphuretted hydrogen, the sulphuretted hydrogen expelled, and the fluid evaporated to ascertain whether a residue remains, which is generally not the case, as sulphuret of lead frequently retains the bodies which were taken up by the charcoal from the watery solution. On this account the sulphuret of lead must be extracted with hot alcohol, and the hot liquid filtered from the sulphuret of lead in a hot-water funnel. *Both precipitates* resulting from sugar of lead and subacetate of lead are *boiled with alcohol* to ascertain whether they dissolve partially or entirely in alcohol. The solutions, if resulting, are treated with sulphuretted hydrogen, the sulphuret of lead heated to the boiling point with the spirit, and filtered hot. In the spirit with which the precipitate which resulted from subacetate of lead was heated, an organic base, or a mixture of several such bodies, may possibly be detected. The *portion of the lead precipitate remaining undissolved in boiling alcohol* is diffused through alcohol, decomposed by sulphuretted hydrogen, the fluid heated with the sulphuret of lead, and filtered hot. These different fluids are evaporated in a water-bath, and the residues preserved for further examination with reagents.

Having spoken of the treatment of the precipitates which are produced by sugar of lead and subacetate of lead in one portion of the watery decoction, and by alum and ammonia in another portion, and described the treatment of a part of the watery decoction with animal charcoal, we will now direct our attention to the liquid *residues* which have been obtained by the methods already related *from the watery decoction after treatment by the two salts of lead or alum and ammonia, and after the substances precipitated by these means have been separated from the lead by sulphuretted hydrogen, and the sulphate of potash and ammonia by alcohol.*

It was mentioned previously that sometimes *crystals* will separate from the *residues*, which by the evaporation of the water or the spirit are left behind, and that these crystals should be removed from the mother liquors from which they have separated.

When the crystals have been separated from the mother liquors, *their degree of solubility* must first be ascertained. That they are soluble in water is evident from their method of preparation, although they may be difficultly soluble in water. The presence of other substances in the watery decoction may considerably increase their solubility in water. If the same crystalline mass had formed from the residues which were obtained from the watery decoction by the salts of lead as from the residues which remained after the treatment of the watery decoction by alum and ammonia, it results that this crystalline mass, which may be one body or a mixture of several substances, is quite as soluble in *alcohol* as in water, because, had it been insoluble in alcohol, it would have been left behind on separating the sulphates of potash and ammonia by anhydrous alcohol, with these sulphates as an insoluble body. It still remains to be ascertained whether the crystalline mass is quite or partially soluble in *ether*, as well as whether *acidulated water* dissolves more of it than pure water. When the degree of solubility has been learnt by these experiments, a method is afforded which had to be found to purify the still impure crystals by recrystallization before they are further investigated.

We first ascertain, with a very small quantity of the *crystals purified by recrystallization, whether they can be partially or entirely sublimed or not, altered or unaltered.* The experiment, which gives in most instances a negative result, can be performed between two small watch glasses fitted to one another.

To arrive at the nature of these crystals, we proceed further, in the following manner:—

We first ascertained *whether an organic base, or a mixture of several organic bases, as an acetate or acetates*, is *contained in the crystalline mass.* To detect these bodies, a portion of the separated crystals is employed, and this is divided into four equal parts.

The *first part* is dissolved in the smallest required quantity of water, and a few drops of hydrochloric acid are added to the solution, then *bichloride of platina.* If no precipitate ensues, a little anhydrous alcohol is added, and then if no precipitate results, a small quantity of ether. The resulting precipitate (if any) is separated by a filter from the fluid, and washed with a mixture of anhydrous alcohol with a little ether. The dried precipitate is tested, to ascertain whether it contains potassa or not, by heating it to redness, and extracting the platina residue with water, and testing for the potash therein, which must be present as chloride of potassium if the crystals contained potash. It is well to examine the portion of crystals employed, to learn their capacity for sublimation, to ascertain whether the residue generally remaining will burn completely, and, when it leaves an ash, whether potassa is present therein.

The *second part* of the solution is mixed with a solution of *bichloride of mercury*. By this means there are several bases precipitated—for example, emetia, &c.

The *third part* of the solution is mixed with a concentrated solution of *caustic soda* in very small quantity. If the crystals were the acetate of a base difficultly soluble in water, or if they contained a little of one or several such salts, the base would be precipitated from its concentrated solution by the alkali, after the neutralization of the acetic acid. In an excess of the alkali, the precipitated base is frequently more soluble than in pure water, therefore the alkali must only be added by drops. Instead of *caustic soda*, carbonate of soda can be employed.

The *fourth part* of the solution is *heated after the addition of an alkali*, and it is ascertained whether the vapor thereby evolved is alkaline. Such a vapor may result when a volatile base is present whose acetate is crystallizable, or when the crystals were, or contained a body analogous to, asparagine; in the latter case, ammonia is evolved under the given conditions.

According to researches of Sonnenschein, phosphor-molybdic acid is a good test to prove the presence of bases. It gives with all bases, almost without exception, precipitates as well with the oxygenated as the non-oxygenated ones; these are generally yellow, but sometimes colored brownish yellow. This compound is prepared by precipitating molybdate of ammonia with c phosphate of soda, suspending the well-washed precipitate in water, and heating it with carbonate of soda, until it is completely dissolved. This solution is evaporated to dryness, and then heated to redness, for the complete expulsion of the ammonia. If the molybdic acid is thereby partially reduced, the heated residue is moistened with nitric, acid, and again heated to redness. The resulting dry saline mass is heated with water, nitric acid is added to produce a strong acid reaction, and then with so much water mixed, that ten parts of the solution contain one part of the dry saline mass. This golden yellow fluid, after filtration, must be preserved, excluded as much as possible from the influence of ammoniacal vapors.

If we have found by this examination whether basic bodies are present or not, it is necessary, in the case of bases being present, to ascertain *whether one or more bases are at the same time present.*

Many vegetable substances contain only a single base. The berries and leaves of coffee contain only caffeina, the berries of cocoa only theobromina, &c. But in cinchona bark, quinia and cinchonia are present; in the strychneæ, brucia and strychnia, besides another base. The papaveraceæ contain at the same time three or more bases.

By the investigation of the degree of solubility, the opportunity has in many cases been given to learn whether we have to do with one or several bodies. To arrive at certainty on the point, the following method of examination is preferable to all others, which is founded on a discovery made by Persoz, and first recommended by C. Oppermann as a method for separating several bases from one another:—

The concentrated aqueous solution of bases is mixed with *tartaric acid*, and then *bicarbonate of soda* is added. Oppermann has found that by this method of treatment quinine, morphine, and brucine are not; on the contrary, cinchonine, narcotine, and strychnine are, precipitated. Thus, in many cases when two bases are present, a separation of one from the other may be effected by this method. By mixing the fluid filtered from the precipitate which may have been produced by bicarbonate of soda with a little hydrochloric acid, and then adding bichloride of platina and alcohol, it can be readily determined whether a base still remains in the solution or not.

If we learn by this treatment that several bases are present, we must still ascertain *whether the precipitated part and the non-precipitated part* consists of *one or more bases*. The examination depends on the principle of *fractional precipitation, and the estimation of atomic weights which are undertaken with the individual portions of the precipitated bases.* For the performance of the examination thirty or forty grains of the substance to be tested is necessary. The part of the solution precipitable after mixture with tartaric acid by bicarbonate of soda is first separated from the unprecipitable part and collected on a filter, then dissolved in dilute hydrochloric acid, and half the quantity of the solution of bicarbonate of soda is added which was required to throw down the entire quantity of bases. This quantity should be previously ascertained with small measured quantities of the solution of the bases and bicarbonate of soda. It is evident that the hydrochloric acid solution of the bases must be quite neutral—that is, must contain no excess of acid.

The substance separated by the first half of the precipitant, and the precipitate produced by the second half of the same, are collected on filters and washed, then dissolved in dilute hydrochloric acid, and mixed with bichloride of platinum and alcohol. Both the platina precipitates are washed with alcohol mixed with ether, dried, and heated to redness.

From the quantity of platina remaining behind, it will be seen whether one or more bases are present. A closer examination with reagents whose behaviour to bases is known, may first be performed with good results when the separation of the different bases has been thus approximately attained.

If we have by these means learnt that the separated crystals are not an organic base, or a mixture of such bases, or rather their salts, with acetic acid, they must be therefore an indifferent organic body, or rarely a mixture of several substances of that kind. The presence or absence of nitrogen —that is, the presence or absence of a body perhaps analogous to asparagine—has been already decided by the experiment with the concentrated solution of caustic soda in the heat.

The preponderating majority of these indifferent vegetable substances has been proved by careful investigation to belong to the class of copulated carbohydrates—as, for example, salicine, phloridzine, populine, arbutine, ononine, æsculine, &c. It is, therefore, our problem to ascertain whether the crystals in question belong or not to this class of bodies—that is, whether by acids (when these do not act in a too concentrated form at high temperatures) they are split into two products, one of which—a carbohydrate—is in the majority of cases sugar, or a similarly composed body. By the action of alkalies on these bodies, two products likewise result—one which is in exceptional instances sugar, but in the majority of cases a carbohydrate, with properties different to those of sugar. Frequently the salt of an acid results, and a product which is decomposed by acids into two products, one of which is sugar.

To ascertain whether a copulated carbohydrate of that kind is present, the crystals under examination are treated in the following manner:—

They are dissolved in the smallest possible quantity of water, and the solution is mixed with a small quantity of *strong hydrochloric acid,* the acid solution is introduced into a flask, and the air drawn out by a stream of carbonic acid gas. The flask is heated on a sand-bath until its contents boil. To intercept the volatile products of decomposition perhaps evolved, the flask is connected with a refrigeratory apparatus and a receiver. In many cases while heating, and in others after cooling, the fluid boiled for some time deposits a product of the decomposition sometimes in the form of distinct crystals, sometimes in the form of amorphous flocks, or in a state of powder. Occasionally a dense oily or resinous mass is deposited, which sometimes, after long standing, becomes crystalline. When *an insoluble* or difficultly soluble decomposition product is separated after the fluid has cooled, this is collected on a filter. It is advisable to cool the fluid down to 32° Fahr., to effect thereby a more complete separation. The filtered acid fluid is then mixed with freshly precipitated moist *carbonate of lead,* until, upon the addition of this salt, no more effervescence takes place. The solution containing the chloride of lead in solution, together with the undissolved chloride of lead is poured into a basin, heated on a water-bath, and in small portions *freshly prepared or still moist* white lead is added. A basic lead salt of very slight solubility results. As soon as by the addition of a fresh quantity of white lead no more change is remarked, the contents of the basin are placed on a filter. The filtered fluid is mixed with *phosphate of silver,* which is prepared by precipitating a solution of phosphate of soda of the Pharmacopœias with a solution of nitrate of silver, and which is preserved *in a moist state,* excluded from the light. As soon as the phosphate of silver and the dissolved chloride of lead come into contact with one another, they are decomposed into insoluble chloride of silver, and into insoluble phosphate of lead. The phosphate of silver is consequently added until the yellow color of the silver salt no longer disappears; the precipitate in the fluid thus assumes a yellowish color. The fluid is filtered from the precipitate, which is washed. The filtered fluid, together with the small quantity of washings, is mixed with pure white lead into a paste, and gently heated for a short time. The white color of the milky fluid begins to pass into a reddish grey by the decomposition of the phosphate of silver, which is soluble in a small quantity in water. The fluid filtered from the insoluble contents is freed from a trace of lead by sulphuretted hydrogen, separated from sulphuret of lead by filtration and evaporated in a water-bath. If sugar has formed by the treatment with hydrochloric acid, it is obtained as a syrupy sweet mass, which crystallizes after standing some days, but requires occasionally some weeks.

When, by the treatment with hydrochloric acid in the heat, *no decomposition products insoluble or difficultly soluble* have separated, and in the receiver furnished with a refrigeratory apparatus, *no volatile products* are to be found, then either no decomposition has ensued, or *both the decomposition products are easily soluble in the water containing hydrochloric acid.* To discover whether soluble decomposition products have been produced, the acidulated fluid is mixed with dry carbonate of lead as long as effervescence results by the addition of a fresh quantity of the carbonate. The hydrochloric acid has a decomposing action on the carbonate of lead, and forms chloride of lead under the development of carbonic acid. The decomposition products of indifferent copulated compounds do not attack, in the cold, carbonate of lead in the majority of cases, because a strong organic acid seldom results from the decomposition of these bodies. Only in the heat do these bodies decompose carbonate of lead. On the contrary, they decompose more readily the freshly precipitated moist carbonate of lead, or that preserved in a pasty wet state after precipitation. The chloride of lead is filtered from the liquid, and thus much hydrochloric acid is separated. The fluid is now concentrated in a water-bath, whereby, especially after cooling, the greater part of the chloride of lead contained in the fluid separates. The separated chloride of lead is filtered off, dried, after it has been well pressed between bibulous paper frequently renewed, and now heated to learn whether it is mixed with an organic substance, which is generally not the case. Should an organic lead compound be admixed with chloride of lead, it is ascertained whether it can be extracted with alcohol from the chloride of lead, wherein the latter is insoluble. When the organic lead compound is not soluble in alcohol, the chloride of lead mixed with the organic lead compound must be decomposed under water by sulphuretted hydrogen, by which means the organic substance and hydrochloric acid are obtained in the fluid filtered from the sulphuret of lead. A small quantity of this fluid is mixed with *baryta water*, to ascertain whether, besides chloride of barium, which remains in solution, a baryta compound of the organic substance, insoluble in water, results. When this is the case, the solution containing chloride of barium is filtered from the baryta compound, which is washed with water, and the organic body which was combined with the baryta, that is, the pure decomposition product, is obtained by decomposing the baryta compound with dilute sulphuric acid. As chloride of barium is almost insoluble in quite anhydrous alcohol, and the majority of the baryta compounds of organic substances, on the contrary, dissolve with great difficulty in weak spirit, we can, when baryta water produces no precipitate in the hydrochloric acid fluid, add absolute alcohol, whereby a baryta compound of the decomposition product is often thrown down before the chloride of barium separates.

It is self-evident that the fluid containing hydrochloric acid, which is obtained by heating the aqueous solution of the crystals under examination with a little hydrochloric acid, may be mixed with baryta water, to observe whether a precipitate, that is, a compound of the decomposition product, insoluble in water, is thereby formed or not; in the latter case, the addition of a little anhydrous alcohol assists the precipitation. If a precipitate is not produced either by baryta water alone, or by baryta water and alcohol, a second portion of the fluid, containing hydrochloric acid, is taken and mixed with freshly precipitated *carbonate of silver*, which is converted into insoluble chloride of silver by the hydrochloric acid, under the evolution of carbonic acid. The chloride of silver is separated by filtration from the fluid, which is now free from hydrochloric acid. Two cases can hereby happen. Either there results, besides the chloride of silver, the silver compound of a decomposition product insoluble in water or not. If no insoluble compound of a decomposition product with silver, has separated with the chloride of silver, the filtered fluid contains silver or not. If it contains silver, the silver must be separated by sulphuretted hydrogen; then we have a watery solution of both decomposition products. If it does not contain silver, the filtrate is a pure solution of decomposition products. Of their further treatment we shall directly speak. When a decomposition product is precipitated, together with chloride of silver, as an insoluble silver compound, and filtered off, the filtered fluid is a solution of sugar, or a solution of a carbohydrate with the same composition as sugar. When the solution of both decomposition products is obtained in a condition free from hydrochloric acid, we must endeavor to effect a separation with *bichloride of tin*, or with *basic acetate of lead*. Many of the decomposition products appearing with sugar are precipitated by bichloride of tin, and most of these bodies are thrown down by basic acetate of lead. The tin and lead compounds obtained may be decomposed by sulphuretted hydrogen, after they have been diffused in water. The fluid filtered from these tin and lead compounds, after treatment with sulphuretted hydrogen, can be employed for obtaining the sugar.

If the research which has been made with both portions of the fluid under examination has lead to no result, a third portion of the fluid, containing hydrochloric acid, is taken and mixed with a solution of *sulphate of silver* as long as a turbidness arises from precipitated chloride of silver. The chloride of silver is removed by filtration, the fluid containing sulphuric acid is mixed with baryta water as long as sulphate of baryta separates, and by filtration a solution of both decomposition products is obtained free from acid.

Another method, which in many cases is easy of execution, depends on the behaviour of many bodies to alumina. The hydrochloric acid of the fluid is precipitated completely with the solution of sulphate of silver; the fluid, now containing sulphuric acid, is mixed with the hydrate of alumina in a moist condition, and ammonia is added to the solution. If a precipitate results which contains the decomposition product obtained with sugar while the sugar and sulphate of ammonia and a little free ammonia remains dissolved in the fluid, this solution is evaporated, and the residue, when it has acquired a syrupy consistence, is mixed with anhydrous alcohol. The sulphate of ammonia remains undissolved, whilst the sugar is taken up by the alcohol containing a little water, and after evaporation remains behind.

If a volatile decomposition product results by the treatment of the crystals with dilute hydrochloric acid in the heat, this is contained in the receiver which was connected with the flask by means of a refrigeratory apparatus, wherein the boiling with the acidulated water took place. A small portion of the fluid is mixed with carbonate of soda as long as effervescence results with this salt, and is then distilled. If the distillate is pure water, the decomposition product is an acid. On the contrary, if the decomposition product is not an acid, it passes over by distillation, while the hydrochloric acid remains in the residue as common salt. When an acid has been obtained, to obtain it free from hydrochloric acid the distillate is mixed with sulphate of silver as long as chloride of silver is thereby precipitated. The chloride of silver is removed by filtration, and the fluid containing sulphuric acid is distilled, by which the acid distils over with pure water.

When we have determined by the above described examination whether the substance under investigation by the action of hydrochloric acid* is decomposed or not into sugar and a second product at an elevated temperature, we have still to ascertain *whether by action of an alkali in the heat an analogous decomposition* is effected or not. Many bodies afford, by the treatment with baryta, a carbohydrate, and the same decomposition product which is obtained by treatment with hydrochloric acid. The tannin of galls affords gallic acid as well by the treatment with hydrochloric acid as with baryta water. Others behave in this respect differently. Æsculine gives, when heated with hydrochloric acid, æsculetine; on the contrary, by treatment with baryta water, no trace of æsculetine is obtained. With reference to the carbohydrates, the copulated substances behave likewise similar and dissimilar. The tannin of galls treated with

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* The hydrochloric may in these investigations be replaced by sulphuric acid with but few exceptions; the latter can be more readily removed when the decomposition has been completed. But in general the decomposition proceeds more slowly and less completely, and often not at all, with sulphuric acid than with hydrochloric acid.

hydrochloric acid gives crystallized grape sugar; on the contrary, by treatment with baryta water, a carbohydrate with the decided character of an acid. The thujine from the green parts of *Thuja occidentalis* treated with hydrochloric acid affords a non-crystallizable carbohydrate; on the contrary, by treatment with baryta water, crystallized grape sugar. Independently of this difference, a number of substances still exists which, by treatment with baryta, do not set free a carbohydrate, as is the case by the action of hydrochloric acid, but an acid results which combines with the baryta, while a substance is formed which, by the action of acids, affords sugar and a second decomposition product. Thus populine, by treatment with baryta, gives, besides benzoate of baryta, salicine, and ononine, besides formiate of baryta affords formonetine. Salicine as well as formonetine are copulated sugar compounds.

It will be seen from the examples cited that the behaviour of a substance of that kind to hydrochloric acid renders in no way superfluous the study of its relations to an alkali.

In consequence of the facility with which organic substances oxydize in contact with an alkali in the oxygen of the air, it is necessary to undertake the treatment with baryta *in an atmosphere of hydrogen*. To accomplish this, an aqueous solution of the substance under examination, as concentrated as possible, is introduced into a flask which is closed with a cork having three perforations. Through one perforation a glass tube passes which is bent at an angle, and serves to connect the flask a with refrigeratory apparatus, and a receiver for the collection of the volatile decomposition products evolved. Through the second perforation, a glass tube bent at a right angle passes almost to the bottom of the flask, through which the hydrogen enters into the flask to drive out the air. The hydrogen is generated from granulated zinc and water by sulphuric acid, and first conducted through a washing bottle containing a solution of bichloride of mercury for the separation of the sulphuretted and arseniuretted hydrogen before it passes into the fluid. Through the third perforation the long beak of a funnel is stuck, which can be rendered air tight by a glass rod ground in above where the beak of the funnel begins. This funnel is filled, when all the air is displaced by hydrogen, with a concentrated hot solution of the hydrate of baryta in water. By raising the glass rod the baryta is allowed to flow into the flask, which is closed before the last drops have run in.* The baryta water may be thus introduced into the flask without a trace of air coming in contact with the contents of the flask. Often an insoluble compound of baryta with the organic substance results, so that a dense precipitate is formed. In this case the flask, which is heated on a sand-bath, must be frequently shaken, to prevent a deposition of the precipitate. Gener-

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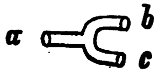
* When the hydrogen gas is evolved from a flask, the necessary mixture of sulphuric acid and water for the continued development of the gas must be passed in through a funnel constructed in the same manner to prevent the ingress of the air into the bottle.

ally, the decomposition proceeds more rapidly with baryta than with hydrochloric acid. Upon the termination of the decomposition the flask is allowed to cool, in a continuous current of hydrogen. Either a clear solution results, consequently no insoluble baryta compound has been formed, or such is suspended in, or deposited at the bottom of, the fluid. Instead of hydrogen gas, either *carbonic acid gas* is conducted into the flask, or *dilute sulphuric acid* is poured in through the funnel which is capable of being closed. Both operations are intended to convert the excess of baryta into a carbonate or a sulphate. By the sulphuric acid always, and sometimes by the carbonic acid, the baryta compound of the decomposition product formed is decomposed. Whether carbonic acid or sulphuric acid should be used must be ascertained by an experiment which is made with a small portion of the contents of the flask. In this preliminary experiment carbonic acid is employed, and it is observed whether by filtering the fluid in contact with the air it undergoes a change. If no change happens, carbonic acid should be conducted through the fluid in a large quantity. On the contrary, if it changes in the air, the bulk of the fluid must be treated with sulphuric acid. Some substances are oxidized in contact with carbonate of baryta, but others are not. Some compounds which result by treatment of the substances with baryta water are almost quite insoluble in water when an excess of baryta is present, and as this separates by the carbonic acid they dissolve, or from the compounds formed with baryta, compounds poor in baryta are produced which are soluble in water, whilst those rich in baryta are insoluble. In such cases it is more advantageous to add alcohol to the contents of the flask, and to filter the whole. The carbohydrate, or its compound with baryta, is dissolved in the spirituous fluid, and the baryta salt of the second decomposition product remains on the filter. The mass changes on the filter when a readily oxidizable substance is contained in it. The carbohydrate is obtained in the solution, and may be obtained pure by distilling off the spirit and carefully precipitating the baryta by sulphuric acid and then evaporating the fluid free from baryta.

As it is desirable by treatment with baryta to test portions of the material, whether treated with carbonic acid or sulphuric acid, or mixed with alcohol, without bringing the whole mass of the fluid into contact with the air, I will here describe a method by which portions can be used for the preliminary investigation without bringing the entire quantity of the fluid from which these portions are taken into contact with the air. For this purpose, the end of the glass tube is closed through which the hydrogen gas and the aqueous vapor pass out, and the glass rod is loosened by which the funnel serving for the conveyance of the baryta water into the flask is closed. By the pressure which the gas and vapor exercise on the surface of the fluid in the flask, the fluid rises up through the beak of the funnel, and fills the funnel more and more after the glass rod is withdrawn.

When sufficient fluid has been forced in this way into the funnel, this is closed with the glass rod, and the glass tube opened. The portion of the fluid in the funnel required for examination may be removed by means of a pipette.

I must also mention a small arrangement which renders easy the displacement of the hydrogen gas by the carbonic acid gas, without permitting the entrance of air into the apparatus. This arrangement consists of a spur made of vulcanized caoutchouc. This forked tube at *a* is to be connected with the glass tube, bent at a right angle, which conducts the hydrogen gas into the flask. The forked tube is attached at *b* to the apparatus for evolving hydrogen, and is at *c*, connected with a gasometer containing carbonic acid. While the tube at *b* is closed with a clamp, carbonic acid is allowed to stream out of the gasometer until all the air is driven out of the conducting tube. The carbonic acid passes at *a* freely, as the tube at *b* is closed by a cock. The tube at *c* is now shut with a clamp, and the cock of the gasometer is also closed. Then *a* is attached to the tube in the flask, and *b* with the hydrogen gas apparatus, and the air expelled from the flask by the hydrogen gas. After the baryta has acted sufficiently long, and it is wished to conduct carbonic acid into the flask, the tube is closed at *b*, which in the mean while was open, and the tube is opened at *c*, and carbonic acid allowed to pass in from the gasometer.



When a clear fluid is obtained by the treatment with baryta, it is ascertained whether, by the addition of alcohol, a baryta compound is precipitated, while the carbohydrate remains dissolved in the spirituous fluid. Often in this way a separation can be accomplished.

If a separation is not effected in this way, *carbonic acid* is conducted into the fluid until all excess of baryta is saturated with carbonic acid. In many cases the baryta compound of the decomposition product is thereby decomposed. The contents of the flask are heated now to the boiling point, while hydrogen gas instead of carbonic acid is passed through the fluid. By boiling, the dissolved bi-carbonate of baryta is converted into the carbonate. The contents of the flask are then filtered. On the filter, carbonate of baryta and a decomposition product remain when the latter is insoluble in water, and was dissolved only as a baryta salt in the water. The carbohydrate is contained in the fluid frequently as a baryta compound (consequently not precipitated from the baryta by carbonic acid), either alone or together with the second decomposition product, which may be dissolved either free from baryta or as a baryta salt. When the substance, as ononine or populine, &c., is decomposed by baryta into a baryta salt and a copulated carbohydrate, a copulated carbohydrate and not a separated carbohydrate is obtained in the filtrate. On this account, we have always to ascertain whether a carbohydrate, or such a copulated compound, is obtained by the treatment with baryta in the heat. If, by heating with baryta, instead of a clear solution a solid compound is obtained, which is suspended in the fluid or is deposited therein, it is separated generally, as above described by filtration from the fluid after the addition of alcohol. When the contents of the flask have been treated with an excess of *sulphuric acid* instead of carbonic acid, and then filtered, sulphate of baryta is found on the filter, and sometimes a decomposition product, insoluble in water, mixed with the sulphate of baryta, and in the filtrate a little free sulphuric acid, and either both or one of the decomposition products dissolved therein. By the careful addition of baryta water the sulphuric acid is separated. The fluid freed from sulphuric acid is heated in a distillatory vessel, and the distillate examined for a volatile acid, perchance resulting from the decomposition of the original substance. The residue of the distillation is further examined by mixing a portion thereof with perchloride of tin, sugar of lead, subacetate of lead, and baryta water. It generally happens that one of the decomposition products is thrown down in the form of an insoluble compound by one of these precipitants, while the other decomposition product remains in solution. The excess of tin or lead salt is removed by sulphuretted hydrogen, and the excess of baryta by sulphuric acid. With perchloride of tin, after the removal of the sulphuret of tin and expulsion of the sulphuretted hydrogen, the hydrochloric acid is to be separated by suitable means.

In individual cases, by *the application of caustic soda or potash* in the place of the hydrate of baryta, perfect solutions are obtained, from which the potash or soda compound of one decomposition product is separated in an insoluble form after the substance under examination has split up. In such cases it is naturally advantageous to employ soda or potash instead of baryta. Generally, the potash or soda compounds separated are insoluble only in potash or soda solutions, but not in pure water. Consequently the washing must be performed with these solutions. The filtered solution is carefully saturated with sulphuric acid, evaporated, and the second decomposition product removed by alcohol from the alkaline sulphates, which are insoluble in that menstruum.

From the results which are obtained by the described investigation it it may be determined whether by the treatment with acids or baryta the substance remains unchanged or not, or whether it is split up into two or more products. *But the case is possible that after the treatment with acids or alkalies, no two decomposition products can be discovered, although the original substance no longer exists.* In this case, where only one substance results in the place of another by the action of acids or alkalies, the original substance is converted into a new body, manifestly under the reception of the elements of water, or the expulsion of oxygen and hydrogen in equal equivalents that is under the separation of water. The substance under exmination, therefore, does not belong to the class of copulated compounds.

When the methods of examination here described have shown that the separated crystals contain no member of the family of organic bases, and no copulated compound which is decomposable by acids into a carbohydrate and a second decomposition product, or by alkalies, can be broken up into an acid and a copulated carbohydrate, we have to do with *an indifferent vegetable substance*, upon whose nature only an extended investigation can afford a conclusion.

There are substances in the vegetable kingdom which must be reckoned among *the copulated compounds, but which do not afford a carbohydrate by splitting up by either acids or alkalies*, for example, athamantine. But as such bodies break up into two products by the action of acids and alkalies, we are already acquainted with their behaviour and nature by the attempts made to decompose them into a carbohydrate and a second body.

When we are thus far acquainted with the crystals, we proceed to the examination of the *mother liquor* from which they have separated, which must always contain still a little of the substance which has crystallized out, as it is impossible for the separation to be total when it has been accomplished merely by crystallization. But if originally no crystals have separated, *the entire amorphous residue* must be examined *which was obtained after the treatment of the watery decoction with sugar of lead and subacetate of lead, and sulphuretted hydrogen, and evaporation.*

It has been previously mentioned that we must endeavor to separate this residue, when it has been suitably concentrated and treated with alcohol, into a soluable and an insoluable portion, and also to treat the alcoholic solution with ether, to ascertain whether one or more constituents are thereby precipitated.

By the treatment of the aqueous decoction with animal charcoal it has been ascertained whether bodies are contained therein which are fixed by animal charcoal or not. When such bodies have been detected in the decoction by means of animal charcoal, we must simplify the method of examining the residue in question of the watery decoction which has been precipitated with acetate and subacetate of lead by the application of animal charcoal. If this residue has been treated with alcohol, and thereby a separation has been effected into a part soluble and a part insoluble in alcohol after the evaporation of the alcohol from the part therein insoluble, and the distillation of the alcohol from the part therein soluble, both the resulting residues are separately dissolved in water and treated with animal charcoal. When a precipitate has formed by the addition of ether to the alcoholic solution of a part of the residue, this precipitate, after it has been collected on a filter, as well as the residue of the filtered liquid freed from alcohol and ether, are dissolved in water, and the solutions treated with animal charcoal. The animal charcoal, as before described, is quite exhausted with alcohol to obtain a solution of the body which it has retained, which, after distilling off the alcohol, is examined for the presence of organic bases and copulated compounds in the same manner as described for the crystals, which sometimes are deposited from the watery decoction after treatment with sugar of lead, subacetate of lead, and sulphuretted hydrogen, and evaporation. As neither all coloring matters nor all bitter principles and organic bases are retained by animal charcoal when their watery solutions are placed in contact with it, a separation of two coloring matters, two bases, or two bitter principles, can often be effected by charcoal, which can only with difficulty be accomplished in other ways.

The further examination for the presence of organic alkaloids, copulated carbohydrates and indifferent organic compounds, is now undertaken in the manner, just now described for the crystals, with those portions which had been absorbed by and were redissolved from charcoal, and with those bodies which remain dissolved in alcoholic ether, and which were precipitated by ether from the alcoholic solution.

In most parts of plants *sugar* is contained which passes into the decoction by boiling with water. It is neither precipitated by sugar of lead nor subacetate of lead, and therefore remains dissolved in the fluid which has been filtered from the precipitate, and freed from lead by sulphuretted hydrogen, and concentrated by evaporation. As this residue always contains acetic acid in rather considerable quantity, derived from the employment of the acetates, the sugar never crystallizes out. At least I have never obtained sugar in this way. By treating this residue with alcohol the sugar dissolves therein, and the acetic acid likewise goes over to the alcohol. On the addition of much ether, the sugar separates from the acetous alcoholic solution as a heavy layer like turpentine at the bottom of the vessel, and adheres to its sides as a gummy covering. With the sugar, under some conditions, other bodies may be precipitated. On that account, the impure sugar is dissolved in alcohol, and mixed with a strong solution of potash. The sugar compound of the potash separates, and most of the other substances remain dissolved in the alcohol containing potash. Whether cane sugar or grape sugar is contained in the watery decoction is not ascertained by this method of proceeding. This may be less easily discovered by the treatment of the watery decoction than by the examination of the spirituous extract of the material under examination. Of this matter we shall speak further on.

It must be observed here, that alcohol will take up almost always the organic bases or their acetates, as well as the copulated carbohydrates, from the residue of the aqueous decoction, left after its treatment with acetate and subacetate of lead and sulphuretted hydrogen. Such bodies are only in exceptional cases found in that portion not dissolved by alcohol; but are frequently precipitated by ether from their alcoholic solution, and are then in most cases intermixed with sugar.

Very frequently a body is contained in the alcoholic extract of the residue in question of the watery decoction which is not precipitated by ether because it is soluble in a mixture of ether and alcohol. Its presence may be easily recognized when the residue which remains after the expulsion of the ether and the alcohol is treated with moderately diluted hydrochloric acid. The fluid becomes turbid when a little of this body is present, and a separation of oily globules on the surface of the acid fluid ensues, and a separation of resinous flocks when it exists in larger quantity, takes place, diffusing a peculiar odor of an ethereal oil. I have met with this substance in plants of the most varied families, so that it may be recognized as one of the most widely-spread constituents of the vegetable kingdom, although it does not exist in all plants. This substance was found by Kawalier in the *Pinus sylvestris,* and analyzed by him, and termed *pinipicrine.* It is a copulated carbohydrate, which is broken up by hydrochloric acid into sugar and an ethereal oil, of which the great part becomes a resin when separated.

As the precipitates which sugar of lead and subacetate of lead produce in the watery decoction of the material under examination are not absolutely insoluble in water, it is intelligible that always after the separation of the lead by sulphuretted hydrogen a fluid is obtained, and by the concentration of the fluid a residue results which contains small quantities of those substances, the bulk of which were precipitated by the salts of lead above named; so that indeed by the addition of a little subacetate of lead always a little precipitate forms in this residue, though not much. When these small quantities of dissolved substances are impeding the separation of other bodies, they must be removed by subacetate of lead, and the lead then separated by sulphuretted hydrogen.

We often find it stated in accounts of analysis that the sugar of the watery decoction, which frequently acts very injuriously in the investigation of the other constituents, must be destroyed by fermentation with the aid of yeast.

But a removal of the sugar in this way can only give occasion too easily to delusions. When no constituents are present which undergo in contact with yeast a splitting up, the constituents still may be decomposed by the yeast and the fermenting sugar. It has been long known that urea, which is not decomposed by yeast, breaks up into carbonic acid and ammonia when it is in a solution of sugar which is set with yeast into fermentation. Other substances also may be decomposed in a similar way when they are contained in a fermenting solution of sugar. On that account this destruction of the sugar by fermentation must only be undertaken as an aid for the isolation of one or more constituents when it has been already discovered that none of the constituents undergo by this method a splitting up or an alteration.

The precipitate which was obtained by sugar of lead in the watery decoction never probably contains an organic base; on the contrary, one or the other constituent which forms with oxide of lead an insoluble compound may be a copulated compound. In the examination of the fractional parts which were prepared from this precipitate according to the method described at page 29, attention should be directed to this point, and the method should be employed with hydrochloric acid and baryta (or soda, or potash) as described at pages 37, 41.

In the same manner as directed for the residue which is obtained from the watery decoction treated with sugar of lead, subacetate of lead, and sulphuretted hydrogen, is *the residue dealt with which remains when the watery decoction was filtered through animal charcoal previous to its treatment with the lead salts, and also the residue which remains behind after the precipitation of the watery decoction with alum and ammonia, evaporating and extracting with alcohol, and distilling off the alcohol.* Thus we have in these three examinations a mutual control of the correctness of the results obtained by each individual examination, and consequently a constituent can scarcely be overlooked, and also conclusions may be drawn on the nature of the individual constituents.

II.—*Examination of the cold watery infusion.*

This fluid, prepared in the manner given at page 12, is divided into several parts.

The *first part* is introduced into a test tube, placed in a beaker glass filled with water, and the water slowly heated. By means of a thermometer inserted in the test tube, the temperature is observed. At a certain heat *a coagulation of one or the other constituents* is produced. When the coagulation of the substance is noticed, the lamp is removed from under the beaker glass, or the latter is taken from the sand-bath on which it has been placed to heat it. The object of this removal is to prevent the temperature of the fluid in the test tube rising any farther, and to retain it some time at the same heat, or rather to cool very slowly. The coagulum is separated after the fluid has cooled by the filtration of the fluid. To promote the filtration, it is better to take a number of small filters instead of a larger one, because the pores of the filter are quickly stopped by coagulated material of that kind, and the filtration then proceeds extremely slowly.

The filtrate is again treated as the original fluid, only the temperature is allowed in this second treatment to rise more quickly to the point where the separation takes place, and then slowly elevated. The fluid heated some degrees higher often throws off a fresh coagulum, which is likewise collected on a filter. The filtrate is again heated, to see whether by a still higher temperature a third coagulum makes its appearance. As all coagulable substances do not lose their solubility in water at the same temperature, several of these bodies may be separated from one another when they are simultaneously present in an aqueous extract.

The *second part* of the fluid is mixed with *acetic acid*, to ascertain whether a precipitate results. If a precipitate ensues, it is collected on a filter, of which several small ones are used, instead of a large one. The filtered fluid is now heated, whereby generally a coagulum is formed. The substance precipitated by a little acetic acid is examined, to learn whether it is quite or partially soluble or not in acetic acid when an excess is added. By these means a separation of several of these bodies may be sometimes effected.

The *third part* is, lastly, mixed with *alcohol*, and it is observed whether a precipitate results, which nearly in all cases makes its appearance thereby in at least a small quantity. The precipitate collected on a filter and washed with spirit, is treated with *water*, whereby only in few cases a complete solution results. The filtered aqueous solution resulting is heated, by which frequently a considerable coagulum is thrown out.

III.—*Examination of the extract obtained by acidulated water.*

As already stated (page 13), this extract is employed for the detection of some organic acids, which *per se* are soluble in water, but are contained in the material under examination in the form of compounds, mostly as lime salts, which are neither soluble in pure water nor in spirit. It is also employed for the detection of organic bases. For example, when a part of a plant contains, as is frequently the case, oxalate of lime, the oxalic acid is neither found in the watery decoction nor in the spirituous extract, because oxalate of lime is equally insoluble in water and in spirit. By its decomposition, by means of sulphuric acid, which is added to the water, we obtained from the salt insoluble in water so much oxalic acid in a free state, that we can detect it in the fluid.

For its further investigation the acid extract is freed from its sulphuric acid by *carbonate of baryta*, which is added in small quantity. A precipitate of sulphate of baryta thereby ensues, mixed with more or less compounds of organic substances, or perhaps with precipitated organic bases, when they were present in the acid solution, and one or more of them were difficultly soluble or insoluble in water. The precipitate is collected on a filter and washed with water. The washed precipitate is *boiled with strong spirit*, and the spirituous solution is separated from the insoluble matter by a filter. It is ascertained whether the spirit has dissolved or not any organic bases. The baryta precipitate, boiled with spirit, is digested with dilute sulphuric acid, to produce sulphate of baryta, which is separated by a filter, and to obtain a solution of the substance which was combined with the baryta. The lime and baryta salts generally exhibit a very analogous degree of solubility, so that by this method mostly those compounds are obtained in solution whose lime salts being insoluble in water and spirit, could not be extracted by these fluids from the material under examination. The fluid which is filtered from the sulphate of baryta, excess of carbonate of baryta and organic baryta compounds, and perhaps precipitated organic bases, is then mixed with *sulphate of copper*, whereby sulphate of baryta is precipitated, when a soluble baryta salt has been formed and is contained in the fluid, as well as many compounds of the oxide of copper with organic substances. The precipitate is filtered off, washed with water, and decomposed under water by sulphuretted hydrogen. The undecomposed sulphate of baryta and sulphuret of copper are filtered off, and a watery solution of the organic substances which were combined with the oxide of copper is thus obtained. The filtrate is heated, for the expulsion of the sulphuretted hydrogen, in a flask or a tubulated retort, in a water bath, during which a stream of carbonic acid is led through the liquid. After this the fluid is mixed with *subacetate of lead* as long as a precipitate ensues. By these means all the acids not precipitated by the copper salt, with few exceptions, are thrown down. The precipitate, after it has been collected on a filter and washed with water, is boiled with *alcohol*, to extract the bases possibly precipitated with the lead compounds. With these some lead salts may of course be dissolved at the same time. The spirit is distilled from the fluid, which has previously been freed from lead by sulphuretted hydrogen, and the bases are sought in the aqueous fluid filtered from the sulphuret of lead. *The fluid filtered from the precipitate produced by basic acetate of lead*, contains in the majority of cases the organic bases. The bases thus separated from most other bodies can be easily discovered therein. A portion of this fluid is employed for the detection of volatile bases, and another portion for the discovery of the bases not distillable with water, according to the directions which are given on these points in the examination of the watery decoction (pages 17, 25, 36.)

The acid fluid which has been obtained by the *digestion of the mixture of baryta salts with dilute sulphuric acid* is, by means of *fractional precipitation*, employed for the detection of the acids contained therein. *Acetate of baryta* is used for the fractional precipitation, which gives better results in this case than acetate of lead.

Volatile as well as non-volatile bases can indeed be separated in a shorter way from the acid extract: the former, by mixing the acid extract with an excess of a solution of potash and distillation: the latter, by infusion of galls and the like precipitants. But thereby we run in danger of overlooking some other constituents. On this account the ceremonious method of analysis here described is to be preferred.

IV.—*Examination of the extract obtained by ammoniacal water.*

This extract, as already mentioned (p. 13), is mixed with dilute hydrochloric acid, and the resulting precipitate, if any, collected on a filter, and washed with water. The precipitate is treated with hot spirit, to learn whether a portion, or the whole, of the precipitate dissolves or not *in* *spirit.* Generally the greater part remains behind, which consists of albuminous bodies which are present in a coagulated condition, or, like legumine, are insoluble in a free condition in alcohol and water, but with ammonia afford compounds soluble in water. They are precipitated from their solutions by hydrochloric acid, and remain undissolved by the treatment with spirit. Among the bodies extracted by ammonia and precipitated by hydrochloric acid, and also in the part soluble in alcohol, of the mixture thus obtained, substances often exist which are extracted by alcohol from the material under examination, because they are not soluble in pure water, but are as soluble in ammoniacal water as in spirit; for example, chinovic acid, &c. We often obtain bodies of that kind purer from this ammoniacal extract than from a spirituous extract of the material, in which they are accompanied with many other substances, while in this case many of these substances are separated for the most part by the previous boiling with pure water, and thus do not interfere with their preparation in a pure state. It often happens *that substances combined with lime or magnesia are quite as insoluble in water and spirit as in ammoniacal water. When the substance combined with lime or magnesia is insoluble in acidulated water,* it can only be obtained in the following way from the material:—A portion of the material, boiled with water, is extracted with water containing hydrochloric acid, whereby the lime and magnesia compounds in question are decomposed, and the lime and magnesia dissolved as chlorides and removed. All that is soluble is separated by washing with pure water, and then the material is extracted with ammoniacal water, which now dissolves the organic body rendered free, which was insoluble as a lime or magnesia compound, and may be precipitated insoluble in water upon the addition of hydrochloric acid. *By the decoction of the material with spirit containing sulphuric acid,* after it has been already exhausted with spirit, these bodies may be obtained likewise; but we are in danger, by the action of the acid in the heat, of producing changes in the bodies we desire to isolate.

V.—Examination of the Spirituous Extract or Decoction.

a.—Deposits from the spirituous extract or decoction.

From the spirituous extract of the substance under examination, when the extract is prepared with hot alcohol, bodies are deposited sometimes by its cooling, or after a portion of the spirit has been distilled off, which must be subjected to a closer examination. With a cold prepared infusion, deposits of that kind make their appearance generally after the distillation of the alcohol, but mostly in smaller quantities. Resins, kinds of wax, fats, with other peculiar bodies which belong to none of these classes—as, for example, saponine—are contained in these deposits, which frequently appear of a dark green color like the spirituous extract itself, when vegetable substances containing chlorophyll have been extracted with spirit.

Probably these might be partially separated by the employment of sulphuret of carbon, and thus the analysis facilitated. Unfortunately, at present such a few data lie before us upon the applicability of this fluid, which was first employed by Lampadius for separations of that kind, that I am not in a position to give more information with regard to the employment of this body in the treatment of the mixtures in question. So much is certain, that the analysis of these mixtures belongs often to the most difficult problems. As all fats, as well as kinds of wax, dissolve at least in hot ether, but only some of the resins, it is convenient to effect a separation by ether into a soluble part, and a part insoluble therein, and to examine both after distilling off the ether more closely, supposing that the whole mass is not soluble in ether, which often happens. Some bodies in such mixtures are soluble in hot or boiling alcohol, and sparingly soluble in cold alcohol, as, for example, some kinds of wax. A partial, though not an exact separation, can be effected by dissolving the mixture in the smallest possible quantity of *boiling alcohol,* and then cooling the solution. I shall come directly to another method for the separation of this mixture into its constituents. But I must here remark that fats, when present in great quantity, as, for example, in the seeds poor in starch or in some roots, are seldom accompanied by resins in considerable quantity, and *vice versâ,* leaves, woods, flowers, &c., rich in resin, contain seldom more than a trace of fat, so that we have to do either with a preponderance of fats, or a preponderance of resins, at least in the majority of cases. On the contrary, with resins, waxy substances frequently exist together. It has been already stated that vegetable bodies rich in fat are freed generally by pressure from the bulk of the fat, and the quantity of fat necessary for its investigation can be obtained almost in a pure condition. And it has likewise been mentioned before that the expressed residues, as well as such material which cannot be freed from its fat by pressure, are to be exhausted with a weaker alcohol in order to obtain alcoholic tincture as free from fixed oil as possible.

I have therefore to give the method by which a mixture of resins containing waxy bodies and a mixture of fats are to be treated, to ascertain the individual constituents of these mixtures. *The mixture of resins,* which contains admixed waxy bodies, must, before it is submitted to investigation, be subjected to some perliminary experiments, which are performed with small quantities of it. *A small portion of the resinous mixture* is treated in a mortar with water to which a little ammonia has been added, and the resinous mass is kneaded with the pestle into the closest possible contact with the alkaline fluid. Many resins possess the character of weak acids. These resins *dissolve in the ammoniacal water,* while the indifferent resins remain undissolved by this treatment. By filtration the undissolved substances are separated from the solution, and from this the dissolved resins are thrown down by dilute hydrochloric acid. By these means the resinous mass is divided into two parts. *A second portion* of the resinous mixture is dissolved in spirit, when the method named effects no separation. But when a separation has been thereby effected, the part soluble in ammonia is dissolved in spirit. The spirituous solutions are mixed with *a solution of acetate of copper*, whereby some resins, but not all, are precipitated. *A third portion* of the resinous mixture is treated with ether, to effect, if possible, a separation. Both portions of resin which have been separated from one another by ammoniacal water are treated with ether, to produce a further separation. *A fourth greater quantity of the resinous mixture* is treated in the following manner:—The mixture is dissolved in spirit, and the solution precipitated with a *spirituous solution of acetate of lead* as long as a precipitate results. The fluid is separated from the precipitate by a filter, and this is washed on the filter with spirit. The washed precipitate is diffused in spirit, and a current of *sulphuretted hydrogen* is passed into the fluid, which is made hot by surrounding the vessel in which it is placed with hot water. After its complete decomposition, the solution is filtered hot from the sulphuret of lead in a water bath funnel. By the cooling of the filtrate the bulk of the substance separates which was previously combined with the lead. A portion often remains dissolved, which may be procured by evaporation. Frequently in this way crystalline waxy compounds are obtained by cooling separated from the resins, while sometimes one resin or the other remains dissolved in the fluid. The fluid which is filtered from the precipitate which has been produced by the spirituous solution of acetate of lead, in the spirituous solution of the resinous mixture, is treated with sulphuretted hydrogen. The lead, as well as the chlorophyll when present, are thereby precipitated from the fluid. The sulphuret of lead is separated by filtration, and the spirit of the solution by distillation, whereby the resins are precipitated. For the prevention of any alteration by heat, the distillation is undertaken in a water bath. The *resins* thereby obtained are treated with a *weak solution of caustic potash*, which separates the soluble from the insoluble part. The resulting solution is mixed with a watery solution of *chloride of calcium*, the resulting precipitate washed on a filter, and then dried by a gentle heat or *in vacuo*. The filtered fluid is mixed with *hydrochloric acid*, whereby a precipitate frequently makes its appearance, which is collected on a filter, washed with water, and then dissolved in *lime water*. A current of *carbonic acid gas* is conducted into the solution, by which a precipitation of organic substances often appears, which are separated from the combinations with lime by the carbonic acid. As this precipitate is contaminated with carbonate of lime, the salt is extracted with *dilute hydrochloric acid*, or the organic substances are separated from the lime salt *by alcohol*. The fluid filtered from the carbonate of lime and the organic substances is heated for the decomposition of the bicarbonate of lime present. The fluid is again filtered, and, when cold, treated with *dilute hydrochloric acid*, by which a precipitate of organic substances results, which, as stronger acids, were not thrown down by the carbonic acid from the lime. The *lime salt*, prepared by precipitating with *chloride of calcium*, the solution which was obtained by means of potash, is after it is dried, treated with *ether*, which generally dissolves a portion of it, which is, left behind by distilling off the ether in a water bath. The portion remaining undissolved in ether is treated with *alcohol*, which sometimes likewise dissolves a small portion. Lastly, that which is insoluble in ether and alcohol, is treated with *dilute hydrochloric acid* without the application of heat, for the separation of the lime. With these individual portions we shall have the opportunity of ascertaining which method of separation possesses the advantage over the others, and to treat correspondingly the whole mass of the resinous mixture.

When we have to operate on a *mixture of fats* which has been procured either by pressure between cold or heated plates, or by the extraction of the material with hot spirit, and distilling off the spirit and filtering the watery residue through a moist filter, whereby the fat remains on the filter, we proceed in the following way:—

A small portion of the fat is saponified with a solution of potash in a dish, *the solution of soap decomposed by a sufficient quantity of dilute sulphuric acid*, and the floating fatty mass separated from the watery fluid by a pipette or a small syphon; this fluid is *subjected to distillation* in a flask or a retort, after a refrigeratory apparatus and receiver have been connected with the distilling vessel. The distillate is tested after about two-thirds of the fluid have passed over, and the distillation is interrupted to ascertain whether it has or not an acid reaction, whether turbid or clear, whether oily globules have separated thereout, and whether it possesses an odor or not. When the distillate exhibits only a slight acid reaction, is almost odorless, quite clear, and no oily globules float on its surface, no glyceryle compounds of the *volatile fatty acids* are present in quantity. On the other side, they are present when the distillate has a strong acid reaction, has thrown out oily globules, or at least when these render the distillate turbid or opalescent, and has a remarkable odor. *If no volatile fatty acids are present, the bulk of the fatty mixture is saponified with a solution of potash, the solution of soap mixed with common salt*, and the soap formed is separated. The soap is removed after some time from the aqueous fluid, and dissolved in water with the aid of heat. The solution is again treated with common salt, and the solution and the salting repeated frequently, until the watery saline fluid takes up no more foreign substances. *In the first ley*, from which the soap has been separated by common salt, is contained the chief bulk of the *glycerine; the soap* which has been purified by repeated solution and salting, is now *dissolved in water*, and precipitated with *a solution of sugar of lead;* the precipitate which results is a mixture of lead compounds, consisting of the lead salts of the fatty acids. This mixture of lead salts, after it has been washed and dried, is treated with *ether,* whereby the lead compounds of the liquid fatty acids are dissolved, but not those of the solid fatty acids, and which, after being washed with ether, are decomposed, which can be accomplished either by spirit containing sulphuric or hydrochloric acid, or by treatment with spirit and sulphuretted hydrogen. The fatty acids, freed from lead, and dissolved in spirit, are, after the greatest portion of the spirit has been distilled off, mixed with a solution of carbonate of potash as long as an effervescence thereby ensues, and then the spirit is entirely expelled by evaporation. A little solution of caustic potash is now added, and the whole boiled to decompose a small quantity of the ethers of the fatty acids, which have formed by the decomposition of the lead salts with the spirit containing sulphuric or hydrochloric acid, and by the distillation of the spirit, have not quite volatilized, and to combine the fatty acids contained therein with potash. The excess of alkali is separated by salting the soap, which is then dissolved in water. *This solution of the potash salts of several fatty acids is now fractionally precipitated with acetate of magnesia, acetate of baryta, or acetate of lead,* according to the method of Heintz, by adding half of a solution of these salts, which would have sufficed to throw down the whole of the fatty acids. The precipitate is filtered off, and washed. To the filtrate, the second half of the solution of the acetate employed is added, and the precipitation is thus completed. Both precipitates are now decomposed, and both resulting portions of the fatty acids are converted into ammoniacal salts in solution, and these solutions each again divided into two parts, and precipitated by the acetate selected. This method of separation is continued until only one fatty acid is in combination with magnesia, lead, or baryta, in the individual parts. We learn whether the separation has been brought thereby to this point by decomposing a portion of a lead, magnesia, or baryta salt, converting the fatty acid or acids into a silver salt, and determining the atomic weight of the acid by heat. The bulk of the lead, magnesia, or baryta salt is then decomposed, of which a small portion has been taken for the preparation of the silver salt used for the determination of the atomic weight; the resulting free acids converted into ammoniacal salts, and these fractionally precipitated. After a silver salt has been prepared from the first and second half, the atomic weights of both silver salts are determined. When the atomic weight or the organic substance of both silver salts is the same, and equal to the atomic weight of the silver salt first estimated, the separation in this examined portion has been a complete one.

If not only *glyceryle compounds* of the non-volatile fatty acids, but those of the volatile acids, are contained in the fats, the method is modified in the following way :—The saponification is performed in a still, the *solution of soap* therein mixed with a solution of *tartaric acid,* and the whole subjected to *distillation.* After the head has been fixed, and a careful arrangement made for cooling, the volatile fatty acids are then found in the *distillate,* the non-volatile ones among the contents of the still. The distillate is so fractioned by *partial combination with a base,* and distillation as described in the examination of the watery distillate (page 24), which is obtained by the decoction of the material under examination with water. The non-volatile fatty acids, partly solid and partly fluid, are treated precisely as though they had been obtained by saponification from the fatty mixture alone, which was above spoken of.

The *liquid fatty acids,* which are obtained as ethereal solutions of their lead salts, by the treatment as above given of the salts of the fatty acids with ether, may be likewise mixtures of several liquid fatty acids. After the expulsion of the ether they must be separated from the lead and thrown down by *fractional precipitation* from one another, precisely as stated for the solid fatty acids.

Since it has been discovered that not only fatty acids, but also benzoic acid, may be contained in fatty mixtures as a glyceryle compound, it is no longer improbable that the glyceryle compounds of other acids besides those of the proper fatty acids, may be found in many fats when attention is directed thereto.

To ascertain *whether other acids besides the fatty are contained or not as glyceryle compounds* in the mixture of fats, *the fluid which is obtained when the fat is saponified, and the soap separated by common salt,* is filtered and evaporated in a water bath until it is reduced to a very small volume. Glycerine and common salt are always found in this residue, besides free potash, carbonate of potash, and small quantities of dissolved soap. If glyceryle compounds of benzoic acid or of other acids were contained besides in the fat, the potash salts of the acids are dissolved likewise in this fluid. *The residue,* which is obtained by evaporation, is divided into two parts. *The first part* is mixed with a solution of chloride of calcium, which precipitates a little carbonate of lime as well as the compounds of smaller quantities of fatty acids with lime, which are insoluble in water. The lime salt of the acid, which is present in addition to the fatty acid, either precipitates or remains dissolved. If it remains dissolved, a solution of the salt of the acid sought for is obtained by filtering the fluid from the carbonate of lime, as well as from the lime salts of the fatty acids; but the solution is contaminated with glycerine and common salt. This fluid is evaporated to concentrate it. The residue is mixed with *hydrochloric acid.* If benzoic acid, or any acid difficultly soluble in cold water, is present, it is precipitated by the addition of hydrochloric acid. When nothing is thrown down, either no acid or one very soluble in water was present. To arrive at certainty on this point, *a second portion* of the residue of evaporation above mentioned is precipitated with chloride of calcium, the resulting precipitate collected and washed with water, diffused in a little water and mixed with *dilute sulphuric acid.* The decomposition is promoted by heat until it is completed. The fluid, still hot, is then filtered through a moist filter. If with the fatty acids, another acid is precipitated by chloride of calcium, as a lime salt insoluble in water, it must be contained in this filtrate with a little free sulphuric acid. To discover the presence of an acid, which is neither difficultly soluble in water, nor gives with lime an insoluble salt, we proceed in the following way:—

A *portion of the fat* under examination *is saponified* by boiling with thin *milk of lime*, and the hot fluid containing glycerine is *filtered* from the lime soap. *Carbonic acid* is conducted into the *filtrate*, heated for the decomposition of the bicarbonate of lime, and filtered. The filtrate contains the lime salt of the acid sought for and glycerine. The fluid is mixed with basic acetate of lead, and the precipitate perchance resulting is separated by filtration from the fluid. The lead salt is washed with water, diffused in water, and decomposed by sulphuretted hydrogen. In the fluid filtered from the sulphuret of lead, the acid sought for is contained. There are only a few acids which produce no precipitate with basic acetate of lead. Should such an acid be present instead of basic acetate of lead, a solution of nitrate of silver mixed with a little ammonia is added, which precipitates a silver salt of the acid. If in this way no precipitation results, the concentrated fluid, wherein the acid and glycerine exist in solution, is digested with freshly precipitated carbonate of zinc or copper, and absolute alcohol is added to the filtered fluid, by which a zinc or copper salt of the acid is thrown down, but not the glycerine. When an acid which is volatile is mixed with the glyceryle compound in the fat, it will have been already found in the examination of the volatile fatty acids.

When *fats and resins* are mixed *with one another*, the mixture is treated with a solution of caustic potash to effect the saponification of the fats. The electro-negative resins dissolve likewise as potash compounds therein, while the indifferent resins remain undissolved. After the insoluble part of the resin has been separated, *the solution of soap and resin soap* is treated with common salt, and the soap of the fatty acids is separated, but not the resin soap. The soap which has separated is treated as previously described (page 7). The solution of resin soap, which at the same time contains the glycerine of the fat, is mixed with *dilute hydrochloric or sulphuric acids*, whereby the resinous acids are separated. They often agglomerate, particularly when heated, and may be easily taken from the fluid and further purified. Sometimes it is necessary to evaporate the liquid, because a milky fluid results with acids which will not filter clear. *The resinous acids* separated are again dissolved in *a solution of potash*, and mixed with an excess of a strong solution of potash. By these means frequently a separation of several resinous acids is effected. Many potash salts of the resins are soluble, while others are insoluble in a concentrated solution of potash.

Before I conclude, the consideration of the mixtures of resins and fats separated from the spirituous extract, by cooling or distilling off the alcohol, I must direct attention to a point in the treatment of resins. *Some resins are copulated compounds.* Two resins are already known which break up into two products one of which is grape sugar. It is therefore probable that not only are other resins such copulated carbo-hydrates, but that some resins are compounds, which, by the action of an acid or an alkali. may be split up into two products, one of which is not grape sugar. The resins must in this respect be more minutely examined.

This examination is conducted in the manner described (pages 40, 55) for the investigation of copulated compounds with acids and alkalies.

It is self-evident that in the presence of *several resinous acids*, their separation can be accomplished in the same manner as this is effected with non-resinous acids, namely, by *fractional precipitation.*

When the spirit is distilled off from the alcohol extract, and the separated resins, fats, and wax-like bodies are separated from the watery residue, and the watery fluid is freed from every trace of suspended substances by a moist filter, this *watery solution* is now a subject for examination.

b.—*Watery residue after the removal of the alcohol from the spirituous extract or decoction.*

This fluid is diluted with a little water, and precipitated with a *solution of sugar of lead,* the precipitate collected on a filter, the filtered liquid mixed with *basic acetate of lead* as long as a precipitate results; and this second precipitate is also separated from the fluid by a filter. The filtered liquid is freed from lead by sulphuretted hydrogen, from sulphuret of lead, by filtration, and from sulphuretted hydrogen by heating it. This fluid, as well as both the precipitates obtained by sugar of lead and subacetate of lead, are treated precisely as the precipitates and fluid were treated which were obtained by the corresponding treatment of the watery decoction of the material to be examined.

It is here to be remarked, that by the examination of this precipitate, as well as those obtained by sugar of lead and subacetate of lead, substances will be found which have been also found by the examination of the precipitates obtained from the watery decoction. Thus far, this examination is a control of the previous one. However, these precipitates generally exhibit a less complicated composition than those obtained from the watery decoction. The spirit does not dissolve many salts—particularly of the inorganic acids, sulphuric acid, phosphoric acid, &c. The pectine bodies are quite as little dissolved by spirit. In the precipitate obtained by sugar of lead, certain bodies are therefore absent which are precipitated by sugar of lead from the watery decoction. On the other hand, no gum is dissolved by spirit, as well as some allied substances, which would be contained in the watery decoction, and then would pass over into the precipitate which subacetate of lead produces in the watery decoction. For the preparation of many bodies it is, therefore, much better to use the precipitates which are precipitated from the watery residue of the spirituous extract than the corresponding precipitates from the watery decoction.

Although we often obtain useful results by following the prescribed method of examination, on the contrary it will happen in many cases that this prescribed method is not the best, and must be replaced by another which renders possible the separation of bodies, which cannot be accomplished with the same precision in the method given. Particularly when coloring matters are contained in the spirituous extract, their isolation by the methods already prescribed cannot be performed quickly or perfectly.

In such cases, *the hydrate of alumina* is often employed with remarkable results for a preliminary separation of the constituents. This is prepared by precipitating a solution of alum with sulphide of ammonium, the precipitate is washed at the commencement by decantation, and then washed on a filter with water, and removed from the filter in a moist, gelatinous condition. It can be preserved in closed vessels for use in a *moist condition,* or at once employed; the gelatinous hydrate is rubbed with water, which is added by degrees in small quantities, to a smooth thin paste. This is added to the watery fluid which has been obtained after the distillation of the spirit from spirituous extract of the material under examination, and after the removal of the fatty and resinous deposits by filtration, the hydrate of alumina is diffused equally through the fluid by stirring, and allowed to remain in contact twenty-four hours, with frequent stirring. At the expiration of this time the fluid is filtered from the alumina, which is washed on a filter with water; the filtered liquid, as well as the alumina on the filter are subjected to further examination. There are bodies which combine with alumina, and others which form no combination with it. The bodies which can combine with alumina are on the filter with the alumina, which has been added in excess, in the form of salts of alumina, or are retained by the alumina in the same way that many bodies are fixed by charcoal or sulphide of lead. *The mixture of alumina and alumina compounds* is treated precisely as the alumina precipitate which has been obtained by the alum and ammonia from the watery decoction. *The liquid which is filtered from the alumina and its compounds* is precipitated with *subacetate of lead;* this precipitate is separated from the fluid by filtration, the fluid from the lead *by sulphuretted hydrogen,* and freed from the sulphuretted hydrogen by heat after the sulphuret of lead has been filtered off. This lead precipitate, and the fluid filtered therefrom, are treated like the corresponding fluid and precipitate were treated when no alumina had been previously added to the aqueous residue of the spirituous extract. Frequently, in the spirituous extract there are two coloring matters present, one of which has the nature of a resin. Such coloring matters separate cotemporaneously with the fats and resins, when the spirit is distilled from the extract, and they are isolated in the examination of the resins. Many coloring matters remain dissolved in the water after the spirit is distilled off. This case often occurs that one of the coloring matters is completely combined and retained by the freshly-precipitated alumina, with other bodies, when a sufficient quantity of alumina has been added to the fluid, while the other coloring matter remains behind in the fluid. The latter is then precipitated with other bodies by the addition of subacetate of lead. In the majority of cases, *the coloring matter* is retained by the sulphuret of lead after the decomposition of the precipitate by sulphuretted hydrogen, so that it can be *extracted by hot alcohol from the sulphuret of lead*, after the removal of the other constituents by water.

Before concluding this chapter, I have to return to the deposits from the alcoholic tincture, which in many instances occur after the cooling, or after the distillation of the alcohol. Occasionally, a body or a mixture of bodies, is separated in the form of powders, which may be readily collected upon a filter for further examination. Sometimes, however, no deposit takes place after cooling, and after most or all of the alcohol has been distilled off, a gelatinous mass or a jelly is obtained after cooling, which, after having been mixed with water, cannot be filtered, or at least clogs the pores of the filter in a short time, thus stopping filtration completely. There remains no alternative in such cases, but to add again the distilled spirit to the residuary liquid, and to warm the whole, in order to effect a solution ; this solution is then precipitated by a solution of acetate of lead in hydrated alcohol, the filtrate precipitated by subacetate of lead; and the liquid filtering from this precipitate, freed from lead by sulphuretted hydrogen. Both precipitates are treated in precisely the same manner as the precipitates obtained by acetate and subacetate of lead, from the aqueous decoction of the material under examination. The liquid which has been freed from lead by sulphuretted hydrogen, may contain substances which yield with lead compounds soluble in alcohol. The alcohol is therefore distilled off, and the aqueous residue is treated with basic acetate of lead, which will produce a precipitate, if the alcoholic solution had contained lead compounds which are insoluble in water. The liquid filtered from this precipitate is freed from lead by sulphuretted hydrogen, and can now be regarded as completely liberated from substances which are precipitated by lead; it is then further examined.

VI.—*Examination of the ethereal extract.*

The extract of the material under examination, after the ether has been separated by distillation in a water bath, will leave mostly fats or resins, or a mixture of both. It frequently contains small, seldom large quantities of other bodies, which are dissolved equally by water or spirit, and are found in the watery decoction or spirituous extract. Free acids, organic bases, and various indifferent bodies may be taken up by the ether. *The residue which remains after distilling off the ether* is consequently first *boiled* with *water*. Tannin and analogous bodies, some vegetable bases and other substances, are taken up by the water, while the fats and resins remain undissolved. The watery solution of the ethereal extract is treated precisely as the watery decoction of the material under examination. *The residue insoluble in water*, after the separation of all the water, is submitted to a further examination. A *portion* thereof is treated with sulphuret of carbon, to ascertain whether a separation can be thereby effected into two parts. If no separation is possible, *the whole residue left, after treating the remaining portion of the ethereal extract with water*, is treated; or when a separation has been accomplished, by sulphuret of carbon; then the portion insoluble in sulphuret of carbon by itself, and the portion which remains after distilling off the sulphuret of carbon by itself, are treated as described for the mixture of fats and resins, which is obtained from the material under examination by extraction with spirit, and cooling the tincture, or by distilling off the alcohol. (See page 11.)

VII.—*Examination of the matter extracted by spirit containing potash or ammonia.*

The solution which is obtained by spirit containing potassa or ammonia is sometimes very suitable for the isolation of substances which could only be procured with difficulty in a pure condition from the material under examination in another way. The substances whose isolation may be attempted from this solution are those which are sparingly soluble in very diluted alcohol, but are dissolved in considerable quantity by potassa or ammonia, so that the greatest portion of them is separated by an acid, while others extracted at the same time are not precipitated after the addition of an acid, because they are soluble likewise in their free state, in very dilute alcohol. Frequently, carbonic acid suffices to decompose the compounds of these substances with potash or ammonia, so that carbonate of potash and the substance which was combined with the alkali are together separated. Sometimes stronger acids, as acetic, sulphuric, or hydrochloric acid, are necessary for the decomposition. At first, therefore, *carbonic acid* is always conducted into the alkaline spirituous extract, to see whether a precipitation of organic substance takes place. When this is the case, the precipitate is filtered from the fluid and examined more closely. The filtered fluid is mixed then with hydrochloric acid, to ascertain whether a precipitate is thereby produced. In this way it is possible to separate one or more weaker acids from stronger ones. The precipitates produced by hydrochloric acid must be separated by filtration from the fluid, which is not further examined. Various peculiar bodies are readily obtained in this way pure; for example, chrysophanic acid from rhubarb and parmelia parietina, also usnic acid and analogous bodies from many lichens. The preparation of these bodies is in no other way so easily and rapidly performed as in this manner. Naturally the precipitates produced by hydrochloric acid, as well as by carbonic acid, may be not only one substance, but a mixture of several bodies, and it is therefore necessary to learn whether by treatment with *alcohol, ether and water*, a separation is possible or not into several constituents. When it is not possible to effect a separation of the mixed bodies, by their unequal solubility in these solvents, then a solution of the mixture is made in that menstruum which most readily effects its solution, such as ammoniacal water or ammoniacal spirit, and the separation is accomplished by fractional precipitation with a suitable metallic salt. In this case it is necessary to take care that no excess of ammonia is present. *Solutions of acetate of copper, acetate of lead, or chloride of calcium* are generally the most suitable salts for fractional precipitation. By a preliminary experiment it may be learnt which is the best to employ.

By the prescribed treatment of the extract whose preparation was explained in page 13, a number of substances have been prepared, not all of which can be regarded as isolated constituents, although such may be the case with many of them. Substances which have been separated from others, by the methods described in the 2nd section, will frequently be obtained in a state of contamination with small quantities of other constituents. But as we have prepared these bodies from different extracts of the same material, according to different methods, generally twice or oftener, their peculiarities may still be recognized, even when the substance has in no case been obtained quite pure, because the impurities from the different methods of preparation must be alike. After following the directions given, and from the evidence thus obtained, it is often impossible to know whether we had to do with one individual body or several bodies. Thus, by the fractional precipitation or solution of precipitates, it must often be felt undecided whether the individual solutions or precipitations contain the same or different bodies; and when the presence of several bodies has been detected in the different solutions or precipitates, whether these individual portions are to be fractionized still further or not by a repetition of this kind of treatment, in accordance with our failure or success in isolating a body from one of these portions. The following section will treat of the manner in which we can obtain information on these points, by the aid of reagents, and of the kind of reagents which in the majority of cases will answer this purpose.

SECTION III.

Reagents and their application.

It has often been stated in the second section, that the further examination of a body, by the observation of its behaviour to reagents, is required, not merely to decide by its reactions the identity of a body with one already known, but chiefly to prevent constituents being overlooked by the aid of their reactions.

If we have obtained a substance by fractional solution of a precipitate, or by fractional precipitation, of which we could not previously know whether it is only one body or a mixture of two, three, or several bodies, and have divided it into several portions, and allowed a number of reagents to act on each portion, we shall be able to ascertain whether we have to do with one or several bodies differing from one another.

I am certainly far from believing that only the reagents described in the following pages are useful means for the attainment of this object, but I have there described a number of reagents which are serviceable in the majority of cases, whose behaviour is known to organic bodies, and which every body is in a position to prepare or to procure more readily than others. I have only appended those remarks to each test which did not appear superfluous in reference to the objects of the present instructions for the analysis of vegetable substances.

1. *Perchloride of iron,* prepared by dissolving dry crystallized perchloride of iron in water. A great number of organic bodies afford with a solution of perchloride of iron, when it is added to their aqueous solutions, neither a precipitate nor a coloration. Many of the most widely-spread constituents of plants behave in their aqueous solution exactly as though this reagent was added to pure water. On the contrary, not a few compounds exist which give this reagent a remarkable coloration, or are entirely precipitated, whereby the color of the precipitate is generally a conspicuous one. There cannot be any conclusion drawn on the nature of a body which is contained in this solution, from the coloration which a solution of perchloride of iron assumes, or from the color of the precipitate produced by this reagent. Morphine, gallic acid, and the aldehyde of salicylic acid, bodies which belong to three different classes, behave very analogous to a solution of perchloride of iron. Nevertheless, this reagent is very serviceable, inasmuch as bodies which produce with other reagents very few characteristic reactions, show by this reagent when they are mixed in very small quantities with other bodies. A great number of vegetable substances afford, when their aqueous solutions are mixed with a solution of perchloride of iron, a dark green or blue coloration, as is well known. Tannin, gallic acid, and many other similar bodies, exhibit this behaviour. Other substances acquire an intense red color when their solutions are mixed with perchloride of iron. It is always advisable to add the perchloride of iron in very small quantities to the fluid under examination, as frequently the color which makes its appearance by a smaller quantity of this salt is destroyed by a larger quantity. There are substances which, by the addition of this reagent, acquire an intense color, but the color soon disappears again, and cannot be reproduced, while with other bodies a coloration results which long remains unchanged. The coloration effected by perchloride of iron is often made to disappear more quickly by the application of heat. The coloration which is developed by perchloride of iron in the solution of a substance is often quite different, according as the substance is present in a free condition, or combined to an acid, or to a base. Frequently it depends on the nature of this acid or base whether a coloration is developed or not. It is a known fact, that not all morphine salts exhibit an equally intense blue coloration when mixed with perchloride of iron, which is shown with some morphia salts every time this reagent is added. Kinic acid in a free state, in an aqueous solution, is colored intensely green by perchloride of iron, while after its neutralization with ammonia it as-

sumes a violet color. Reference must be made to these circumstances in the employment of perchloride of iron. The perchloride of iron itself is distinctly colored yellow in considerably diluted aqueous solutions. On this account, it is necessary to prevent any excess of this solution, as otherwise misconceptions will arise; for example, a blue coloration should be observed, but instead of it a green makes its appearance, because the blue coloration which the substance and the perchloride of iron produce is converted into green by the yellow of the solution of perchloride of iron which has been added in excess. Further, it is always convenient to add a little ammonia to the fluid which has assumed a distinct color with perchloride of iron, to observe the appearances which are thereby developed. The green or blue coloration is changed by perchloride of iron sometimes into a dark violet, sometimes into a black, and sometimes into a red. Thus the presence of two substances can be rendered evident, which behave in a free state quite the same as perchloride of iron.

2. *Perchloride of tin.*—The aqueous solution of perchloride of tin produces no coloration in the watery solutions of many substances, and also no precipitates; on the contrary, in the solutions of other bodies, a characteristically colored precipitate frequently results thereby, sometimes only after the addition of a little ammonia. Frequently, by heating a solution after the addition of perchloride of tin, a precipitation results which contains no longer the original substance, but a decomposition product of the substance combined with oxide of tin.

3. *Protochloride of tin.*—The protochloride of tin, as a powerful agent of reduction, produces, particularly at elevated temperatures, changes of color, which indicate the presence of a body which otherwise might have been overlooked. By this reducing action a colored fluid often results. In many cases the addition of a little free alkali assists considerably the action of the protochloride of tin.

4. *Nitrate of silver.*—By the watery solution of this salt a precipitate of a silver compound, insoluble in water, often results in solutions, particularly after the addition of a little ammonia. Many of these silver salts are almost immediately decomposed under the separation of metallic silver, others only under the influence of a higher temperature. The silver separates thereby sometimes as a shining mirror, sometimes as a pulverulent black mass. This varied behavior of the different constituents of vegetable substances to the solution of nitrate of silver, by the presence and absence of an alkali, permits the employment of this salt likewise for the detection of individual constituents in a mixture.

5. *Acetate of lead.*—The neutral acetate of lead is employed as a watery as well as a spirituous solution; for the latter spirit of specific gravity ·825 is used. The majority of organic substances are precipitated by sugar of lead from a watery or spirituous solution. One part of the lead compound, insoluble in spirit or water, dissolves in acetic acid: another

part does not. A part of the lead compound insoluble in water, dissolves in alcohol; on the contrary, a part of the lead compound, insoluble in spirit, dissolves in water. By the decomposition of lead compounds which are precipitated from their watery solutions by alcohol, and by the decompositions of lead compounds which are precipitated from their alcoholic solutions by water, the separation of substances is effected which were contained in the lead precipitates together at the same time. When the decomposition is performed with sulphuretted hydrogen, the sulphuret of lead, like charcoal, retains often one or more of the constituents, while other constituents pass over into the fluid in which the lead compound was diffused before treatment with sulphuretted hydrogen.

6. *Basic acetate of lead.*—In general, what has been stated of the neutral acetate of lead is applicable to this reagent. A number of substances which are not precipitated by the neutral salt, give insoluble compounds by the addition of subacetate of lead to their watery or spirituous solution. As many organic substances which have a great tendency to reduce the oxides of the noble metals, and in combination with alkalies and alkaline earths absorb oxygen from the air, form with lead compounds which are less subject to such changes. both the lead salts are more suitable, in many cases, than other metallic salts to effect the decomposition and separation of substances. Concerning the basic acetate of lead, it is particularly to be mentioned that it precipitates substances from acid solutions because it saturates the free acid, and is converted into the neutral salt. These substances are *per se* insoluble in the fluid, and are only dissolved therein by the agency of an acid, so that the precipitate may contain substances which do not form compounds with oxide of lead.

7. *Acetate of copper* can be used in many cases as the neutral acetate of lead, but seldom offers any advantage over it.

8. *Sulphate of copper* is employed in the same cases in which acetate of copper or acetate of lead is used, when the presence of acetic acid should be prevented in the fluid, because the sulphuric acid which is here introduced into the fluid by the reagent can be more easily and quickly removed than acetic acid. The application of sulphate of copper for distinguishing grape sugar and milk sugar from gum-cane sugar, and analogous bodies, is, of course, well-known; but I may mention that the *alkaline solution of copper* as a reagent demands great care, because many substances effect a reduction and separation of the suboxide of copper, like grape sugar or milk sugar; on the contrary, other substances have not this reaction.

9. *Chloride of platinum*, and

10. *Bichloride of mercury.*—These salts serve for the detection and separation of organic bases. (For the same object, under certain conditions, infusion of galls, nitro-picric acid, and sometimes sulpho-cyanuret of potassium are employed.)

11. *Carbonic acid, metallic oxides insoluble in water, carbonate of lead, carbonate of silver, carbonate of copper, and basic carbonate of lead.* are often employed for the separation of bodies. *Carbonate of zinc* and *carbonate of cadmium* are seldom serviceable. Many substances expel the carbonic acid from the carbonates, and form compounds partly soluble and partly insoluble; other substances drive off the carbonic acid quite as little at the boiling heat of water as at ordinary temperatures, whilst some other bodies are able to expel the carbonic acid in the heat, but certainly not in the cold. When, therefore, one or the other of the metallic carbonates named are brought into a solution of different bodies, compounds result partly soluble and partly insoluble, while a part of the organic substance remains dissolved in a free state. Many of the dissolved compounds are precipitated by alcohol from their watery solutions, and others are not, whereby a further separation is rendered possible.

12. *Bisulphites of potash, soda, and ammonia.*—These salts are prepared in solution, as concentrated as possible, by conducting sulphurous acid into concentrated solutions of the corresponding carbonates. They are partly employed to produce, with certain substances, compounds which are easily separated from the other constituents, which are not capable of combining with alkaline bisulphites. This is the case in the separation of the aldehydes from indifferent bodies which possess equal solubility in various fluids with the aldehydes. They are partly used with the co-operation of heat to change individual substances, whilst others remain thereby unaltered. Many substances which possess the same solubility as others, by this change lose their solubility in a fluid, so that the bodies remaining unchanged may now be readily separated from the unaltered ones.

It is necessary, when changes are produced by the action of the materials which afford a solid body by separation from a fluid, to always observe whether the separated substance contains or not sulphurous acid and an alkali. By this it may be concluded whether an insoluble compound, with alkaline bisulphites, results or not. As Knop has shown, many bodies break up by the action of alkaline bisulphites in the heat in a manner analogous to the action of free alkalies and acids in the heat. By this capacity to produce decomposition products, the alkaline bisulphites are quite as useful in investigations as by their capacity to form with many bodies alkaline salts under the expulsion of sulphurous acid, whose oxidation by the oxygen of the air is prevented by the presence of sulphurous acid, as Knop has observed with gallic acid and analogous bodies.

13. *Hypochlorite of lime.*—The chlorinated lime is employed as watery solution which has been separated from the undissolved hydrate of lime by filtration through clean asbestos. With many organic substances it produces characteristic colorations, which are often so very intense that a small quantity of a body can be recognized thereby in the presence of other substances. Lichens contain peculiar crystalline materials, some of which

are remarkably colored by chlorinated lime. With many bodies chlorinated lime produces no coloration. The chloride of calcium admixed has no influence in these reactions.

14. *Bichromate of potash.*—Bichromate of potash acts on many organic substances at ordinary temperatures, on others only at a boiling heat. Many bodies undergo no change at higher temperatures with this salt· By this unequal behaviour of bodies to this oxidizing salt, it is suitable for the detection of many substances. Either changes of color only, or also the separation of precipitates, are thereby observed, which latter consist frequently of a combination of oxide of chromium with a newly-formed product of oxidation. Frequently, peculiar odorous volatile oxidation products are formed, which are readily-detected by reagents. When the salt does not act on a solution of one or more bodies even at the boiling heat of water, a little sulphuric acid is then added, by which an oxidation is effected, except in a few cases. Only a few bodies withstand the action of chromic acid, which is rendered free by the addition of sulphuric acid. The experiment with bichromate of potash, as well as with chromic acid, is best undertaken in a retort, or a flask connected with a refrigeratory apparatus and a receiver, to intercept the bodies which are volatile. Salicylic acid, kinone, &c., can be thus easily detected in the distillate. Substances which—as, for example, limonine—withstand theaction of chromic acid even at high temperatures, are easily isolated from all other accompanying constituents, which thereby undergo decompositions.

15. *Caustic alkalies, the hydrates of potash and soda, as well as baryta,* are often very serviceable as reagents, partly in the form of an aqueous, and partly in the solid condition. Substances are dissolved by a solution of an alkaline hydrate which are insoluble in a free state in water or spirit; while other substances, insoluble, *per se,* but dissolved in the form of a compound, are separated and precipitated by the alkaline solution. Potash, soda, and baryta, effect changes by bodies being heated in their solutions, which often afford conclusions on the nature of the bodies, and quite as often draw attention to the existence of a body which otherwise had remained unobserved. Ammonia, methylamine, and similar bases, are often thereby set free from nitrogenous bodies, sometimes affording a decomposition product which, with the alkali, forms an insoluble compound which separates. This takes place more frequently with baryta, than with soda, or potash. Indeed, often no such insoluble compounds result, but a soluble salt of a decomposition product is formed, which is, *per se,* insoluble in water, so that only after saturation with an acid a decomposition product is separated. As organic substances in contact with the air more readily take up its oxygen in the presence of strong bases than happens without the agency of these bases, it is necessary to exclude the air when the action of alkalies on organic substances is to be observed. Consequently, the bodies are heated with alkalies in vessels which are filled with

hydrogen gas, in the manner explained in the treatment of certain bodies with baryta (page 42.)

The disposition of many organic substances to oxydize with oxygen in contact with alkalies, can likewise be used for the detection of bodies. In these processes of oxidation changes of color generally appear which are not easily overlooked,

16. *Ammonia.*—In its method of action, ammonia is closely allied to the bases above mentioned. In many cases it possesses a preference over them, in so far as an excess of it can be easily removed. Its action is generally less energetic than that of the fixed alkalies and baryta. Ammonia frequently acts in a peculiar way on organic substances, for many organic substances combine therewith under the absorption of oxygen and the separation of water, and produce sometimes brilliantly colored compounds. In contact with many compounds, ammonia produces immediately characteristic colorations. The treatment of dry substances with dry ammoniacal gas, sometimes at ordinary and sometimes at higher temperatures, serves frequently for the detection of bodies which would otherwise remain unobserved, and for the recognition of bodies in other respects similar.

17. *Nitric acid.*—The acid acts in a concentrated condition very vehemently on almost all organic bodies. Their oxidation products, or substitution products, which contain NO_4 in the place of hydrogen, are thus produced. The body often splits up, and the products of this decomposition then undergo further changes. By the action of nitric acid many bodies assume very intense characteristic colorations, others do not; so that this acid can be used by this property for the recognition of bodies in mixtures with others. Nitric acid mixed with sulphuric is particularly suitable for the development of nitro-compounds.

18. *Sulphuric acid* is employed in a diluted as well as a concentrated condition. The heated dilute acid splits up many bodies into decomposition products, although in this respect hydrochloric acid is much to be preferred. But it may be more readily and quickly separated from a liquid than hydrochloric acid, which in many cases demands care. In a moderately concentrated state it precipitates many forms of tannin from concentrated aqueous solutions, particularly when no acetic acid is present. It gives crystallizable salts with many organic bases, which, with the exception of the salts of methylamine, are soluble in alcohol. The dilute acids often effect in the heat, with some organic substances, an absorbtion of water, or rather of its elements; with others, an expulsion of hydrogen and oxygen in equal equivalents. In this respect its action has much resemblance to the action of alkalies.

The concentrated acid dissolves many organic substances without exercising any influence on their composition. When the substance is insoluble in water, it is often precipitated unchanged from such solutions by water. Sometimes the solutions even of colorless bodies are strongly colored. Generally, the color of the solution appears red; more seldom, violet or blue. The yellow or brownish-yellow color is quite as frequent as the red. By the addition of water a more or less complete decolorization then generally ensues, with or without the formation of a precipitate. Sometimes, by the solution of a substance, a so-called copulated sulphuric acid is produced, which is found when the solution, diluted with water, is mixed with carbonate of baryta, lime, or lead, and the sulphuric acid salt, insoluble in water, separated by filtration from the fluid, which is then evaporated, whereby the salt of the copulated acid is left behind.

19. *Hydrochloric acid.*—The concentrated acid precipitates many organic substances from their aqueous solutions, but the precipitation is not generally so complete as that with sulphuric acid. More of the substance to be precipitated remains dissolved in the hydrochloric acid solution than is the case with the use of sulphuric acid. Acetic acid prevents generally the precipitation more or less, and sometimes entirely. The tannic acid of galls, and other analogous bodies, may be precipitated by hydrochloric acid. The dilute hydrochloric acid, at the boiling heat of water, splits up bodies, and in this respect it is not surpassed by any other reagent. Decompositions of this kind are most suitably undertaken in an atmosphere of carbonic acid. A more thorough decomposition, as happens so readily with sulphuric acid at the margin of the liquid, is not to be feared with hydrochloric acid. Hydrochloric acid affords with these decomposition products very little occasion for the formation of bye-products. Through the separation of a difficultly soluble or insoluble decomposition product, and by the peculiar color of many such products, the means are given frequently to recognize and to direct attention to a body. Concentrated hydrochloric acid, as well as hydrochloric acid gas, like concentrated sulphuric acid, produce often a conspicuous coloration of bodies, which sometimes disappears on the addition of water, but sometimes is only slightly changed thereby, and in a few cases undergoes no alteration at all. Hydrochloric acid gas may be employed for the determination of the atomic weights of substances with which it combines; as, for example, organic bases and many hydrocarbons, of which some give therewith a crystalline, and others a volatile compound. In the latter case, hydrochloric acid may be employed for the separation of several such indifferent bodies. Hydrochloric acid is consequently the most generally applicable means for the recognition and separation of organic materials.

Before I pass to another reagent, I will only just remark, that different organic substances which are split up by hydrochloric acid require an unequally long time for their decomposition, so that, by a gentle heat and a sufficiently diluted acid, one of the compounds is often entirely decomposed before the decomposition of the second has begun. In this way, consequently, it is frequently possible to recognize two substances mixed with one another whose solution could easily have been regarded as the solution of a single substance.

20. *Peroxide of lead, and peroxide of manganese.*—Both these superoxides, in a finely divided condition, frequently produce an oxidation of one or the other constituent in the heated watery solutions of substances, while some bodies are not thereby attacked. A few organic compounds withstand this oxidizing agent after the addition of dilute sulphuric acid. Volatile bodies are often thereby formed, as formic acid, kinone, &c., and frequently characteristically-colored oxidation products; as, for example, with strychnine. The formation of colored oxidation products from many organic bases, which are produced by the action of peroxide of lead and sulphuric acid, depends, with the majority of these substances, upon an illusion. Quinetine, cinchonetine, morphetine, &c., result, by the action of sulphuric acid and peroxide of lead, from the bases concerned, only when the sulphuric acid or the peroxide of lead is contaminated with nitric acid. By the employment of pure reagents other decompositions are produced.

21. *Chlorine, bromine, and iodine.*—These three elements produce, partly by the indirect oxidation of the substance in the watery solution in which they are introduced, and partly by the substitution of hydrogen which they call forth, characteristic appearances of color, or precipitations of insoluble oxidation or substitution products; consequently, they serve often for the detection of substances in mixtures.

22. *Gelatin.*—Solution of gelatin is employed for the precipitation of the different forms of tannin. A pure solution of gelatin is prepared by precipitating a solution of gelatin, to which a little hydrochloric acid has been added, with alcohol, washing the precipitate with spirit, an ddissolving the washed gelatin in water.

23. *Infusion of galls* serves for the precipitation of organic bases, as well as for throwing down some albuminous substances from their solutions.

The employment of reagents will never lead to a complete knowledge of the composition of a vegetable substance, because, from the similar behaviour towards some reagents of a body discovered with one already known, no conclusion can be drawn on their identity. Reagents are serviceable for directing attention to the presence of substances, and reagents should show us the way of separating bodies which exist in a mixed state. In the second section it has been explained how we are to proceed with different decoctions and infusions of a material under examination, to separate up to a certain point the constituents from one another. Thereby it was necessary to speak of the application of some reagents. The description of the method of separating mixtures was often interrupted, and it was there stated that the further examination must be continued with the aid of reagents. If we had described in every case the method to its termination, a numberless quantity of repetitions would have been unavoidable. Besides, that which has been indicated above concerning the individual reagents, clearly shows in what manner and to what purpose each reagent shall be used, where in previous paragraphs it has been only briefly pointed out that reagents should be used for the further investigation. Assuming that by treatment of the precipitate with acetic acid, which sugar of lead produced in the watery decoction of the material under examination, we have the precipitate separated into a part soluble and a part insoluble in acetic acid, the part soluble in acetic acid precipitated by subacetate of lead into two portions, because by subacetate of lead a precipitate results when the fluid still reacts acid, while a second precipitate makes its appearance when the acid fluid is neutralized by the addition of subacetate of lead: assuming that by treatment of both lead salts with alcohol, we have separated them into a part soluble and a part insoluble in alcohol, and thus obtained four portions of lead salts of the precipitate from the part soluble in acetic acid produced by sugar of lead in the watery decoction of the material under examination; assuming that we have decomposed the part of this precipitate insoluble in acetic acid under water by sulphuretted hydrogen, the fluid filtered from the sulphuret of lead, freed from the excess of sulphuretted hydrogen, and thrown down ten lead salts by fractional precipitation with sugar of lead; we have prepared in this way fourteen lead salts from the single precipitate thrown down by sugar of lead in the watery decoction of the material under examination. By the decomposition of these lead salts with sulphuretted hydrogen, we have fourteen aqueous solutions, which are now to be tested with reagents. It is self-evident that certain reagents are not here required to be employed, because no representative can be contained in these fluids of the class bodies for which they could be used with results. We have found in the precipitate produced by sugar of lead partly inorganic and partly organic acids combined with lead, no indifferent carbohydrates and no bases, because their precipitation is prevented by the acetic acid rendered free. The vegetable acids existing generally as malic acid, citric acid, tartaric acid, fumaric or aconitic acid, the tannic acids, the acids corresponding to gallic acid, substances which are so widely spread in the vegetable kingdom, are contained in this precipitate, by the investigation of the bark, the leaves, the stems, and the flowers of plants. Coloring matters, often formed by the oxidation of the various forms of tannin or their splitting up, are produced from colorless bodies. Gelatinous bodies of the class of pectine compounds are frequently present in this precipitate. Coloring matters and pectine bodies, by the decomposition of the lead compound with sulphuretted hydrogen, are often entirely retained in the sulphuret of lead, partly because sulphuret of lead acts analogous to animal charcoal, and partly because they were present in the watery decoction in the form of soluble salts. By precipitation with sugar of lead the base of the soluble salt is separated as an acetate, the acid precipitated with the oxide of lead, and retained by the sulphuret of lead, because in a free state it is insoluble in water. We return now to the fourteen fluids.

It is self-evident that we have not to deal with the solutions of fourteen peculiar bodies. Several bodies may be contained only in one, or at the most two of these solutions, but another constituent may exist in six or eight of the fluids, and each contaminated with one or more constituents, and perhaps in one of these fluids quite pure. It is only by a number of reagents that the truth can be learnt. It is clear that the same reagent must be always applied to all portions of the fluids. For example, we add a few drops of a solution of perchloride of iron to a little of each of the fourteen fluids which have been taken for this purpose. In several of the portions there results an intense, in some portions a less intense, in other portions no coloration, or there results in some of these fourteen fluids a different coloration by this reagent to that of the remainder. In the same manner we add a second reagent to portions of these fourteen fluids, and so forth. By these means it may be ascertained how many different constituents are contained in the fourteen fluids. It may further be discovered by what means each of the constituents present can be separated from the remainder. The examination can only be conducted further by the aid of elementary analysis. By elementary analysis alone can the identity of a discovered body, separated from its accompanying constituents, be proved and established with a known body. The similarity of many reactions is so great with many bodies, that we should regard those as identical which elementary analysis shows us are very different bodies: for example, two members of a series of homologous substances which stand next to one another in the series, &c. On the contrary, bodies often appear different in many of their properties from a known body, while we by elementary analysis are taught that a complete identity exists, and the difference in many properties is due to impurities which are present in such small quantities, that they have exercised no noticeable influence on the result of the analysis.

§ 6.—*Quantitative estimation of the constituents.*

For the completion of a work on the analysis of vegetable substances, it is appropriate to describe the methods which are employed to determine the quantities of individual constituents which have been found in a plant or in a part of a plant. It is often of importance in pharmaceutical or technical relations to know correctly the quantity of one or more constituents of a vegetable substance, or more rarely those of a whole plant. Instruction for the complete *quantitative* analysis of a vegetable substance cannot be given at the present time, as scarcely a complete *qualitative* analysis of any one plant, or part of a plant, exists. It is self-evident that it is impossible to describe methods for the separation of bodies which are unknown, whose proportions of solubility are quite as unknown as their combinations, and of whose existence we know nothing. With vegetable substances also which contain only known bodies, a method for their quantitative determination cannot be supplied, because the bodies most known are still too little investigated with exactness to afford grounds for the construction of a method of separation from a knowledge of their properties, and the properties of their compounds. Another circumstance renders a quantitative estimation almost impossible, even when we know the means of separating the constituents from one another: namely, a complete exhaustion of a vegetable substance under examination is almost impracticable, because it is not possible to comminute a substance in such a way that each cell is broken and its contents exposed to the action of a fluid. There also always remains behind a quantity—sometimes greater, sometimes smaller—of the constituent to be estimated in the material under examination. It may be easily determined by an experiment how much quinine can be *extracted* from a sample of cinchona bark, while the difficulties of the experiment would be considerably increased to determine how much quinine is *contained* in such sample of bark, as a little quinine always remains in the bark. I believe that it is quite useless to give the methods here which have been devised to determine quantitatively one or the other constituent in a certain vegetable substance; for example, the starch in seeds or bulbs, the sugar of beetroot, the quinine in cinchona bark, &c. To conduct a quantitative analysis, a complete qualitative analysis must first be undertaken, and the individual constituents must be accurately studied, and not only must their relations to solubility and their combinations be known, but their decomposition products, the properties of the same, and the quantity in which they appear, &c., must have been correctly studied. In a particular case, a method for the quantitative analysis of an individual part of a certain plant may be devised when the troublesome and tedious labor above mentioned has been performed in that particular case. But it is not impossible to supply a general method for this purpose, because a single body previously unknown, when present with other well-known constituents, must always cause an alteration in the entire order of the analysis. The majority of quantitative analyses, of which we have no deficiency, are regarded as useless. They can only claim to be considered as qualitative analyses. Independently of pharmaceutical or technical bearings, which in particular instances may render desirable an approximately correct quantitative determination of one or the other constituent of a certain material, an exact quantitative analysis can only have for its object the construction of a true representation of the normal constitution of the parts of a plant. But this object has never been accomplished by an analysis, however correct. We are far from being in a position, from a dismembered analysis of an ash, to draw a valid conclusion on the normal soil constituents of a plant, and quite as far from being able, from the individual analyses which have been performed with especial reference to its organic constituents, to form a conclusion on the normal composition of a plant or one of its parts. In such analyses, whether we find ten or thirty per cent. of sugar, is of no importance. We only learn by this estimation that ten or thirty per cent. of sugar are contained in a certain part of a certain plant under certain circumstances, but we do not learn whether this quantity of sugar remains constant under all conditions, or whether the quantity found is the maximum or minimum quantity of sugar, or whether it lies between both extremes. That which has been stated with regard to sugar is applicable to every other constituent. Whether with the increase of one constituent the quantities of a second and a third increase or diminish, this and the like are questions which remain unanswered. Quantitative analyses will only then afford us information—that is to say, will be able to teach us the normal constitution of a vegetable substance—when they have been performed, in greater number, with materials which have been collected from plants at certain epochs of their development, and from plants which, under various climatic relations, have been developed in various positions, and from plants whose age we know correctly, &c.

These investigations, which are necessary to afford information on the normal constitution of a single vegetable structure, would claim the industry of a chemist for years. Consequently, there is little prospect existing that we shall be in possession of the results of such investigations in our time.

On the grounds just explained, we have also no rule for judging of the correctness or incorrectness of the results of quantitative analyses, when several of them have been performed on one and the same material by several chemists, and when the quantities of the different constituents in the various analyses differ considerably. Individual exact quantitative analyses, consequently, in proportion to the time and labor bestowed upon them, are of such little service, that it is advisable to neglect them. Under some circumstances the quantitative estimation of a constituent in a material may appear constantly necessary, to determine accordingly its value as a medicine or an article of commerce. Estimations of that kind of constituent, with the neglect of all others, possess proportionately little difficulty, and the corresponding method may be easily devised when a good qualitative analysis lies before us.

With regard to these quantitative estimations of individual constituents, attention may here be directed to circumstances of particular importance. The knowledge of the constituents of a material to be examined teaches us frequently that it is quite impossible to separate two constituents from one another in such a manner that one of them can be obtained pure without any loss. In such cases, or also when the separation can only be accomplished by tedious operations, the possibility of the *indirect estimation of a constituent* deserves our attention. This method for the estimation of a constituent is by no means new. For a long time we have known how to estimate the contents of sugar from the quantity of alcohol which is obtained by the fermentation of the sugar. We have had processes for the estimation of starch from the quantity of sugar which can be produced from starch by various agents. Indirect estimations of this kind are often very easily performed in cases where a direct determination is endlessly difficult, or quite impossible. To estimate the quantity of caincic acid in the roots of *Chiococca racemosa* belongs to the impossible; the caffeo-tannic acid cannot be so exactly separated from the caincic acid, that the latter is obtained pure without loss. The caffeö-tannic acid mixed in its watery solution with hydrochloric acid and heated, does not give an insoluble or difficultly soluble decomposition product, but simply caincic acid. When a mixture of both substances is treated in the heat with dilute hydrochloric acid, the decomposition product of caincic acid is easily obtained, and its quantity can be estimated. This product is very difficultly soluble, but not insoluble, in the fluid from which it has separated. We know, by the examination which has been made, how much per cent. of the difficultly-soluble decomposition product is afforded by the pure caincic acid, and we know the solubility of this decomposition product as well as the quantity of fluid, consequently know the quantity of the decomposition product which remains dissolved therein; and thus we can estimate, in a short time, the quantity of caincic acid with the greatest facility and exactness. Indirect determinations of that kind may be performed, in a number of cases, without any difficulty and in a very short time. The correction first employed by Fresenius in mineral analysis for the solubility of difficultly soluble precipitates must not be passed over here without attention being drawn to it.

MICROSCOPIC EXAMINATION WITH THE AID OF REAGENTS.

Repeatedly the assertion has been made, that a chemical analysis can only be considered as completed when it not only enables us to learn the constituents of a vegetable substance, but, with the assistance of the microscope, renders us so experienced that we know in which form, and at what place, to find the individual constituents in the material under examination, and make out whether they are in the form of crystals or in the form of amorphous masses, or exist in a dissolved form in the contents of the cells, or as a constituent of the walls of the cell; also the density of its layers, and so forth. It is certain that we can only then say we know a plant or its parts when our investigations in chemical and anatomical directions are equally complete, and at the same time consolidated to a whole. But the assertion quoted is decidedly untrue from a chemical point of view, if correct from a botanical or a vegeto-physiological one. The chemical investigation has only to teach us the problem what constituents a plant contains, and in what quantities which naturally fluctuate between two certain extremes.

Whatever relates to the place in which a constituent exists is certainly not a chemical question, even when it lies in the nature of things that with chemical assistance, or perhaps alone, or at least more easily and certainly than without such assistance, this question can be answered.

In physiology, in geology, and other sciences, there is an abundance of problems which only those are in a position to solve who possess a certain sum of chemical knowledge. On this account, these problems are merely physiological or geological ones, and the physiology or geology is, on this account, no chemistry, although when not studied with chemical knowledge, they are less essentially advanced. When the chemist takes the arithmetical mean of the results of three elementary analyses, he is not necessarily an arithmetician, although he must have learnt to calculate to perform this operation; and when a chemist arrives at the remarkable idea of calculating the mean of his analysis according to the method of the smallest quadrate, nevertheless he is not a mathematician. The mineralogist is not a chemist when he tests a mineral with the blowpipe.

To return to the microscopic examination with the aid of reagents. It will be self-evident that it can only be undertaken when a correct qualitative analysis has already been performed with the material under examination, and the behaviour of the individual constituents with reagents has to be inquired into with exactness. It is also self-evident that we cannot conduct an examination of that kind with five or six reagents, as some persons still appear to consider at the present day. We must have confidence in the idea that we must test under the microscope in the same manner as without it. No one believes that simpler methods are employed in such chemical analysis, and that several reagents can be used when spectacles are worn. But a microscope is nothing else than spectacles which permit us to observe things which we are not able to see with our naked eyes on account of their smallness; it saves us chemical operations and chemical reagents quite as little as the spectacles of a short-sighted or long-sighted chemist are in a position to spare him such things. What we see under the microscope with the aid of reagents is only understood when we have been able, by a previous analysis, to know with precision the constituents. Whoever endeavors to learn anything under the microscope with the aid of reagents without a previous analysis and without a preliminary study of the constituents, is like a man who strives to read a book which is written in a language unknown to him, and therefore unintelligible to him with the assistance of lens. The result is precisely the same. He will know as little after the labor has been done as he did before the commencement. The vegetable anatomist is quite right when he endeavors to accomplish his object by the application of some few reagents, and facilitates and renders possible his observations, because by a few chemical agents he makes certain outlines appear more defined, or compels some bodies to disappear, which prevent such observations. In chemical relations merely, nothing results from these observations, as bodies are present which behave towards certain reagents precisely as many hundred other bodies, some of which we know accurately, others very little or not at all. Of bodies which are colored brown by iodine, and such as are colored red by sulphuric acid with the addition of sugar, there is an innumerable quantity. From such reactions on certain bodies, to establish certain classes of bodies, is folly.

To give a method for the microsopic examination of vegetable substances whose composition has been previously ascertained with exactness, and whose constituents have been accurately investigated with regard to their behaviour to the various reagents, is at the present time an impossibility. We have a mass of difficulties therein to overcome, and the result of an investigation is frequently a doubtful when even a probable one, as we may have often and cautiously made observations, at least with regard to one or more constituents, when there was also frequently no difficulty in procuring certainty concerning other constituents.

§ 8.—*Conclusion.*

So far as was practicable in the present position of our knowledge, I believe that I have supplied a method for the examination of plants or their parts which does not easily permit a body to be overlooked which exists therein as a constituent. I believe, also, that by following the method given with some attention, suitable methods of separation can be easily devised to procure as many of the individual constituents as are necessary for the performance of a more minute examination of them, which will afford us again useful hints for devising improved methods of separation. When a minute examination of a constituent is intended, and consequently a sufficient quantity is to be prepared for this purpose, it is an unnecessary labor and a useless loss of time, when the order of analysis here described is pursued, to separate and prepare all the bodies which are contemporaneously present. We often attain this object very quickly when a certain quantity of the material is employed for the preparation of a constituent, and in this undertaking we have only a regard to this one constituent, and are disposed to sacrifice the remaining ones. This shorter and simpler method for the preparation of individual constituents can only be devised from the experiences which we have made by a systematic analysis, which has enabled us to learn all the constituents present, and given us the means to prepare smaller quantities of the individual constituent for the examination of its behaviour with other bodies, as far as it is necessary, to discover methods of preparation based on these experiences, which will enable us to procure larger quantities of the constituent for further investigation in the shortest possible time and with the least expense. When we have prepared sufficient quantities of all the constituents in an approximately pure condition, the next problem is to completely purify these bodies. This completely pure preparation of bodies is attended often with no difficulty, as, for example, is the case with easily crystallizable bodies or with volatile bodies when they exist with non-volatile bodies, or even with volatile ones if in reference to their chemical characteristics they are widely different. Generally, bodies of the opposite character of an acid and a base are easily obtained pure when they are at the same time present with indifferent substances; likewise all bodies which are not *per se* crystallizable when they are capable of forming compounds, which can be readily obtained in a crystalline state. On the contrary, it is extremely difficult to completely separate indifferent amorphous substances when they exist mixed with one another, and to prepare in a state of purity the individual constituents of such mixtures. But the pure preparation is often not the greatest difficulty, but the establishment of the proof that the substance has been prepared in a state of purity. It is often possible to effect the pure preparation of a substance, but we have no index of the purity of the prepared substance. This is often the case with the amorphous and indifferent constituents of vegetables. There is frequently no other means for obtaining certainty with regard to the purity of a substance than by elementary analysis, conducted with portions of the substances which have been prepared in different ways from the same part of the plant, or where possibly taken from different parts of the plant. The complete agreement in the results of the analysis of the different portions of the same substance affords a proof of its purity. The individual constituents which we have prepared in a pure isolated condition are submitted to a further chemical examination. The elementary analysis of these substances combined with their reactions, will supply us with an evidence whether the constituent found is or not identical with a body already known. A close examination, to the execution of which the previous analysis will afford assistance, will now teach us the constitution of the individual constituents. From this knowledge an insight is obtained into the connection between the individual constituents, that is to say, our investigation will afford results quite as useful for vegetable physiology as for chemistry itself. We secure an important advantage by these investigations, when we make the objects of our studies not only the various individual parts of a plant, but also the various individual parts in different epochs of their development. Observations on the formation of a body from one or several others will bring, most easily, light into the darkness in which the transformation of vegetable bodies is wrapped up. Correct analyses of plants, or rather of their parts, in their various relations, and their gradual development consequently, are a means to enlarge in a very productive manner, not only our chemical, but also our physiological knowledge. In the hope of having, by the present work on the analysis of plants and their parts, contributed something towards the accomplishment of these aims, I submit these pages to the considerate judgment of the experienced chemist, and to the zealous student in this field of inquiry, who has had no opportunity from his own experience to devise a method for the analysis of vegetable substances.

Ether sol - cryst evap to dryness.
Dissolve in alc.
Precip. 3 vol. ether + enough pet. ether
to cause partial precipitation
Colored body separates with some cry
Clear supernat. fluid (yellow) precip
with Pet. ether till marked cloud.
Warm mixture on bath with coole
till redissolved
Cryst. separate on cooling
Let stand in dark several days
adding Pet. ether from time to time
Pour off -
Cryst. from boiling abs. alc.
Amorphous alk. prec. by Pet. ether
Cryst - prec. by HCl. ether from the ether sol.