THE LABORATORY GUIDE.

PREFACE.

In preparing for the press this, the Seventh, Edition of the Laboratory Guide, it has again been carefully revised. An additional Lesson on Soils has been introduced in Part I., while some improved quantitative methods have been described in Part III. On the other hand, the accounts of three processes, which are practically obsolete, have been removed from the volume. These are the citric-acid method for determining phosphorus pentoxide, the old process of extracting fat from milk-residues, and the sulphuric-acid method for the isolation of indigestible fibre.

A. H. C.

Kew, April 1894.

PREFACE

TO THE SIXTH EDITION.

THIS little book of directions in Practical Chemistry differs in several particulars from ordinary manuals of laboratory practice; otherwise I should not have added to the number. After the lapse of nearly a quarter of a century, it still remains the only English work in which a complete course of laboratory practice is provided for the use of agricultural students.

The elementary lessons on Manipulation are drawn chiefly from familiar, important, or interesting materials with which every one ought to be acquainted.

In the Qualitative Part, not only all the rare elements, but also nearly all those which are not important constituents of any agricultural material or product are omitted, and thus many of the processes of analysis have been simplified. As, however, this section of laboratory practice is often felt to be irksome by agricultural students, a judicious teacher may further reduce its complexity by passing over, at least for a time, the less important parts of the "Preliminary Examination," as well as those "Reactions" and "Tables" which include what may be called *non-agricultural* elements, such as antimony, arsenic, copper, mercury, tin, &c.

In giving Quantitative Methods, examples have been selected from the most important substances likely to engage the attention of the agricultural analyst. By reference to the Table of Contents it will be seen that the examination not only of soils, manures, and cattle-foods, but also of dairy-produce, of bread, and of waters, is included. The student who carefully and intelligently carries out the processes described, will be able to extend their application to many materials which are not referred to specifically in the following pages.

The various processes given in this volume for the estimation of the several constituents of cattle-foods, manures, &c., have been personally tested over and over again. They will be found to yield trustworthy results with the expenditure of such an amount of skill, attention, and time as can reasonably be demanded of agricultural students during their course of scientific training. The rough and inaccurate methods of analysing manures which were too often employed when this Guide was first published, have been excluded from the present volume.

The notation and nomenclature used in the following pages are nearly identical with those employed by the majority of English scientific chemists—exceptional usages of terms are in most cases explained or justified. The Centigrade thermometric scale and the metric system of weights and measures have been employed almost exclusively; but, in a few instances, where comparison with other results, with existing data, or with common standards would have been rendered inconvenient, the grain, the inch, and the gallon have been exceptionally retained. Sometimes, for example, the weight in grams, or a measured volume in cubic centimetres, of a substance with which experiments are to be performed, is followed by a weight in grains, or by a measure in ounces, which is given as a suitable but by no means identical quantity.

In preparing the present edition of the Laboratory Guide for the press it has been once again subjected to revision; fuller explanations, directions, and tables have been inserted, and some new processes have been introduced. The section of the work devoted to the analysis of milk and dairy-products has been almost entirely re-written. In the previous edition I drew particular attention to the various classes of nitrogen-compounds which occur in vegetable foods, and gave some suggestions as to their discrimination and separate estimation. The first process published in this country for the determination of true albuminoids was that which I called "The Carbolic-Acid Method." After much experimenting I still place more confidence in the results of this process than in those obtained by the use of tannin, ferric acetate, or lead acetate—these reagents precipitating, along with the true albuminoids, other nitrogenous bodies of no ascertained alimentary value. The method of separating albuminoids by the use of moist copper hydrate is not faultless, for it yields results which, in the presence of certain nitrogenous acids, are decidedly too high, yet it presents the advantage of permitting the filtrate from the precipitated albuminoids to be tested and further analysed. The use of phosphotungstic acid, as a precipitant for the peptones, which are now known to occur in many seeds, I have not described, because my limited experience of this reagent has not been satisfactory. I have introduced, in deference to the opinion of several correspondents, a slight alteration in the factor used in calculating the albuminoids from the ascertained percentage of nitrogen. This is now given as 6·25 instead of 6·33.

Some persons using this manual may regret the absence from its pages of information which they expected to find therein. And, on the other hand, I anticipate that objection will be taken to some of the Lessons in Part I., and to some of the analytical directions given in the succeeding sections of the volume. Yet nothing has been inserted and nothing omitted without careful consideration, nor have I failed to appropriate to the utmost the advice of those teachers who, in many parts of the world, have been in the habit of using the book in their laboratory classes. I trust that, on the whole, the volume as it now stands will be found to merit the increasing favour with which each successive issue has been received. From a small privately printed pamphlet of some forty pages, the Guide has grown, in six subsequent stages, to a volume of nearly seven times its original bulk. I have, however, endeavoured to limit the expansion of the work by keeping continually in view its original scope as set forth in this Preface and in the Introductory Chapter.

The Guide was intended primarily for use in the Royal Agricultural College, as a help in carrying out the system of practical instruction of chemistry there pursued. Experience has confirmed my conviction that the publication of the plan of laboratory practice which I had developed at Cirencester would not only be helpful to my own pupils, but would also render a wider service in extending the study of practical chemistry in relation to agriculture. The Laboratory Guide has been adopted as the text-book not only in our Agricultural Colleges at home, but also in Australia, India, Italy, and Japan.

It was so long ago as 1864 that my then assistant, Mr. Robert Warington, drew up, at my request, some directions in quantitative analysis which once formed a considerable part of the third division of the Laboratory Guide. During the twenty-four years which have passed since that time, many new processes of analysis have been developed or adopted, and many old processes simplified or improved under my personal supervision. It would be impossible to acknowledge specifically the source of each analytical detail or method; but the labours of many well-known chemists have been utilized in the preparation of my little volume, and in the improvement of each successive edition. I cannot, however, refrain from expressing the obligations which I am under for special help accorded to me in the preparation of the present issue by Professor Kinch of Cirencester and Dr. Munro of Downton, who have furnished me with notes, hints, and emendations, suggested by their experience in the use of the book. I am indebted to Mr. R. H. Harland and to the authors of papers in recent volumes of 'The Analyst' for improvements in the section "On Dairy Products;" the Reports issued by the United States Association of Official Chemists have also been laid under contribution.

A. H. C.

Kew, June 1888.

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CHAPTER II.

THE LABORATORY GUIDE.

INTRODUCTION.

Chemistry is essentially a science of experiment. The Laboratory is as important as the Lecture-room. It is not sufficient to have an experiment described, nor even to see it performed; the student must repeat it for himself. And he must apprehend all the conditions of the experiment and the laws which it illustrates. Thus only can the science be thoroughly learnt so as to be of real service in practical life; thus only can be fully realized its beneficial effects in training the mind to accurate observation and close reasoning. Besides these chief advantages of practical chemical work others may be mentioned. For instance, actual repetitions of leading experiments give sharpness and precision to the memory; and, at the same time, the unexpected results, and even the mishaps that attend laboratory practice, afford a certain amount of play to ingenuity in contriving new arrangements of apparatus and new conditions of experiment. In this way it has happened that the stimulus to original endeavour which accidents give has resulted in discoveries of great scientific or economic importance.

But just as lectures may become too theoretical, so laboratory work may become too practical. The student in the laboratory must never forget that the experiment is the means, not the end. An experiment rightly tried is a question properly put to nature; and though its results may be striking or beautiful, it is to their meaning or interpretation that we look. Merely to make a coloured precipitate or a flash of bright flame is not the end of experimenting, but to identify facts by means of phenomena is.

We read in our text-books that sulphuric acid dissolves zinc and gives off a light and combustible gas; but it is not till we have watched the bubbles rise from the mixture, collected them, burnt them, and otherwise tested them, that we realize the properties and relations of zinc and acid and hydrogen. But our books tell us something more about this experiment. We not only have to learn *how* to make it, and the *qualities* of the materials taken and of those formed, but we see that we have to do with *quantities*. We learn that 65 parts by weight of zinc will dislodge only 2 parts by weight of the gas hydrogen, yet that these two parts by weight of gas will occupy more than 2300 times the bulk of the solid zinc used. These considerations enable us to divide the work of practical chemistry into 3 sections:—

1. Manipulation, which includes the management of apparatus and tests.

2. Qualitative Analysis, by which the constituents of substances are separated and identified by appropriate methods.

3. Quantitative Analysis, by which the quantities of the several constituents of the substance examined are ascertained, either by weighing or measuring.

These sections are found in practice not to be absolutely distinct; indeed, the study of the first of them, Manipulation, involves both Qualitative and Quantitative work, while the third necessarily includes the other two. But it is, after all, not only usual, but very convenient to divide Laboratory practice into these sections, and the plan has accordingly been adopted in the pages which follow.

For whatever occupation in life a student may be destined, the foundations of his chemical knowledge must be laid in the same way. Yet there is a mode, and a perfectly legitimate one, of giving a special character even to early scientific instruction. In a medical school the more elaborate illustrations of chemical facts, both in lecture and lesson, may be selected mainly from substances with which the physician or surgeon is more immediately concerned, and thus a medical *bias* be given to the whole course. The great facts concerning the elements and their combinations would be duly explained in all cases; but while a subject should be illustrated by potassium iodide or magnesium sulphate when addressing medical students, potassium chloride or calcium phosphate should be specially dwelt upon in the case of agricultural students. The latter, too, would have the laws of diffusion illustrated to him by the processes which go on in the soil and in the plant; the medical student, on the other hand, would study the same laws as they work in the liquids and gases concerned in the functions of the human body. The agricultural student would devote particular attention to those compounds of nitrogen which are used as manure, while the medical student would make the acquaintance of those which are of importance in the treatment of disease. Both students follow the fortunes of nitrogen till it appears as ammonia, then the former combines it with sulphuric acid, the latter with citric. Both will study analysis, one to detect and estimate phosphoric acid, and the other arsenic. But as the whole of the present volume affords an illustration of this method as applied to agricultural teaching, it is unnecessary further to explain it here.

The student using this Guide will do so with the greatest effect if, while he is going through the experiments on manipulation described in Part I., he will attend a course of Lectures on Inorganic Chemistry, and study the corresponding chapters of a text-book of Chemistry. The lessons on Manipulation may then be readily mastered by two or three hours' practice in the laboratory each week during a period of four months; an additional hour or so each week will be requisite for posting up the 'laboratory book' with the results of the practical work. This time is exclusive of that which lectures require. This Guide *can* be used without the personal help of a teacher; but the progress of the student will then be less sure and rapid, especially where, as in the processes of analysis, the operations described are very delicate or complicated.

When the student has prepared and examined the common gases, hydrogen, oxygen, nitrogen, carbon dioxide, sulphur dioxide, &c., and has studied, by actual practice on suitable (often agricultural) examples, the processes of solution, evaporation, distillation, precipitation, filtration, decantation, crystallization, drying, ignition, and weighing, he must next acquire an exact acquaintance with the various substances with which the analyst is concerned. More than this, he must become familiar with the tests and reagents employed either to separate or discriminate the several constituents of any ordinary solid or liquid material which may be submitted to analysis. By the use of these tests or reagents different effects ensue: gases are evolved, precipitates are formed, or colours are produced; from these phenomena definite inferences are drawn as to the nature of the substance or substances present. These reagents do not, except in a few instances, separate a body in the elementary or uncombined state, but in some characteristic and easily identified form of combination. As, however, the simple element is occasionally eliminated in the free state, a list of the most salient properties of each important element is given further on: a reference to this list will enable the experimenter to identify any particular element.

When the student has become familiar with the behaviour of each metallic or basic, and of each acid constituent, when acted upon by the reagents in use, he proceeds to the systematic part of Qualitative Analysis. This, the method of analysis, consists of the application, in a fixed order, of certain tests. But the schemes which have to be here followed are often modified to suit the particular state and nature of the material to be analysed.

When the schemes are mastered, and the student has successfully analysed the various simple and complex substances that have been selected as examples, he commences the study of the third part of this work, which is devoted to Quantitative Analysis. This section of the Guide commences with minute directions for the estimation of potassium, nitrogen, and other important constituents of foods, soils, and manures, and it then gives numerous examples for the practice of quantitative analysis. All these examples are drawn from the produce of the farm, or from those materials which are of the highest importance to the agriculturist.

PART I.

CHEMICAL MANIPULATION.

THE Lessons which follow have been so devised as to illustrate and confirm some of the chief truths learnt during the course of lectures on Inorganic or Mineral Chemistry, which they are intended to accompany. The usual introductory lectures of such a course will refer to Chemical Physics. The corresponding Lessons are devoted to Solution, Crystallization, Sublimation, and so forth. Next in order, both at lecture and in lesson, come hydrogen, oxygen, and other important non-metals and their compounds; afterwards the chief metals. Here and there throughout the series it will be well to introduce one of the special agricultural lessons, in order to connect, even in the early stages of instruction, chemical science with the commonest and most familiar materials of life on the farm.

To show the mode of carrying on a class of practical chemistry in the most effective way a few words of general description are necessary. The lesson having been selected, the teacher will suspend in some conspicuous place in the laboratory a diagram embodying the chief operations to be performed. He will read this, commenting upon it as he reads, and illustrating apparatus and methods by sketches on the black-board, and in many cases by going through the experiment, or making the apparatus to be employed, before the class. This done, the class is told what materials and apparatus will be required. Part of this will belong to the student's set, part will be found on the shelves above his bench, and part will be specially provided for the use of the class, according to the demands of each lesson. Work may now be commenced.

The student should bear in mind the great importance of (1) cleanliness, (2) order, (3) quietness, (4) exactness.

All apparatus must be made clean before being used, and must be kept clean. A test-tube washed out three times with a little water is really cleaner than if washed once with much. When work is over, put the apparatus away, dry as well as clean. Pour away all residues, unless the contrary be specially directed at the time of the lesson: clean up all messes.

As to order, never have anything on the bench which is not required, but never omit anything that is. Arrange your apparatus so as to be most convenient for work, so as not to prevent your getting reagents from the shelves, and so as not to be liable to be upset.

Hurry and noise prevent the successful performance of experiments. Give every experiment time. If you are told to let a liquid cool, give it time to do so. If you are told to heat a substance till it becomes dry, give it time to get so.

By exactness, we mean the use of the right materials in the right way. If you are directed to warm a liquid, don't boil it. If you are directed to add five drops of some test, don't let an uncounted number tumble into your test-tube: economy is not only better, it is more successful than waste. Be careful to see that you add the right test: don't use ferrocyanide for ferricyanide, nor sulphate for sulphite. If you are directed to use strong sulphuric acid in any experiment do not spill it about, nor mix it suddenly with any liquid, and above all never allow it to come in contact with hot water, or, if it be itself hot, with hot or cold water.

But cleanliness, order, quietness, and exactness will be of small avail unless the student accurately observe the result of each experiment, grasp its meaning, and make a full record of all his work. Rough notes should be taken in the laboratory, to be afterwards copied into a book. In making and transferring such notes, remember that the actual results of your own experiments, not the directions given you for carrying them out, are of the first importance. See that you understand the reason of each step taken, of each addition made, and of each change effected: write out the chemical equations for such changes. Be careful to spell chemical words exactly as given in the lessons and on the labels of the laboratory. The names of chemical substances and processes have been formed (sometimes awkwardly enough) chiefly from Latin and Greek words; and their derivations as well as meanings are obscured or lost when through inattention a letter is omitted or altered. For instance, never spell *chlorine* without an *h*, nor *analyse* with a *z*.

Seeing now what we have to do, and how to do it, we may begin work. Each of the following lessons will require from one to two hours for its successful completion.

LESSON I.

SOLUTION AND FILTRATION.

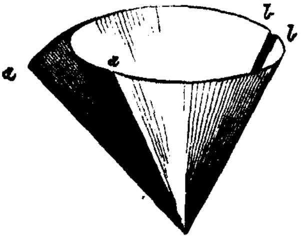
Apparatus required.—Retort stand; funnel; filter-papers; spirit-lamp; porcelain bason; two beakers; wash-bottle; scales and weights.

Ordinary reagent.—Dilute hydrochloric acid (HCl).

Special materials.—A mixture, in known proportions, of sand and salt, to be labelled A; a mixture, in known proportions, of sand and chalk, labelled B; a feather.

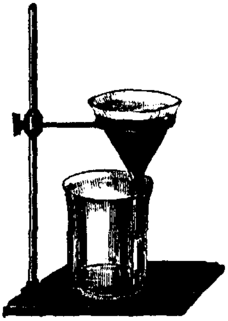
1. Weigh out 10 grams (or 100 grains) of a mixture (A) of sand and salt. Place the weighed substance on a filter fitted in a funnel and pour water gently into the funnel. The filter-paper used above is folded first into halves along the line *a*, *a*, then into quarters from the centre to *b*, *b*. It is opened partially when in the funnel, so as to bring *a* and *a* together and to leave *b* and *b* similarly placed. When the liquid that drops from the funnel (called the *filtrate*) no longer tastes salt, syringe out every particle of the sand, which alone remains on the filter, into a bason: this washing

Fig. 1.



out the residue on the filter is easily done by the wash-bottle jet being allowed to play upon it, the funnel being held upside down over the bason. Pour off the water, leaving the sand in the bason. Turn the bason about, so that the wet sand forms a thin layer all over it: then heat it cautiously, to avoid spirting, until the sand is dry; sweep it, when cold, with a feather into one of the pans of the scales, and weigh it. Its weight, multiplied by 10, if grams have been used, gives you the *percentage* of sand in the original mixture.

Fig. 2.



2. Weigh out 10 grams (or 100 grains) of a mixture (B) of sand and chalk. Place the weighed substance in a beaker, and pour upon it a little hydrochloric acid: shake the mixture. Continue to add hydrochloric acid, drop by drop, till all frothing (due to the escape of carbon dioxide, CO_2) ceases; shake the mixture from time to time. Add water to the residue that has not dissolved, and gently decant it off again. This pouring on and off of water is to be repeated twice, taking care to lose none of the sand at the bottom. The sand should now be syringed, as before described, into a porcelain bason: it is to be dried and weighed as in experiment 1.

The student learns by this lesson that substances differ in solubility, some being soluble in water, some in acids, some insoluble in both. He also learns that a filter separates solid particles from liquids.

The only *chemical* change in these experiments occurs during the solution of the chalk in the hydrochloric acid. It is represented thus:—

$$CaCO_3 + 2HCl = H_2O + CaCl_2 + CO_2$$

$CaCO_3$	$2HCl$	H_2O	$CaCl_2$	CO_2
Chalk, insoluble in water.	**Acid.**	**Water.**	**Calcium chloride, dissolved in the water.**	**Carbon dioxide, goes off as gas.**

LESSON II.

CRYSTALLIZATION.

Apparatus required.—Furnace-support; wire gauze; spirit-lamp; wash-bottle; two porcelain basons; porcelain crucible; triangle; test-tubes; scales and weights; filter-papers.

Special Materials.—Solutions of copper sulphate, sodium sulphate, calcium chloride, and potassium dichromate; piece of wire.

1. Evaporate $\frac{1}{2}$ of a test-tube full of a solution of copper sulphate over the lamp in a porcelain bason until the crystals which form round the margin of the solution cease to dissolve when pushed into it: set it aside to cool.

2. Add 30 drops of sodium sulphate solution to a test-tube about $\frac{1}{8}$ full of calcium chloride solution. The white substance which gradually separates from the mixture will be found to be made up of small crystals which can be seen with a pocket lens. These crystals are calcium sulphate (=gypsum, $CaSO_4$, $2H_2O$).

3. Weigh out in a crucible of known weight 2 grams (or 30 grains) of crystals of copper sulphate ($CuSO_4$, $5H_2O$), from *experiment 1.* The crystals must first be pressed between filter-papers, and then lightly powdered in a mortar before weighing. Heat the weighed salt and stir it with a wire; continue to heat it until its blue colour has entirely disappeared. When the crucible is cold weigh it again. The difference in weight will be the *water of crystallization* lost by the salt.

4. A solution of potassium dichromate, when evaporated as in experiment 1 above, will deposit on cooling crystals ($K_2Cr_2O_7$) which contain no combined water.

LESSON III.

SUBLIMATION.

Apparatus required.—Retort-stand; triangle; spirit-lamp; scales and weights; porcelain crucible; test-tubes and stand.

Special Materials.—Iodine; pure ammonium chloride; adulterated ammonium sulphate.

1. Into a dry test-tube drop a crystal of iodine and gently heat it. Purplish-violet vapours will be produced which will condense on the cooler parts of the tube into small crystals of iodine. This physical change of a solid into a gas, followed by the *re-formation of the original* solid, is unaccompanied by any chemical change: it is called 'sublimation.'

2. Take 1 gram (or 10 grains) of ammonium chloride (NH_4Cl), place it in a porcelain crucible which has been counterpoised, or the weight of which has been ascertained, and then heat it over the spirit-lamp till no more fumes are given off. When the crucible is cold weigh it again. The salt, if pure, will have left no residue, having been entirely sublimed. A cold surface, say, a test-tube, placed in the fumes will be covered with minute crystals of sublimed and condensed ammonium chloride.

3. Take 1 gram (or 10 grains) of adulterated ammonium sulphate and heat it exactly as above. The materials used to adulterate this valuable salt are generally non-volatile, and will be left behind. The amount of adulteration will be learnt by finding what weights have to be added to the counterpoise in order that it may balance the crucible and the non-volatile residue in it. The student must, however, remember that many substances used as adulterations *are* volatile. Vegetable and animal substances and water itself are amongst these, and must be looked for in making an analysis of any ammonia salt used as manure.

LESSON IV.

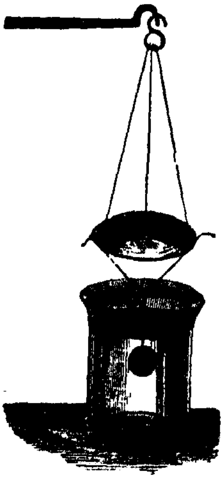
SPECIFIC GRAVITY.

Apparatus required.—Scales and weights; a large beaker nearly full of water.

Special materials.—Pieces of lead, glass, apatite, aluminium, and iron; thread; and a gold or silver coin.

1. Tie a piece of iron by means of a thread so that it shall hang about 3 inches below one pan of the scales. Place weights in the other pan to counterpoise the iron, noting the number of grams or grains required. Now lower the beam of the scales until the piece of iron is wholly immersed in water contained in a beaker, taking care that the iron does not touch the sides or bottom, and removing any air-bubbles that may adhere to it by means of a small brush. Remove weights from the pan till those left again balance the iron. Subtract the second weight from the first; the difference is the weight of the volume of water displaced by the iron—that is, the weight of an equal volume of water. To find the specific gravity of the iron, water being taken as unity, divide the weight in air by the above difference, the quotient will be the required specific gravity.

Fig. 3.



The following is an example of the working of this problem:—

Weight in air of a piece of gold (a sovereign)	7·971 grams.
Weight in water of the same	7·517 „
Difference	·454 gram.

This difference, ·454 of a gram, represents then the weight of the volume of water displaced by the immersion of the gold—that is, the weight of an equal volume of water. We have now nothing to do but to divide the weight of the gold in air by this difference; and the dividend will express how many times the weight of the volume of gold contains the weight of an equal volume of water:—

$$\frac{7{\cdot}971}{{\cdot}454} = 17{\cdot}56, \text{ spec. grav. of standard gold.}$$

Or we may express the same facts in another form. We may say that the weights of equal volumes of water and gold are in the ratio of ·454 to 7·971; and then, assuming the specific gravity of water to be 1, we have the following proportion :—

$$\underbrace{\cdot 454}_{\text{Weight of water displaced by gold.}} \quad : \quad \underbrace{1}_{\text{Spec. grav. of water.}} \quad = \quad \underbrace{7\cdot 971}_{\text{Weight of gold.}} \quad : \quad \underbrace{x}_{\text{Spec. grav. of gold.}}$$

$$x = \frac{1 \times 7\cdot 971}{\cdot 454} = 17\cdot 56.$$

The specific gravity of standard gold, which contains 8·33 per cent. of copper, is lower than that of pure gold, which is 19·3.

2. The same experiment is to be tried with a piece of lead, and,

3, with a piece of glass; 4, with a silver coin; 5, with a crystal of apatite; 6, with a piece of aluminium.

The specific gravity of a body is the ratio of the weight of any volume of that body to the weight of an equal volume of water. It is expressed by a number which shows how many times the weight of any volume of the body contains the weight of an equal volume of water. *e.g.* A cubic foot of lead weighs 11,400 ounces; a cubic foot of water weighs 1000 ounces: therefore the specific gravity of lead is 11·4.

The following proposition expresses the principle involved in the method of taking specific gravities above described. Every body immersed in a liquid is subjected to an upward vertical pressure, equal to the weight of the liquid displaced, and applied at its centre of gravity: or, the weight of a body immersed in a liquid is diminished by a weight equal to the upward pressure. Strictly, we should take into account the weight of the air displaced by the body when weighed in the usual manner; but this correction may generally be neglected: the temperature of the water and of the body weighed is of more importance. We have considered no case but that of solid bodies heavier than water, and not dissolved or chemically affected by that liquid.

LESSON V.

WASHING BY DECANTATION.

Apparatus required.—Wash-bottle; pestle and mortar; beakers; scales and weights; porcelain bason; furnace-support and wire gauze; glass rod; spirit-lamp.

Special materials.—Dried soil, or mixture of sand and clay; guano adulterated with sand; feather.

1. Take 10 grams (or 100 grains) of a dried soil containing clay and sand, put them into the mortar and add a little water. Stir the mixture without grinding it, add more water, and, after a minute's rest, pour off the turbid liquid (along a glass rod applied to the lip of the mortar) into a beaker; take care that none of the sandy sediment is poured off as well. Continue to wash the soil in this manner until the water that flows away is no longer turbid. Gently crush any remaining lumps in the mortar, and pour more water into it. If this water remains clear the sand must now be syringed into a porcelain bason, dried cautiously over the lamp, and, when cold, brushed into one of the scale-pans and weighed. It is well to examine the sediment from the wash-waters in the beakers, and if any sandy grains be seen in it, they must be rinsed out with water, and added to the main bulk of sand in the bason before drying it.

Fig. 4.

2. Take 10 grams (or 100 grains) of adulterated guano and treat them exactly as directed above, the treatment being continued till the residual sand is uniform in appearance; any white or brown lumps that remain are to be pressed with the pestle, and then the washing is to be continued: the heavy granular residue which remains, if entirely freed from guano, will not be altered by heat.

LESSON VI.

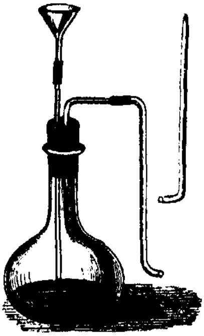
PREPARATION OF HYDROGEN.

Apparatus required.—Flask or bottle; small funnel; mortar; wash-bottle; test-tubes; sheet india-rubber or tubing; rat-tail file; beaker; platinum wire.

Ordinary reagent.—Sulphuric acid (dilute).

Special materials and tests.—Granulated zinc; 3 pieces of quill tube, each about 6 inches long; cork; wide tube, open at both ends; splints of wool.

Fig. 5.



1. A cork is to be fitted to the flask or bottle chosen for the experiment. Two holes are to be bored in this cork. Into one of these holes a straight tube is to be inserted, so as nearly to touch the bottom of the flask: into the other hole an elbow-tube (bent once at right angles) is to be placed, the whole fitting quite air-tight. To the upper end of the straight tube previously mentioned, a funnel is to be joined by wrapping round both a warmed strip of sheet india-rubber, or by slipping over them a piece of vulcanized tubing. Similarly, to the elbow-tube, a second elbow-tube, bent into a shape somewhat like the letter *l*, is to be joined. A thistle-head funnel may be used instead of the funnel and tube above described.

2. Put a little granulated zinc into the flask, insert the cork with its tubes, then add a little sulphuric acid through the funnel. When the gas has been given off for a few minutes, collect some of it in a test-tube filled with water, and standing, inverted, over the end of the delivery-tube, which must be just under the water of the pneumatic trough (a bason of water or the mortar will answer). When the test-tube is full of gas remove it from the water, closing its mouth with the thumb and applying a light to

its contents. Collect two or three tubes of gas thus, till it is found to burn with a pale flame and without explosion: great attention should be paid to this point, as if any air remains in the flask, the mixture of air and hydrogen is sure to explode when a light is applied in experiment 3. Observe that a lighted splint of wood, though it sets fire to the gas, is itself extinguished.

3. Remove the delivery-tube, and put another elbow-tube, terminating in a jet, in its place. Wrap the flask round with a cloth, pour in a little more acid, light the jet of gas, and hold a dry beaker over the flame; observe the formation of dew. If a good-sized tube, a few feet long and open at both ends, be lowered over the flame, a musical note may be produced. Hydrogen may be lighted by means of platinum sponge or a warm platinum wire.

When zinc and sulphuric acid react the following is the final change which occurs:—

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

When hydrogen burns in air, two volumes of hydrogen unite with one of oxygen; thus—

$$H_2 + O = \underset{\text{Water.}}{H_2O.}$$

As 100 measures of air contain about 21 measures of oxygen, they will furnish enough oxygen to combine with twice that number or 42 measures of hydrogen.

LESSON VII.

PREPARATION OF OXYGEN.

Apparatus required.—**Scales and weights; spirit-lamp; retort-stand; test-tube; rat-tail file or rasp; mortar; litmus paper; wash-bottle; large beaker half full of water.**

Special materials.—**1 foot of quill tubing; corks; splint of** wood; red phosphorus; sulphur; a blue or purple flower; oxygen mixture*; piece of iron wire with a loop at one end.

1. Select a stout, short, and dry test-tube. Knead a suitable cork between the fingers till it becomes soft and elastic. Perforate the cork very carefully with the round file, so that a piece of glass tube may be tightly inserted into the hole. This tube is to be bent, in the most luminous part of the flame of a batswing burner, in two places. One bend should be made downwards, about 1½ inch from one end of the tube; the other bend should be upwards, as near the other end of the tube as possible. The downward bend should then be passed through the cork; from the opening at the extremity of the other bend the gas will issue and be collected. The next step is to weigh out 3 grams (or 40 grains) of the oxygen mixture, chiefly potassium chlorate, to introduce them into the test-tube, to insert the cork and bent delivery-tube, and to suspend the apparatus on a ring of the retort-stand. Have ready a beaker half full of water: also 4 test-tubes perfectly full and placed close at hand in the test-tube stand. On applying a gentle heat by means of the spirit-lamp, oxygen gas will be given off. The end of the delivery-tube should dip under some water contained in the mortar. Allow a few bubbles of gas to escape, and then adjust, over the opening of the delivery-tube, an inverted test-tube full of water till the gas has displaced its contents. Fill the other test-tubes in the same way. Each test-tube as it becomes full of gas should be removed (with its mouth downwards, and closed, during removal, by the thumb) to the beaker half full of water previously mentioned.

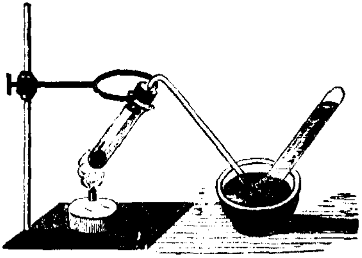


Fig. 6.

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* The oxygen mixture is made of 10 parts of potassium chlorate in powder and 1 part of ferric oxide (jewellers' rouge).

2. Light a splint of wood, blow out the flame, and insert the glowing end into one of the test-tubes of oxygen.

3. Light a little red phosphorus, placed on a loop of iron wire, and quickly introduce it in a test-tube of oxygen. When the combustion is over, pour a little water into the tube, and then drop in a slip of blue litmus paper.

4. Light a bit of roll sulphur on an iron wire and introduce it into oxygen. When the combustion is over, pour a little water into the tube and drop in a blue flower.

5. Fix a small fragment of charcoal to the end of a piece of iron wire, heat it in the flame of the spirit-lamp, then introduce it into a test-tube of oxygen gas. Withdraw the wire when the combustion is over, and test the gas in the test-tube for carbon dioxide by pouring in a little lime water.

In the foregoing method of preparing oxygen, the final result of the reaction which occurs may be expressed thus:—

$$KClO_3 = KCl + 3O.$$

LESSON VIII.

PREPARATION OF SULPHUR DIOXIDE.

Apparatus required.—Retort-stand; test-tubes; spirit-lamp; wire gauze.

Ordinary reagent.—Ferric chloride (Fe_2Cl_6).

Special materials and tests.—Perforated cork; piece of quill tube, about 10 inches long; strong sulphuric acid; charcoal; hydrosulphuric acid (H_2S); potassium ferricyanide; blue flower; blue litmus paper; chromic acid solution.

1. Fit a short, stout test-tube with a perforated cork, as in Lesson VII.: the delivery-tube used in the preparation of oxygen may be employed, if its smaller elbow-bend be removed by means of a stroke or two with the triangular file. Introduce into the selected test-tube a few fragments of charcoal and enough strong sulphuric acid to half cover them; fit in the cork and delivery-tube, and gently heat the mixture. Conduct the evolved gas

into a flask one-third full of distilled water. Shake the flask occasionally; and when the water in it smells strongly of sulphur dioxide, remove the flask and pour its contents into five test-tubes.

2. Into one test-tube put a piece of blue litmus paper.

3. Into another test-tube put a blue flower and apply heat.

4. Into another test-tube pour a little solution of hydrosulphuric acid. The following change (with others) occurs:—

$$SO_2 + 2H_2S = \underset{\text{Precipitate.}}{S_3} + 2H_2O.$$

5. Into another test-tube pour 5 drops of chromic acid solution; note the change of colour due to reduction.

6. To another test-tube add one drop of ferric chloride (note the darkening of the colour), boil (note the disappearance of the colour). The ferric chloride has been reduced by the SO_2 to ferrous chloride, and will now give a rich blue precipitate (Turnbull's blue) with potassium ferricyanide.

7. In order to show what reaction ensues when ferric chloride (without SO_2) and potassium ferricyanide are mixed, add to half a test-tube of pure water, 2 or 3 drops of ferric chloride and 5 drops of potassium ferricyanide; instead of a deep blue precipitate, a clear green colour only will be produced.

When charcoal and sulphuric acid are heated together, the following change occurs:—

$$C + 2H_2SO_4 = \underset{\text{Carbon dioxide.}}{CO_2} + 2H_2O + \underset{\text{Sulphur dioxide.}}{2SO_2}.$$

But as water dissolves 44 times as much of sulphur dioxide as of carbon dioxide, and as the latter gas does not interfere with the experiments above given, our solution may be regarded as one of SO_2 only. Mercury or copper heated with H_2SO_4 gives off pure SO_2.

LESSON IX.

PREPARATION OF AMMONIA.

Apparatus required.—Retort-stand; spirit-lamp; wire gauze; scales and weights; wash-bottle; 3 narrow test-tubes; 1 stout test-tube; perforated cork; mortar full of water; slips of turmeric paper and of reddened litmus paper; glass rod.

Special materials and tests.—Ammonium chloride (NH_4Cl); slaked lime (CaH_2O_2); strong hydrochloric acid; 8-inch piece of quill tubing.

1. Fit a dry test-tube with a perforated cork and straight quill tube 6 or 8 inches long. Weigh out 1·5 gram (or 20 grains) of ammonium chloride and 3 grams (or 40 grains) of slaked lime (= calcium hydrate CaH_2O_2); mix these materials on a piece of paper, and introduce them into the tube. When the mixture is heated ammonia gas (NH_3) will be evolved; it is to be collected in dry narrow test-tubes, which are to be successively placed (mouth downwards, as NH_3 is lighter than air) over the quill tube, so that the open upper end of the quill tube may nearly touch the inside of the rounded end of the test-tube.

2. Drop a piece of turmeric paper, and also a piece of reddened litmus paper, into a tube of the gas.

3. Remove a tube of the gas, tightly closed with the thumb, to the mortar full of water, remove the thumb while the mouth of the test-tube is immersed, and observe the absorption of the gas by the water. 1 volume of water at 15° C. dissolves no less than 783 volumes of ammonia.

4. Into a tube of the gas introduce a rod, moistened with strong hydrochloric acid; observe the white fumes of ammonium chloride (NH_4Cl) formed.

The reaction by which ammonia is separated in the foregoing process is thus expressed:—

$$2NH_4Cl + CaH_2O_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

Ammonia may be detected in peat and other soils by warming the soil with caustic magnesia and water, and holding a piece of turmeric paper in the vapours evolved.

LESSON X.

PREPARATION OF CARBON DIOXIDE.

Apparatus required.—2 flasks; test-tubes; litmus paper.

Ordinary reagents.—Hydrochloric acid; lime-water.

Special materials and tests.—Perforated cork, tube bent twice at right angles; marble or limestone in fragments; quill tube 6 inches long; splint of wood.

1. Fit a flask with a perforated cork and a tube bent twice at right angles, one of the bends being about 1 inch from one end of the tube, and the other about 4 inches from the opposite end. Gently slip into the flask a few pieces of limestone or marble ($CaCO_3$), and pour upon them dilute hydrochloric acid. The gas evolved is CO_2, or carbon dioxide: its separation is represented by the equation $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$. The gas being heavier than air, is collected by downward displacement in dry test-tubes, the mouths of which are directed upwards.

2. Into a test-tube of the gas drop a piece of wet blue litmus paper.

3. Into a test-tube of the gas lower a lighted splint of wood.

4. Into a tube of the gas add some lime-water (CaH_2O_2) and a little distilled water; then allow the gas to bubble into the mixture for some minutes; observe whether the precipitate first formed redissolves. If so, divide the clear solution into 2 portions: to one add some more lime-water, drop by drop;—an abundant and bulky precipitate separates. This is calcium carbonate removed from solution in accordance with the following equation:—

$$\underset{\text{Calcium carbonate, dissolved by carbon dioxide.}}{CaCO_3, CO_2} + \underset{\text{Calcium hydrate in the lime-water.}}{CaH_2O_2} = \underset{\text{Precipitate.}}{2CaCO_3} + H_2O.$$

This process of softening water is called Clark's process. Boil the other part of the solution, when the calcium carbonate comes down, but in a more compact and less conspicuous form than in the previous experiment. Here the precipitation is due to the expulsion of carbon dioxide on boiling. The fur on kettles and boilers, produced by boiling hard water, is formed for the same reason.

5. Examine the air expired from the lungs for carbon dioxide, by breathing through a tube into a small flask half filled with lime-water.

6. Prove that the gas is heavier than air by carefully pouring it from a test-tube full of the gas into an empty one, and then testing for its presence in the latter with lime-water.

LESSON XI.

DISTILLATION OF NITRIC ACID.

Apparatus required.—Retort and stand; scales and weights; mortar; wire gauze; flask; filter-papers; spirit-lamp; silver nitrate solution; test-tubes; wash-bottle.

Special materials and tests.—Nitre (KNO_3); sulphuric acid diluted with its own bulk of water; concentrated sulphuric acid; ferrous sulphate, $FeSO_4$, 7aq., in crystals; barium nitrate ($Ba2NO_3$) solution; solution of indigo; copper foil.

1. Weigh out 7 grams (or 100 grains) of potassium nitrate, place them in a retort, and add carefully 60 cub. cent. (or 2 ounces) of moderately strong sulphuric acid: apply heat to the retort, and collect the nitric acid which distils in a flask half-immersed in water, and covered over with a wet filter-paper so as to condense the nitric acid vapours (see fig. 7, p. 24). Reject the first portion of the distillate. The action which takes place in this experiment is as follows:—

$$\underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Nitric acid = distillate.}}{HNO_3} + \underset{\text{Acid potassium sulphate.}}{KHSO_4}$$

2. When a sufficiency of the acid has been collected, it should be tested and identified as follows:—

a. To one portion add 2 or 3 drops of silver nitrate solution; if any chlorine be present as an impurity, a white curdy precipitate of silver chloride will fall.

b. To another portion add 5 drops of barium nitrate solution; if any sulphuric acid be present, a fine white precipitate of barium sulphate will fall.

c. To another portion add a crystal of ferrous sulphate; after a minute or two pour in gently 20 drops of strong sulphuric acid, holding the tube in a slanting position; let the mixture rest: a ring of purplish-brown colour on the sulphuric acid layer shows the presence of nitric acid (nitric oxide and nitrates produce the same effect).

d. To a few drops of the acid add concentrated sulphuric acid and a little solution of indigo, then heat. Note the change of colour, due to the oxidation of the blue indigo.

e. Slip a small piece of copper foil into a test-tube containing a few drops of the distilled acid. Pour the brown fumes given off into a second test-tube containing a solution of green vitriol. Note the colour produced.

LESSON XII.

DISTILLATION OF ACETIC ACID.

Apparatus required.—Retort and flask; retort-stand; mortar; spirit-lamp; funnel; wash-bottle; filter-paper; silver nitrate; test-tubes; scales and weights; test-papers.

Ordinary reagents.—Barium chloride ($BaCl_2$); ammonium hydrate; ferric chloride (Fe_2Cl_6).

Special materials and tests.—Sodium acetate ($NaC_2H_3O_2$); sulphuric acid mixed with an equal bulk of water; pure alcohol (C_2H_6O).

1. Weigh out 7 grams (or 100 grains) of sodium acetate, put them carefully into a retort. Pour in with a funnel 60 cub. cent. (or 2 ounces) of moderately strong sulphuric acid so as not to soil the neck of the retort: distil. Reject the first part of the distillate, and divide that which comes over afterwards into three parts, *a*, *b*, and *c*.

a. To this part add some barium chloride solution: should a white precipitate occur, it indicates that the acid is impure from the presence of sulphuric acid.

b. To this part add a few drops of silver nitrate solution: should a white cloudiness or a curdy precipitate form, it shows that the acid is impure from the presence of hydrochloric acid.

c. Into the third part put a piece of blue litmus paper.

2. To a few crystals of sodium acetate add a little concentrated sulphuric acid and a few drops of pure alcohol; warm, and notice the apple-like odour of ethyl acetate evolved.

3. To a small quantity of a solution of sodium acetate add one or two drops of ferric chloride; notice the deep brownish-red colour due to ferric acetate. If a few drops of an acid, say dilute hydrochloric acid, be now added, the colour will disappear.

The reaction in experiment 1 above is thus expressed:—

$$2NaC_2H_3O_2 + H_2SO_4 = 2C_2H_4O_2 + Na_2SO_4.$$

LESSON XIII.

TESTING OF WATERS.

Apparatus required.—Retort-stand; furnace-support and gauze; spirit-lamp; porcelain bason; silver nitrate solution; test-tubes; flasks; retort; mortar; wash-bottle.

Ordinary reagents.—Ammonium oxalate; dilute nitric acid; dilute hydrochloric acid; barium chloride; dilute sulphuric acid.

Special materials.—Four samples of water; potassium permanganate solution containing ·395 of a gram per litre; Nessler's test.

Several of the following experiments (namely 2, 3, 4, and 5) are to be tried with three or more samples of water. In each case it is better to place the same quantity of each of the waters to be tested in separate vessels, and then to add the test to each sample at the same time; thus an idea of the comparative purity of the several waters is obtained.

1. Evaporate 30 cub. cent. (or 1 ounce) of well- or river-water just to dryness in a porcelain bason. Note the colour and other characters of the residue left, as well as of any deposit which may have occurred during evaporation. Now heat the residue still more, and observe if it blackens, or gives off fumes or an

2. To test-tubes half full of each water, add ammonium oxalate solution; a white precipitate indicates *lime.*

3. To test-tubes half full of each water, add 20 drops of nitric acid and 5 of silver nitrate solution; a white precipitate indicates *chlorides.*

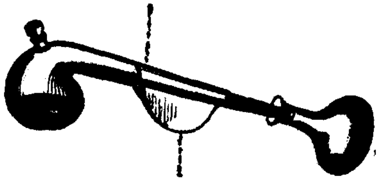
4. To test-tubes half full of each water, add 10 drops of hydrochloric acid and 10 drops of barium chloride solution; a white precipitate indicates *sulphates.*

5. To a test-tube half full of rain-water (or of water contaminated with sewage), add 5 drops of Nessler's test; a yellow or brown colour indicates *ammonia.*

6. To 65 cub. cent. (or 2 ounces) of each water warmed till the temperature of about 27° C. has been reached and contained in flasks or beakers, add 60 drops, or 4 cub. cent., of pure dilute sulphuric acid and 1 drop of potassium permanganate: if the colour disappears, add more permanganate until the purple colour is permanent after the lapse of 10 minutes: note how many drops each water has required. The usual cause of the disappearance of the colour is the loss of oxygen, or *reduction,* which permanganate undergoes when in presence of organic matter. Chalybeate waters and those containing nitrites exert the same effect upon this reagent.

7. Place 130 cub. cent. (or 4 ounces) of well- or river-water in a retort and distil: the figure shows how a large filter-paper kept constantly wet may be made to aid in condensing the steam. Repeat experiment 5 above with the first portion of the distillate, and test some of that which comes over afterwards in the same manner for ammonia; also test another portion of this distillate for lime by ammonium oxalate, as in experiment 2.

Fig. 7.



LESSON XIV.

DETECTION OF ARSENIC.

Apparatus required.—Spirit-lamp; test-tubes; wash-bottle; filter-paper; blowpipe.

Ordinary reagent.—Ammonium hydrate.

Special materials and tests.—Solution of arsenic trioxide in HCl; fine copper wire; subliming-tubes; mixture of dry sodium carbonate and potassium cyanide; hydrosulphuric acid; pure sulphuric acid; pure zinc.

1. Boil a little of the arsenic solution with two or three short pieces of bright copper wire; after a few minutes a dark grey compound of arsenic and copper will form on the wires. Remove the wires from the tube, rinse them with water, and dry them gently between filter-papers. The wires are now to be introduced into a small tube closed at one end and heated. As the arsenic is driven off in vapour it unites with oxygen and forms small brilliant crystals of arsenic trioxide, which will condense upon the cooler part of the tube, and may be seen to be octahedra under a lens.

2. Mix a very small quantity of arsenic trioxide with about three times its bulk of a mixture of dry sodium carbonate and potassium cyanide. Introduce the dry and slightly warmed mixture into a bulb subliming-tube. This is best done by means of a paper *gutter*. Heat the bulb gently at first; and if moisture comes off, sop it up with a slip of filter-paper rolled up so as to go into the tube. When the heat is increased, a dark but lustrous ring or mirror of sublimed metallic arsenic will be found in the cooler part of the tube.

3. To a little of the arsenic solution add some hydrosulphuric acid and warm; a yellow precipitate (of As_2S_3), dissolved on adding ammonium hydrate, indicates arsenic.

In addition to the above methods another and most satisfactory way of identifying arsenic exists. Fit up the hydrogen-apparatus exactly as used in Lesson VI., employing pure zinc and pure sulphuric acid. When the hydrogen has been evolved freely for a few minutes, and all air has been driven out of the apparatus (see § 2 of the Lesson on Hydrogen, p. 14), light the jet and depress into the flame for a few seconds one or two fragments of clean hard porcelain; no stain should appear on them. Now introduce through the funnel tube a few drops of the arsenic solution; note the increased size and the altered colour of the flame. This flame is due to the combustion of a mixture of hydrogen and hydrogen arsenide (AsH_3). If pieces of porcelain be depressed for a few seconds into the flame, so as nearly to touch the orifice of the jet, dark-brown stains of arsenic will be deposited upon them; for when the flame is cooled the hydrogen alone of the AsH_3 burns, and an arsenic-soot, similar in mode of formation to carbon-soot from an ordinary candle, is formed upon the cold porcelain. Antimony produces quite similar stains: but:—

a. The arsenic stains dissolve in calcium hypochlorite solution; antimony stains do not.

b. The arsenic stains do not dissolve in yellow ammonium sulphide solution; antimony stains do; but the ammonium sulphide must not be very strong or contain much sulphur in excess, or both stains will disappear.

Arsenic may be further identified by heating a tube through which hydrogen arsenide (arsenietted hydrogen) is passing, and experimenting with the black arsenic mirror which will be formed in the tube; or by allowing hydrogen arsenide to bubble through acid silver nitrate solution.

LESSON XV.

EXAMINATION OF BRONZE COIN.

Apparatus required.—Flask; furnace-support; spirit-lamp; blowpipe; funnel and filter; wire gauze; wash-bottle; test-tubes.

Ordinary reagents.—Dilute nitric acid; sodium acetate; potassium ferrocyanide; ammonium hydrate.

Special materials and tests.—About $\frac{1}{8}$ of a bronze halfpenny piece; potassium cyanide; piece of charcoal; piece of bright iron wire.

1. Slip a small piece of bronze gently into a flask, cover it $\frac{1}{4}$ of an inch deep with nitric acid, and heat it gently. When the metal has been completely acted upon, add a little water and allow the white particles of tin dioxide (SnO_2) to settle. Pass

the blue solution through a filter, leaving as much as possible of the tin dioxide in the flask. Test the filtrate, which will contain copper nitrate ($Cu2NO_3$), as follows:—

a. Pour one drop of the blue solution into a test-tube half full of water, add a few drops of sodium acetate, and 1 drop of potassium ferrocyanide: a purple-brown precipitate indicates copper.

b. To a small quantity of the blue solution add ammonia in excess: a clear deep blue colour indicates copper.

c. Dip a piece of bright iron into a small quantity of the blue liquid: a coating of metallic copper will form upon the iron.

2. As to the white residue (of SnO_2) mentioned above (1);—rinse it from the flask into a porcelain bason, pour some water on it, and when the particles have subsided decant it off: repeat this washing of the white residue, then dry it, mix it with twice its bulk of potassium cyanide and place the mixture in a small hole made in a piece of charcoal. Heat the mixture in the reducing flame of the blowpipe: add water to the fused mass, and extract and examine the globules of metal (tin) produced.

The bronze alloy of which English coins are made contains, in 100 parts, 95 parts of copper and 4 parts of tin, with 1 part of zinc.

LESSON XVI.

EXAMINATION OF SILVER COIN.

Apparatus required.—Flask; furnace-support; wire gauze; spirit-lamp; porcelain bason; funnel and filters.

Ordinary reagents.—Dilute nitric acid; dilute hydrochloric acid; potassium ferrocyanide.

Special materials and tests.—Silver coin; strip of sheet zinc.

1. Take a small silver coin (economists may be content with half a threepenny piece), slip it gently into a flask, and cover it half an inch deep with dilute nitric acid. Keep the flask warm over the spirit-lamp, but do not boil the liquid. When the

metal has completely disappeared, add hydrochloric acid to the solution until it ceases to produce a precipitate.

2. Shake the liquid and precipitate in the flask, allow the white particles of silver chloride ($AgCl$) to aggregate together, and pour the liquid, which contains all the copper of the original coin (7·5 per cent.), into a wetted filter placed in a funnel. The silver chloride should now be rinsed out of the flask on to the same filter. Continue the washing of the precipitate on the filter until the washings (the filtrate) no longer give a purple-brown precipitate with potassium ferrocyanide and sodium acetate (see experiment *a*, Lesson XV.).

3. The silver chloride is now to be washed out of the filter into a small dish, a drop of hydrochloric acid and a small piece of sheet zinc added. When the silver chloride has become uniformly brown, it is no longer chloride but pure metallic silver, and must, when the piece of zinc has been taken out, be thoroughly washed, by decantation, with much water. If pressed between pieces of agate, it may be made to assume the beautiful white lustre proper to pure silver. It may be dried and fused (after adding a little borax) into a button on a piece of charcoal before the blowpipe; or it may be dissolved in a little nitric acid, evaporated to dryness, and dissolved in a few drops of water; it constitutes then a pure solution of silver nitrate.

The following are the chemical reactions which occur during the foregoing experiments. The silver coin in dissolving forms silver and copper nitrates. These salts on the addition of hydrochloric acid are differently affected, the copper remaining dissolved, for its chloride is soluble, the silver coming down because its chloride is insoluble:—

$$\underset{\text{Silver nitrate.}}{AgNO_3} + HCl = HNO_3 + \underset{\text{White precipitate.}}{AgCl}$$

The zinc in the next stage of the experiment seizes the chlorine of the silver chloride, either directly—$2AgCl + Zn = ZnCl_2 + Ag_2$—or indirectly:—

$$\begin{aligned}&(1)\ 2HCl + Zn = ZnCl_2 + H_2;\\&(2)\ 2AgCl + H_2 = 2HCl + Ag_2.\end{aligned}$$

In dissolving silver plate and coin in nitric acid, while the silver and copper dissolve, a black powder generally remains unaffected: this consists chiefly of gold.

LESSON XVII.

EXAMINATION OF CAPSULE METAL.

Apparatus required.—Furnace-support; wire gauze; spirit-lamp; flask; wash-bottle; test-tubes; bason; funnel; filters.

Ordinary reagents.—Dilute sulphuric acid; dilute nitric acid.

Special materials and tests.—Strip of capsule metal; potassium cyanide; hydrosulphuric acid; piece of charcoal.

1. Warm a small piece of capsule metal with dilute nitric acid in a flask. When nothing but a white powder remains in the flask add water, and allow the white particles of the tin peroxide (SnO_2) to subside. Pass the solution, which contains the lead of the alloy, through a wetted filter, leaving as much as possible of the tin peroxide in the flask. Test the liquid which runs through for lead by dividing it into three parts (*a*, *b*, *c*), and adding to

a. A little dilute sulphuric acid: a white precipitate ($PbSO_4$) indicates lead.

b. Add some hydrosulphuric acid: a black precipitate (PbS) indicates lead.

c. Concentrate this portion; allow it to cool, and add a few drops of hydrochloric acid: a white crystalline precipitate, soluble in boiling water, indicates lead.

2. Rinse the white residue, obtained in (1) above, from the flask into a bason, wash it with water by decantation, dry it, mix it with twice its bulk of potassium cyanide, and place the mixture in a small hole made in a piece of charcoal. Heat the mixture in the reducing blowpipe-flame. Add water to the fused mass, and extract and examine the globules of metal (tin) produced. See for identification of tin and lead Lessons XV. and XVIII.

LESSON XVIII.

EXAMINATION OF TYPE-METAL.

Apparatus required.—Flask; furnace-support and gauze; spirit-lamp; funnels and filters; test-tubes; wash-bottle.

Ordinary reagents.—Dilute nitric acid; dilute hydrochloric acid; dilute sulphuric acid; sodium acetate; hydrosulphuric acid.

Special materials and tests.—Potassium dichromate solution; tartaric acid solution; fragments of type-metal.

1. Place a small piece of the metallic alloy, which consists chiefly of lead and antimony, in a flask, cover it ½ an inch deep with dilute nitric acid, and heat it gently till nothing but a white residue remains. This residue will contain the antimony, and the solution all the lead. Decant the solution on to a wetted filter, leaving the white residue in the flask.

2. Test the filtered solution for lead by applying to separate portions *a*, *b*, and *c* the following tests:—

a. Add a little hydrosulphuric acid; a black precipitate (of PbS) indicates lead:—

$$Pb2NO_3 + H_2S = 2HNO_3 + PbS.$$

b. Add a little dilute sulphuric acid; a white precipitate (of $PbSO_4$) indicates lead:—

$$Pb2NO_3 + H_2SO_4 = 2HNO_3 + PbSO_4.$$

c. Add a little potassium dichromate and some sodium acetate; a precipitate of chrome-yellow ($PbCrO_4$) indicates lead.

3. Wash the residue in the flask several times with water, by decantation, then add to it a little hydrochloric acid, also some tartaric acid, and warm; finally filter the solution, and add to it hydrosulphuric acid; an orange-red precipitate (of Sb_2S_3) indicates antimony.

LESSON XIX.

EXAMINATION OF A ZINC ALLOY.

Apparatus required.—Flask; retort-stand or furnace-support;

wire gauze; spirit-lamp; funnel and filter; test-tubes; wash-bottle.

Ordinary reagents.—Dilute nitric acid (HNO_3); ammonium hydrate (NH_4HO); dilute hydrochloric acid; sodium acetate ($NaC_2H_3O_2$); potassium ferrocyanide ($K_4[FeCy_6]$); ammonium sulphide (NH_4HS); sodium phosphate (Na_2HPO_4); acetic acid.

Special materials.—Zinc alloyed with 5 or 6 per cent. of iron, or clippings of galvanized iron. The former material is more convenient, and is easily obtained from galvanized-iron manufactories. Potassium ferricyanide ($K_6[Fe_2Cy_{12}]$); potassium sulphocyanide (KCNS).

1. Dissolve a small fragment of the alloy in dilute nitric acid; a flask is best suited for the purpose, a gentle heat only being employed. To the solution add ammonia solution in excess; a considerable quantity is required in order to re-dissolve all the zinc oxide which it at first precipitates. When enough ammonia has been added, there will remain, after the mixture has been thoroughly shaken, nothing of the original thick and pasty precipitate but some reddish-brown flocks of ferric hydrate ($Fe_2H_6O_6$). Filter these off, and divide the clear filtrate into two parts, *a*, *b*. To

a add a little ammonium sulphide; white *zinc* sulphide will fall. To

b add a little sodium phosphate and a little acetic acid; white *zinc* phosphate will fall.

2. In order to identify the *iron* in the alloy, the brown precipitate (obtained in 1 above) is to be washed, while still on the filter, with water, and then dissolved by pouring upon it the smallest quantity of warm hydrochloric acid that will effect the purpose. Divide the solution into 4 parts, *a*, *b*, *c*, *d*: to

a add one drop of potassium ferrocyanide: to

b add one drop of potassium ferricyanide: to

c add one drop of potassium sulphocyanide: to

d add some sodium acetate.

LESSON XX.

REDUCTION AND OXIDATION.

Apparatus required.—Flask; furnace-support and wire gauze; spirit-lamp; test-tubes; wash-bottle; funnel and filter; silver nitrate; methylated spirit; platinum foil; tongs.

Ordinary reagents.—Ammonia; dilute hydrochloric acid.

Special materials and tests.—Potassium dichromate (K_2CrO_4, CrO_3); lead acetate ($Pb2C_2H_3O_2$); alcohol; sulphurous acid solution; potassium nitrate in crystals.

The metal chromium affords a good illustration of the power which many metals possess, of combining in several proportions with oxygen or other non-metals. Some compounds of chromium are green; the sesquioxide (Cr_2O_3) and its solutions in acids are examples; other compounds of chromium containing more oxygen, &c. are yellow, orange, or red; of these latter, chromic peroxide (CrO_3) and the chromates may be mentioned. We shall proceed to show how one series of these salts may be changed, by addition or removal of oxygen, into the other. In order to be able to identify *chromic* compounds, when obtained, it is better to begin this lesson by trying the following experiment:—

1. To two test-tubes, each half full of water, add a few drops of potassium dichromate solution, then to one of the test-tubes add a few drops of lead acetate; yellow lead chromate falls: to the other tube add a few drops of silver nitrate; deep-red silver chromate falls.

2. Put into a flask a little potassium dichromate solution, a little spirit of wine, and about the same bulk of dilute hydrochloric acid. Boil the mixture until it has become grass-green; let it cool, and add ammonia in slight excess, *i. e.* until the liquid, after shaking, just smells of ammonia gas. Filter off the green precipitate, which is chromium sesquioxide (Cr_2O_3), reduced by the alcohol from the higher oxide (CrO_3), which may be regarded as present in the dichromate taken. The alcohol gains oxygen in the process, and is partly converted into acetic acid. Potassium dichromate solution is changed from orange to green when mixed with sulphurous acid solution, owing to the same reduction taking place.

3. Scrape the green residue just obtained off the filter on to platinum foil, add a few crystals of potassium nitrate, and hold the foil over the lamp. The potassium nitrate will give up oxygen to the green oxide, and turn it into the higher one, the colour changing to yellow. Wash the yellow mass off the foil into a tube, divide the solution of it into two parts, and add to one a few drops of lead acetate, to the other a few drops of silver nitrate. Exactly the same precipitates will be formed now as in experiment 1 above; for the lower oxide has been reconverted into the higher.

LESSON XXI.

MANGANATES AND PERMANGANATES.

Apparatus required.—Retort-stand; spirit-lamp; triangle; porcelain crucible; wash-bottle; flask; funnel and filter; scales and weights.

Ordinary reagents.—Dilute sulphuric acid; hydrosulphuric acid.

Special materials and tests.—Mixture of equal parts of potassium chlorate and sodium hydrate; oxalic acid solution; ferrous sulphate in solution Manganese dioxide (MnO_2).

The metal manganese forms numerous combinations with oxygen and other non-metals. In consequence of the instability of most of these compounds, it is found that those of them which contain little oxygen may be easily made to take up more, while those which contain much readily part with some. The first and second experiments below show absorption of oxygen, while the several reactions given under experiment 3 show how the loss of oxygen which a manganese compound suffers in contact with organic matter or certain iron salts may be utilized in analysis.

1. Weigh out ·7 of a gram (or 10 grains) of manganese dioxide, and 1·4 of a gram (or 20 grains) of a mixture of potassium chlorate and sodium hydrate; mix the two substances, and place them on a fragment of porcelain. Heat the mixture gently at first, afterward increase the heat until the mass acquires a green colour throughout.

$$6NaHO + KClO_3 + 3MnO_2 = 3Na_2MnO_4 + KCl + 3H_2O.$$

2. Dissolve the green mass in cold water, filter the liquid into a flask, and add a *very small* quantity of dilute sulphuric acid to it; warm. Observe the change from the green manganate to the violet permanganate.

$$\underset{\text{Manganate.}}{5Na_2MnO_4} + 4H_2SO_4 = \underset{\text{Permanganate.}}{4NaMnO_4} + MnSO_4 + 3Na_2SO_4 + 4H_2O.$$

If, as commonly occurs, brown manganic hydrate be precipitated, the liquid should be filtered again.

3. Add a little of the violet permanganate solution to the following substances dissolved in water, and note the results :—

a, hydrosulphuric acid, in presence of a little sulphuric acid.

b, oxalic acid, in presence of sulphuric acid.

c, ferrous sulphate, in presence of sulphuric acid.

d, ferrous sulphate, without addition of H_2SO_4.

LESSON XXII.

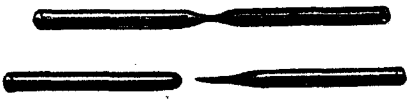
BLOWPIPE EXPERIMENTS.—PART 1.

Apparatus required.—Blowpipe; spirit-lamp; litmus paper; turmeric paper; crucible tongs; triangular file.

Special materials.—Quill tubing; sawdust; hay; gelatin; gypsum; mercuric oxide; red lead; white arsenic; paper gutters.

1. Take a length of quill tubing; cut it, by means of the triangular file, into four pieces, each about 5 inches long. Direct the point of the blowpipe-flame upon the middle of one of these pieces, rotating it at the same time. When the glass is softened draw the ends apart quickly, and by further heating close the fused points so as to make two tubes, each closed at one end. Eight tubes will be required for the following experiments, one of which should, however, be open at both ends, though drawn to a point at one end.

Fig. 8.



2. Introduce, by means of a paper *gutter*, a little longer than

the tube, some sawdust into one of the tubes: heat it, and observe that it chars and gives off vapours of acetic acid ($C_2H_4O_2$), which redden blue litmus paper.

3. Heat a fragment of gelatin similarly in another tube; introduce a piece of turmeric paper, which will be turned brown by the ammonia evolved.

4. Heat a little gypsum in a tube, and notice its change of aspect and the appearance of water in the cooler part of the tube. The change which gypsum suffers on moderate heating is thus represented:—

$$\underset{\text{Gypsum.}}{2(CaSO_4, 2H_2O)} = \underset{\text{Plaster of Paris.}}{2CaSO_4, H_2O} + \underset{\text{Water.}}{3H_2O}.$$

5. Heat a little mercuric oxide (HgO); observe its gradual disappearance, and the formation of globules of mercury.

6. Heat half an inch of dry grass in a tube open at both ends: observe the charring, the burning away of the charcoal, and the residual fixed matter or ash, which consists in great part of silica (SiO_2).

7. Heat a little red lead (Pb_3O_4) in a small tube; observe the altered colour of the residue:—

$$\underset{\text{Red oxide.}}{2Pb_3O_4} = \underset{\text{Yellow oxide.}}{6PbO} + O_2.$$

8. Heat a little white arsenic (As_2O_3) in a small tube; observe the crystalline sublimate.

It is of great importance, in all the above experiments, that the several substances used should be so introduced into the tubes as not to soil the inner walls of the tube. This is best accomplished by means of a small paper gutter.

LESSON XXIII.

BLOWPIPE EXPERIMENTS.—PART 2.

Apparatus required.—Blowpipe; spirit-lamp; cobalt nitrate solution; platinum wire; test-tubes and stand; wash-bottle.

Ordinary reagent.—Dilute hydrochloric acid.

Special materials.—Small tubes closed at one end, as used for Lesson XXII.; zinc oxide (ZnO): chalk ($CaCO_3$); alum ($AlK2SO_4$, 12aq.); zinc sulphate ($ZnSO_4$, 7aq.); magnesium sulphate ($MgSO_4$, 7aq.): lead acetate ($Pb[C_2H_3O_2]_2$): charcoal; barium sulphate ($BaSO_4$): a silver coin; borax; solutions containing copper, iron, manganese, chromium, and cobalt; also potassium, barium, strontium, and calcium.

1. Select a piece of charcoal free from bark and cracks: cut one end of it in a slanting direction, and make a small shallow hole near the middle of the sloping surface. Into this hole put a little zinc oxide (ZnO), moisten it: note the colour it assumes when hot.

2. Heat a small piece of marble or chalk ($CaCO_3$) on charcoal prepared as for experiment 1; note the brilliant light emitted; take the residue, which is now lime (CaO), and place it on a piece of wet turmeric paper.

3. Heat a fragment of alum, which contains alumina (Al_2O_3), on charcoal, moisten the residue with a drop of cobalt nitrate solution, and heat it again.

4. Moisten a crystal of zinc sulphate with a drop of cobalt nitrate, and ignite it in the blowpipe-flame on charcoal: observe the colour of the mass.

5. Ignite some magnesium sulphate on charcoal; moisten the residue with cobalt nitrate solution, and ignite it again: observe the colour of the mass.

6. Heat a little lead acetate on charcoal. Observe the malleable globules of lead separated, and the yellow ring of oxide.

7. Mix together a little barium sulphate, $BaSO_4$, and powdered charcoal. Heat the mixture, which should be just moistened with water, on a piece of charcoal, in the reducing flame. Allow the ignited mass to cool, place it upon a silver coin, and moisten it with a drop of dilute hydrochloric acid; observe the effervescence, caused by the escape of hydrosulphuric acid gas (H_2S), which may be recognized by its characteristic odour, and by the black stain (Ag_2S) which it produces upon the silver.

In this experiment (7) the charcoal removes oxygen from the $BaSO_4$, and makes it into BaS. This compound is then decomposed by HCl, thus:—$BaS + 2HCl = H_2S + BaCl_2$.

8. Make a loop (about twice the size shown in fig. 9) near the end of a piece of platinum wire, heat it to redness, dip it into powdered borax, and fuse the borax to a clear glass in the blowpipe-flame.

Fig. 9.

9. Dip the borax bead just made into a solution of copper, and heat it both in the inner and outer blowpipe-flames. Four other beads are to be successively made, and dipped respectively into solutions of salts of iron, manganese, chromium, and cobalt; and then each is to be heated as in the first case. Note, in each instance, the colour of the bead. To remove the bead and clean the wire plunge it red-hot into hydrochloric acid; the bead will then be loosened, and may be removed by pressure between the fingers and washing with water.

10. Dip the end of the platinum wire (which must be so clean as to give little or no colour when heated alone in the blowpipe-flame) into a solution of potassium chloride, and heat it in the blowpipe-flame: note the colour imparted to the flame. Repeat the experiment with solutions containing barium, strontium, copper, and sodium respectively, noting the colour in each case. The wire must be cleaned between each experiment, by dipping it in dilute hydrochloric acid and then heating it to redness and washing it with water. Repeat this treatment several times, until the wire imparts no colour to the flame, and then try the next experiment.

LESSON XXIV.

MANUFACTURE OF SUPERPHOSPHATE.

Apparatus required.—Spirit-lamp; test-tubes; funnels and filters; wash-bottle; scales and weights.

Ordinary reagent.—Dilute nitric acid.

Special materials and tests.—Bone-ash; ground coprolites: ammonium molybdate; superphosphate of lime; sulphuric acid of specific gravity 1·7.

1. Boil ·2 gram (or 3 grains) of bone-ash in water in a tube, filter through Swedish paper, and to a few drops of the filtrate, which must be perfectly clear, add a few drops of nitric acid, and of ammonium molybdate; heat nearly to boiling. The bone-ash consists chiefly of tricalcic phosphate, which is nearly insoluble in water, so that the above test for phosphoric acid will produce little or no effect in the watery extract of the bone-earth.

2. Boil ·2 gram (or 3 grains) of dissolved bone-ash or superphosphate of lime in water in a tube, filter, and add to a few drops of the perfectly clear filtrate a few drops of nitric acid and the same quantity of ammonium molybdate; heat nearly to boiling; a yellow precipitate will be formed, indicating the presence in the superphosphate of a soluble phosphate, which was extracted by the water.

3. Weigh out ·2 gram (or 3 grains) of ground coprolites (which chiefly consist, like bone-ash, of insoluble tricalcic phosphate): put it in a test-tube, and pour upon it a drop or two of moderately strong sulphuric acid: warm the mixture. Finally add water to the tube, but not until it is nearly cold; agitate the mixture, and pour it on to a wetted filter. To ten drops of the clear filtrate add a few drops of nitric acid and some ammonium molybdate, and heat nearly to boiling; a yellow precipitate shows that sulphuric acid converts the insoluble phosphate of coprolite and bone-ash into a soluble one.

The change of the originally insoluble tricalcic phosphate into the soluble monocalcic phosphate, which is one of the chief changes occurring in the manufacture of superphosphate and in experiment 3 above, is thus shown :—

$$\underset{\substack{\text{Insoluble tricalcic}\\ \text{phosphate.}}}{Ca_3 2PO_4} + 2H_2SO_4 = \underset{\substack{\text{Soluble monocalcic}\\ \text{phosphate.}}}{CaH_4 2PO_4} + 2CaSO_4.$$

LESSON XXV.

EXPERIMENTS WITH LIME.

Apparatus required.—Test-tubes; funnel and filters; turmeric and litmus paper; piece of quill tubing; flask; wash-bottle and distilled water. Corks.

Ordinary reagents.—Dilute hydrochloric acid; ammonium oxalate solution; dilute sulphuric acid; barium chloride solution.

Special materials and tests.—Freshly burnt lime (that prepared from Iceland spar is best); copper sulphate solution; chalk; earthenware plate or tile; powdered white marble; gypsum in coarse powder.

There are four common and important substances which consist mainly of compounds of the element calcium—the metallic basis of lime. These four substances are:—

1. Lime, quicklime or burnt lime = CaO.
2. Slaked lime or calcium hydrate = CaH_2O_2.
3. Mild lime or calcium carbonate = $CaCO_3$.
4. Gypsum, selenite, alabaster or hydrated calcium sulphate = $CaSO_4, 2H_2O$.

1. Put a hard lump of freshly burnt lime upon a plate and drop water upon it a little at a time until no more is absorbed. The lime combines chemically with a definite amount of the water (56 of lime combine with 18 of water) and produces calcium hydrate:—

$$CaO + H_2O = CaH_2O_2.$$

Much heat is given out during this combination, and some of the excess of water present is driven off as steam.

2. A small portion of the calcium hydrate, or slaked lime, formed in experiment 1, should be placed in a test-tube with some distilled water, corked, and then shaken up. Allow the mixture to settle, and then pour the clear liquid through a filter. A very weak solution of calcium hydrate in water, called lime-water, is thus obtained: the presence of an alkaline earth in this solution may be shown by dividing it into 3 parts and testing the first with a piece of red litmus or turmeric paper, the second

with a few drops of copper sulphate solution, and the third with a few bubbles of air from the lungs, blowing through a small quill tube.

3. When slaked lime, that is calcium hydrate, is exposed to the ordinary air it slowly parts with its water and combines with carbon dioxide thus—

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

The calcium carbonate thus formed is identical in composition with the chief constituent of chalk, limestone and marble—white Carrara or statuary marble being almost pure calcium carbonate. Two instructive experiments may be made with some chalk or powdered marble:—*a*. Shake up a little powdered marble with recently boiled distilled water in a test-tube, filter the liquid, and add to half of the perfectly clear filtrate a few drops of ammonium oxalate solution. Owing to the almost complete insolubility of calcium carbonate in pure water, no visible precipitate will be formed, though a slight cloudiness may be observed after some time. Into the other half of the filtrate drop a piece of red litmus paper, its colour will not be perceptibly altered: these negative results should be contrasted with those obtained with lime-water in experiment 2 above.—*b*. Dissolve a small piece of chalk in dilute acetic acid, filter the liquid and divide the clear filtrate into two portions. To one add a little ammonium oxalate solution; to the other a little dilute sulphuric acid.

4. Place some coarsely powdered gypsum in a bottle or flask half full of distilled water and shake it for a few minutes. Pour the liquid on to a filter and divide the clear filtrate into two portions, to one of which ammonium oxalate solution, and to the other barium chloride solution is to be added. One part of gypsum dissolves in about 420 parts of water: the solution is strong enough to give a decided precipitate with both these tests, the insoluble calcium oxalate falling in the first reaction and barium sulphate in the second.

LESSON XXVI.

LIME IN SOILS.

Apparatus required.—Scales and weights; spirit-lamp; test-tubes; funnels; wash-bottle; cut filters.

Ordinary reagents.—Hydrochloric acid; ammonium hydrate (NH_4HO); ammonium oxalate ($[NH_4]_2C_2O_4$).

Special materials.—Dried and powdered samples of four kinds of soil.

1. Boil ·5 gram (or 8 grains) of a calcareous soil (A) with a little weak hydrochloric acid in a test-tube until the effervescence ceases. Add ammonium hydrate in excess to the mixture, shake it—note whether, after shaking, the mixture stills smells of ammonia, and if it does not, add more ammonium hydrate—and then filter. The ammonium hydrate precipitates as hydrates any alumina and ferric oxide which have been dissolved, and thus the filtrate will contain scarcely anything save salts of the calcium and magnesium present in the soil. The next step is to add to the filtrate some solution of ammonium oxalate, when a white precipitate of calcium oxalate will fall if lime was present in the soil tested.

2. Try exactly the same experiment with a clay soil (B), a loamy soil (C), and a peaty soil (D). Care should be taken to obtain comparable results. The several filtrates should be made up to the same bulk, and they should be treated with ammonium oxalate in test-tubes of the same size.

LESSON XXVII.

EXPERIMENTS WITH SOILS.

Apparatus required.—Two beakers; a flask; spirit-lamp; funnels and filters; test-tubes; wash-bottle; litmus paper; scales and weights.

Ordinary reagents.—Ferric chloride (Fe_2Cl_6); sodium hydrate ($NaHO$); dilute hydrochloric acid; ammonium hydrate.

Special materials and tests.—Loam; peat; decoction of logwood; two wide-mouth 4 oz. bottles.

1. Boil 2 grams (or 30 grains) of peat with water in a flask or beaker. When the mixture has boiled five minutes, pour it on a wetted filter, and divide the filtrate which passes through into two parts, *a* and *b*.

a. To one part add a few drops of ferric chloride (Fe_2Cl_6); a black colour or precipitate shows the presence in the soil of organic acids similar to those of oak-bark and gall-nuts (tannic and gallic acids).

b. Into the remainder of the filtrate drop a piece of blue litmus paper; if the blue colour becomes reddish, it is a sign of the "sourness" of the soil, and that the application of a base such as lime will be beneficial to it.

2. Warm 2 grams (or 30 grains) of peat in a flask with enough sodium hydrate solution to cover it. When the mixture has been heated five minutes, add a little water and pour the mixture on a wetted filter. If the filtrate is dark brown and gives a brown flocky precipitate when it is made acid with excess of dilute hydrochloric acid, it is a sign of the presence of certain organic acids (humic &c.), which are nearly insoluble in water, but form soluble salts with alkalies. They are derived from the decay of organic matter.

3. To about 3 oz. of water add five drops of ammonium hydrate; the solution will turn turmeric paper brown. Now put into a 4 oz. wide-mouth stoppered bottle some loamy or peaty soil, and add the weak ammonia solution prepared above: shake the mixture and pour it on to a wetted filter. Good soils have so strong an absorptive power for ammonia, that when such a solution as that mentioned is allowed to remain in contact with them, the ammonia is so far removed that the filtrate no longer smells of ammonia, nor turns turmeric paper brown.

4. Shake another portion of the same soil with a weak decoction of logwood (or other coloured liquid), and presently pour the mixture on to a wetted filter. The filtrate will be colourless or nearly so. Liquid sewage and the drainage of manure-heaps

lose by the same treatment their colour and odour, owing to the absorptive power of peat.

LESSON XXVIII.

ACTION OF SOILS ON SALTS.

Apparatus required.—Furnace support; spirit-lamp; wire gauze; porcelain bason; test-tubes and rack; funnels and filters; wash-bottle; turmeric paper.

Ordinary reagents.—Sodium hydrate; sodium phosphate; ammonium oxalate; barium chloride.

Special materials and tests.—Wide-mouth 4 oz. bottles; ammonium phosphate solution; potassium nitrate solution; ammonium sulphate solution; ferrous sulphate; oil of vitriol; air-dry sifted soil.

1. Into a wide-mouth bottle introduce some sifted soil, cover it with water (about 3 oz.), add 5 drops of sodium phosphate solution, and shake the mixture for 5 minutes. Pour the contents of the bottle on to a wetted filter and test the clear filtrate for phosphoric acid by "magnesia mixture." The soil should have withdrawn much of the phosphoric acid from the solution.

2. Repeat the experiment with ammonium phosphate solution: test one part of the filtrate for ammonia by boiling it with sodium hydrate solution, and the other part for phosphoric acid: much of the base as well as of the acid will have been withdrawn by the soil from the solution.

3. Repeat the experiment with a very weak solution of potassium nitrate. Test one part of the filtrate (after evaporation) for potash by tartaric acid and half of the remainder for nitric acid by means of ferrous sulphate and oil of vitriol: much of the base, but little of the acid, will have been withdrawn by the soil. The rest of the filtrate will be found to give a precipitate when tested for lime by means of ammonium oxalate, showing that the soil has yielded calcium while withdrawing potassium from the solution.

4. Repeat the experiment with a very weak solution of ammonium sulphate. Test one part of the filtrate for ammonia by means of sodium hydrate; another part for sulphuric acid with barium chloride, and another part for lime with ammonium oxalate. While much of the ammonia will have been withdrawn, much sulphuric acid and some lime will be found in the filtrate.

LESSON XXIX.

STARCH AND SUGAR.

Apparatus required.—Retort-stand; spirit-lamp; test-tubes; two flasks; cut filters; funnels; pestle and mortar; wash-bottle.

Ordinary reagents.—Sodium hydrate solution; sulphuric acid (H_2SO_4), concentrated and dilute.

Special materials and tests.—Starch; a raisin; the "sugar test"; tincture of iodine; cane- or beet-sugar in crystals; maltose; grape-sugar; milk-sugar; solution of 40 grams of phenylhydrazine and 40 grams of glacial acetic acid in 10 c. c. of water.

1. Crush a fragment of starch, shake it up in a test-tube half full of water, and boil, constantly shaking the tube. Pour the starch paste thus formed into three test-tubes, *a*, *b*, and *c*.

To *a*, when cold, add one drop of tincture of iodine: observe the production of a blue colour and its disappearance on warming the mixture.

To *b* add ten drops of the "sugar test," and boil carefully.

To *c* add a few drops of dilute sulphuric acid and some water, boil for ten minutes in a flask, then add ten drops of the "sugar test" and enough sodium hydrate to produce a clear blue colour; boil.

2. Place ¼ of a small dry filter in a dry mortar, just moisten it with strong sulphuric acid, and then grind it to a paste; add water, pour the mixture into a flask, boil it five minutes, filter it, add ten drops of sugar test and enough sodium hydrate to produce a clear blue colour; boil.

3. Cut a raisin in pieces, boil it in a flask with a little water, filter, and then add to the filtrate twenty drops of the sugar test; boil.

4. Dissolve a little grape-sugar in water, and add the solution to a mixture of phenylhydrazine and acetic acid; boil and allow to cool. The yellow crystalline precipitate which falls is phenylglucosazone.

5. Dissolve a crystal of cane- or beet-sugar in water, add ten drops of "sugar test"; boil.

6. Dissolve a crystal of beet- or cane-sugar in a little water, add 2 or 3 drops of dilute sulphuric acid or a small crystal of citric acid, boil for a few minutes, and then add sodium hydrate in excess and apply the "sugar test."

7. Try the action of the "sugar test" when boiled with milk-sugar, and also with maltose, in the presence of water.

By this lesson the student learns how to detect and distinguish starch and sugar, and thereby to discover certain adulterations in cattle foods; he also learns how to turn starch and paper into sugar. The "sugar test" named above gives a yellow, orange, or red precipitate of copper suboxide (Cu_2O) only when certain sugars, as grape-sugar and milk-sugar, are present. The sugar from the sugar-cane or beet-root gives no precipitate until it has been treated as in Expt. 6. The preparation of the "sugar test" is described further on amongst the "special reagents."

LESSON XXX.

EXPERIMENTS WITH MILK, BUTTER, AND CHEESE.

Apparatus, &c. required.—Test-tubes; funnels; beakers; spirit-lamp; wash-bottle; filters; porcelain bason; retort-stand; gauze; furnace-support; silver nitrate solution.

Ordinary reagents.—Dilute sulphuric acid; sodium hydrate.

Special materials and tests.—Milk; butter; cheese; "sugar test"; soda-lime.

1. To half a test-tube full of milk add five or six drops of dilute sulphuric acid; agitate the mixture well, and pour it on a wetted filter; the curd will remain on the filter, while the whey will pass through as the filtrate. Add to the filtrate a little sodium hydrate solution and twenty drops of the "sugar test"; boil. A yellow or red precipitate of cuprous oxide (Cu_2O) shows the presence of sugar (a particular kind, called *lactose*).

2. Take the curd which remains on the filter used in experiment 1, place it in a porcelain bason, and warm it gently on the top of a beaker half full of hot water, supported on wire gauze over the spirit-lamp. As the filter-paper and curd get dry the former will acquire greasy stains from the true fat or butter melting out and leaving the true curd (casein).

3. Fill a beaker half full of water, warm it, and, before the boiling-point is reached, plunge into it a narrow test-tube containing a small lump of butter. The true fat or butter melts at about 36°·5 C. into a clear oil, while the casein sinks below this layer, the water remaining at the bottom of the tube. The salt present may be detected by adding a little cold water to the tube, shaking the mixture, pouring out the aqueous part into a clean test-tube, and then adding to it a few drops of silver nitrate solution, when a white curdy precipitate of silver chloride will fall.

4. The presence of nitrogen, the characteristic constituent of casein or true curd, may be detected by mixing a grain or so of grated cheese with a little soda-lime in a small tube, and heating it strongly: ammoniacal vapours will be given off.

LESSON XXXI.

DEXTRIN AND GUM.

Apparatus required.—Furnace-support and gauze; spirit-lamp; bason; wash-bottle; test-tubes; funnel and filter; retort-stand.

Ordinary reagent.—Ammonium oxalate.

Special materials and tests.—Starch; gum-arabic; piece of wire; tincture of iodine.

1. Place a small quantity of starch in a porcelain bason, and cautiously heat it, with constant stirring or shaking, until it has all acquired a pale fawn-colour. Allow the bason to cool completely, and then pour half a test-tube full of distilled water upon the roasted starch. Filter the cold-water solution of dextrin

thus prepared, and divide the filtrate into two parts, *a* and *b*. To *a* add a few drops of tincture of iodine: a plum or brownish-purple colour is observed if the dextrin be free from starch: this colour is produced by one of the two kinds of dextrin (erythrodextrin) present in the above product. To the other portion of the solution, *b*, add a few drops of ammonium oxalate: the liquid remains clear.

2. *Dissolve a few lumps of crushed gum-arabic in a test-tube* half full of boiling distilled water. Divide the solution, when cold, into two parts, and test them exactly as in the case of *a* and *b* above. Iodine tincture produces scarcely any change, while ammonium oxalate gives a white cloudiness, due to the presence of calcium compounds in the gum-arabic.

LESSON XXXII.

EXPERIMENTS WITH BREAD.

Apparatus required.—Beakers; furnace-support and gauze; spirit-lamp; scales and weights; bason; test-tubes; wash-bottle; funnels and filters; retort-stand.

Ordinary reagents.—Acetic acid; potassium ferrocyanide; ammonium hydrate; ammonium chloride; barium nitrate; dilute nitric acid.

Special materials and tests.—Bread-crumb; grated bread-crust; bread adulterated with blue vitriol and alum; iodine solution; sugar-test; linen filter; 4 °/₀ carbolic acid solution.

1. In order to ascertain roughly the amount of water present in bread, weigh out 10 grams (or 100 grains) of bread-crumb, put them into a porcelain bason, which is placed on the top of a beaker containing hot water, and kept hot by the lamp. When the bread is completely dried, it will be found to have lost about 38 to 40 per cent. of its total weight; but it is not possible to complete the drying with the simple contrivance just mentioned, the *water-oven* or even a temperature a little above that of boiling water being requisite for this purpose.

2. To show that the heat of the baking-oven has changed one

important constituent of the flour greatly, agitate a small quantity of rasped bread-crust with cold water in a beaker for five minutes, throw the mixture on a filter, and evaporate the clear filtrate nearly to dryness over the lamp. A gummy and sticky residue remains, which is chiefly dextrin or transformed starch. The crumb of bread contains a much smaller quantity of dextrin than the crust, while the original flour contains a still smaller proportion.

3. Boil a little bread in water, filter the solution, and divide the filtrate into two parts. To one of these add a few drops of solution of iodine, to the other a few drops of the alkaline solution of copper tartrate and boil. For the meaning of the results obtained refer back to Lesson XXIX. on Sugar and Starch.

4. Blue vitriol (copper sulphate, $CuSO_4$, 5aq.), as well as alum (potassium and aluminium sulphate [$AlK2SO_4$, 12aq.]), have been often fraudulently used by bakers, chiefly to enable them to employ damaged flour in bread-making. Even when the quantity of blue vitriol in a quartern loaf does not exceed a grain, it may be thus shown :—A large piece of the crumb is to be placed in a porcelain bason containing distilled water, to which a drop or two of acetic acid and of potassium ferrocyanide have been added. The rose- or purple-brown colour of copper ferrocyanide will gradually make its appearance.

5. Alum may generally be detected in bread by agitating the crumb for some time with a cold 4 $^o/_o$ solution of carbolic acid, pressing the mass in a linen cloth, and filtering through paper the liquid expressed. Nitric acid and some barium nitrate should be added to half the filtrate thus obtained; a white precipitate of barium sulphate will usually be obtained if alum, itself a sulphate, has been added to the flour. A precipitate of alumina may be got from the rest of the filtrate by adding to it ammonium chloride and hydrate: but the nature of the precipitate thus obtained must be exactly ascertained by further experiment. Alumed bread usually yields, when burnt, more ash than genuine bread: 100 parts of genuine bread will yield, on an average, 1·3 part of ash. But the constituents, and not the quantity of the ash, are of

importance in discovering adulterations. Naturally, wheaten flour contains the merest trace of aluminium.

In order to obtain adulterated bread for the above experiments (4 and 5), a quartern loaf may be made with the introduction of ·3 of a gram (or 5 grains) of blue vitriol, and 3 grams (or 50 grains) of alum. Further and more precise directions for the detection of adulterations in bread will be found in the Third Part of this volume.

LESSON XXXIII.

ASHES OF PLANTS.

Apparatus required.—Spirit-lamp; retort-stand; platinum foil and wire; triangle; watch-glasses; funnel and filter; turmeric and litmus paper; wash-bottle; platinum tetrachloride.

Ordinary reagents.—Dilute nitric acid; dilute hydrochloric acid; acetic acid; ammonium oxalate.

Special materials and tests.—Ammonium molybdate; dried beech-leaves, hay, &c.

1. Roll up some dried beech-leaves, grass, or other suitable vegetable matter, within a spiral of platinum wire. Place a triangle upon a ring of the retort-stand, and upon the triangle a piece of platinum foil. Heat and set fire to the vegetable matter, and continue the heating until nothing remains but a white or grey ash. The substance to be burnt should be held over the platinum foil in such a way as almost to touch it, and so as to avoid the loss of any of the ash that may drop out of the platinum spiral. With the ash or mineral matter thus obtained the following experiments may be tried :—

2. Place a minute particle of the ash in a watch-glass, add one drop of dilute nitric acid, and 10 drops of ammonium molybdate; a yellow precipitate coming down on warming indicates the presence of phosphates in the ash.

3. Place a minute particle of the ash upon a piece of turmeric paper, and let a drop of water fall upon it; a reddening of the paper indicates the presence of an alkaline carbonate.

4. Add ten drops of water to the whole of the remaining ash, pour the mixture upon a very small wetted filter, and collect the filtrate in a watch-glass; add to it 3 or 4 drops of hydrochloric acid and the same quantity of platinum tetrachloride: a yellow crystalline precipitate forming slowly proves the presence of potassium compounds in the ash.

5. The residue on the filter will probably contain some charcoal and calcium carbonate. Pour upon it ten drops of acetic acid, collect the filtrate in a watch-glass; add to it 3 or 4 drops of ammonium oxalate: a white precipitate indicates the presence of calcium compounds in the ash.

LESSON XXXIV.

VEGETABLE COLOURS.

Apparatus required.—Spirit-lamp; test-tubes; mortar; flask; funnel and filters; bason; retort-stand; wash-bottle.

Ordinary reagents.—Sodium hydrate; dilute sulphuric acid; ammonium carbonate.

Special materials and tests.—Alcohol; concentrated hydrochloric acid; fragment of zinc; cream of lime; solution of lead acetate; powdered madder-root; solution of indigo or sulphindigotic acid; dahlia-flower; turmeric root; litmus; wool; black paper.

1. Some leaves of grass, mangolds, or nettles, are to be employed for the first experiment. They should have been dried as quickly as possible after having been gathered, but at a lower temperature than 100° C. A small quantity of the dry material having been crushed and placed in a test-tube, it is to be warmed with alcohol till the latter has become a rich green colour. This solution, which contains *chlorophyll*, the green colouring-matter of leaves, should now be passed through a filter which has been previously dried, and the clear filtrate viewed, in sunlight if possible, with a piece of black paper behind the tube containing it. It will exhibit, owing to the action of the

chlorophyll in changing the refrangibility of some of the solar rays, a beautiful red *fluorescence*, as it is called. When this effect has been noticed, some water should be added to the solution; the chlorophyll, being insoluble, will be precipitated.

2. Crush the petals or florets of any dark-red or purple flower, such as a rich coloured dahlia, and warm them with water in a flask. Filter the liquid, and divide it into 3 parts. To one part add a drop or two of dilute sulphuric acid, to another a drop of sodium hydrate, and to the third a drop of lead acetate solution. The changes of colour in 1 and 2 thus produced afford a convenient method of ascertaining whether a solution is acid, alkaline, or neutral.

3. Boil some powdered root of madder, *Rubia tinctorum*, with water and some sodium hydrate, in a flask, filter the liquid, and make the filtrate acid with dilute sulphuric acid. The orange precipitate which falls after a few minutes contains *alizarin* ($C_{14}H_8O_4$), the chief colouring principle of madder; this important substance, however, has been made artificially from anthracene ($C_{14}H_{10}$), a constituent of coal-tar. Alizarin is used in dyeing Turkey-red; and if a piece of cloth so dyed be warmed in hydrochloric acid, washed, and then boiled in sodium hydrate solution, its colour may be removed.

4. Pour a little sulphindigotic acid into a bason of distilled water, warm the liquid, and immerse in it a few wet strands of wool which have been thoroughly washed previously; the colouring-matter present will attach itself to the wool. The wool is now to be removed, rinsed with water, and transferred to a test-tube containing a little ammonium carbonate solution. The colouring-matter will now leave the wool.

5. Boil a little turmeric root, *Curcuma longa*, with water, filter the liquid, and add to it first sodium hydrate, and then dilute sulphuric acid.

6. Repeat experiment 5 with litmus instead of turmeric.

LESSON XXXV.

EXPERIMENTS WITH BONE AND FLESH.

Apparatus required.—Flask; funnel and filter; spirit-lamp; test-papers.

Ordinary reagents.—Dilute hydrochloric acid; ammonium hydrate; sodium carbonate; dilute nitric acid; ammonium carbonate.

Special materials and tests.—Bone-meal; uncooked lean beef; strong nitric acid; piece of muslin; saturated solution of common salt.

1. Put a small quantity of bone-meal into a flask and warm it with dilute hydrochloric acid for ten minutes; decant the liquid on to a wetted filter, and then add to the filtrate excess of ammonium hydrate: a white gelatinous precipitate will separate; this consists chiefly of tricalcic phosphate (bone-earth). The residue in the flask consists chiefly of ossein, the characteristic nitrogenous matter of bone: wash it with abundance of water, until the wash-waters no longer react acid with blue litmus paper. It may be dissolved by long boiling with water, especially at an increased pressure, and is then turned into gelatin. Like other substances of similar origin and character, it is turned yellow by the action of strong nitric acid; this experiment should be tried with a few particles of the residue in the flask. The presence of nitrogen in these particles of ossein may be easily proved by heating 2 or 3 of them in a test-tube with soda-lime: ammonia will be given off and will turn red litmus paper blue.

2. By chopping up some raw beef, enclosing it in a muslin bag and washing it in a stream of water until the liquid flows away clear and colourless, a pale mass is left, consisting chiefly of a kind of fibrin. It may be purified from fat &c. by dissolving it in a ·1 per cent. solution of hydrochloric acid, exactly neutralizing the solution with ammonium carbonate, and collecting the flocculent precipitate which forms. This precipitate, after washing with water, consists of syntonin and myosin, the former sub-

stance being an alteration-product of the chief constituent of muscular fibre, and the latter being ready formed in it. A saturated solution of common salt will dissolve out the myosin from the mixture.

LESSON XXXVI.

EXPERIMENTS WITH BLOOD.

Apparatus required.—Three beakers; test-tubes; spirit-lamp; test-papers.

Ordinary reagents.—Dilute nitric acid; sodium carbonate solution.

Special materials and tests.—Fresh blood; coagulated blood; bundle of birch twigs; spectroscope.

1. If perfectly fresh blood be violently stirred with a bundle of clean birch twigs, a substance known as fibrin is gradually formed, and separates, attaching itself to the twigs as an irregular network of whitish filaments: the red liquid remaining consists of the serum and the corpuscles.

2. If some blood be allowed to curdle spontaneously, it will gradually separate into two parts, a yellow liquid or serum, and a red clot which contains both fibrin and corpuscles.

a. The serum may be proved to be alkaline by dipping a piece of turmeric paper into it.

b. If some of the serum be heated to 60° or 70°, a separation of albumen will take place: nitric acid (not acetic) and metaphosphoric acid produce the same result.

c. A dilute cold solution of sodium carbonate readily extracts the red colouring of the blood from the clot. This colouring-matter, called hæmoglobin, shows a spectrum characterized by two dark absorption-bands, situated respectively about the solar lines D and E.

LESSON XXXVII.

COTTON, WOOL, AND SILK.

Apparatus required.—Furnace-support; spirit-lamp: wire gauze; filters and funnels; porcelain bason; wash-bottle; test-tubes.

Ordinary reagents.—Sodium hydrate; dilute sulphuric acid.

Special materials and tests.—Cupric hydrate dissolved in ammonia; sodium plumbate solution; concentrated nitric acid; oil of vitriol; concentrated hydrochloric acid; solution of magenta; cotton; wool; silk.

1. Cotton, one of the forms of cellulose, a most important constituent of plants, may be separated from wool by means of an ammoniacal solution of freshly precipitated and moist cupric hydrate. This reagent dissolves cotton and linen fibres with great ease. This may be shown by shaking a piece of filter-paper in a test-tube half full of this reagent till no more paper dissolves, filtering the liquid through a double filter, and then adding dilute sulphuric acid to the clear filtrate: flocks of cellulose will be re-precipitated. In this experiment carded cotton may be substituted for the paper with the same result; or the cotton fibres in a piece of inferior cloth may be dissolved out and detected. Carded cotton and some other forms of cellulose dissolve perfectly in cold sulphuric acid of spec. grav. 1·53.

2. Wool and silk both dissolve when boiled with sodium or potassium hydrate solution of specific gravity 1·05. Cellulose is unaffected by this treatment. Wool, however, may be distinguished from silk by immersion in sodium plumbate solution (made by adding to a solution of basic lead acetate enough sodium hydrate solution to redissolve the precipitate first formed), which turns wool brown, but does not change the colour of silk. Silk is readily dissolved by an ammoniacal solution of nickel oxide; but the best solvent for it is cold concentrated hydrochloric acid. Both wool and silk are coloured yellow by immersion in nitric acid; cotton and linen are not. A weak warm solution of magenta dyes wool and silk permanently; but cotton

or linen immersed in the same solution becomes nearly white again when rinsed in water.

2. *An instructive experiment consists in burning a single filament of wool or silk by the side of a cotton or linen fibre; the differences in the odours evolved and the cinders and ashes produced are quite characteristic.*

4. Advantage may be taken of the different solvents named in paragraphs 1 and 2 above in order to separate from a mixed fabric its constituent fibres and to identify them in succession. The following plan answers well. A textile fabric containing cotton, wool, and silk, is first soaked in cold concentrated hydrochloric acid until the silk has been dissolved out. The acid liquor is then poured off, while the remaining fibres, after a thorough washing with hot water, are boiled with a ten per cent. solution of sodium hydrate, which dissolves the wool. The cotton now alone remains, and may be recognized in the following manner:—Wash and dry it, and then immerse it for five minutes in a mixture of 2 measures of oil of vitriol and 3 measures of strong nitric acid; this treatment converts cotton into gun-cotton, which may be readily recognized when clean and dry.

LESSON XXXVIII.

WINE AND BEER.

Apparatus, &c. required.—Retort and stand; spirit-lamp; flask; test-tubes; mortar; porcelain bason; blowpipe; platinum wire; spirits of wine; glass rod.

Ordinary reagents.—Hydrochloric acid; sodium hydrate.

Special materials.—Potassium dichromate solution; sugar test; glass measures; wine, beer, and cider.

1. Pour 50 cub. cent. (2 ounces) of claret or other light red wine into a retort and distil over about 10 cub. cent.: pour this distillate into two test-tubes *a* and *b*.

***a*. Warm this tube and apply a lighted spill to its mouth when**

the liquid begins to boil; the spirits-of-wine or alcohol vapour will burn with a pale flame.

b. To this tube add a little hydrochloric acid and some potassium dichromate solution; then boil it: the production of a green colour is due to the reducing effect of the alcohol (see Lesson XX.).

2. Pour half the residue in the retort (from experiment 1) into a flask, add a little sodium hydrate and some sugar test, and then boil: a red precipitate indicates sugar.

Evaporate the remainder of the residue in a porcelain dish till it is reduced to about 10 cub. cent.; then dip a platinum wire into the remaining liquid and hold it in the blowpipe-flame, in order to ascertain, by the lilac tinge, the presence of potassium. The acid reaction of this residue is due to hydro-potassium tartrate, which may be precipitated as cream of tartar by the addition of strong alcohol and stirring.

3. The above experiments may be repeated with beer and with cider.

Other very useful lessons in Chemical Manipulation may be devised by the adoption of the same style of treatment as that which has been pursued in the present Part of this work. The analysis of atmospheric air; the separation of colloids from crystalloids by dialysis; the use of the spectroscope, and the tests for uric acid, hippuric acid, urea, with the artificial formation of the latter compound, suggest themselves as suitable subjects for class-teaching.

PART II.
QUALITATIVE ANALYSIS.

CHAPTER I.

§ i. INTRODUCTION.

The object of qualitative analysis is the discovery of the constituents of an unknown substance. By suitable treatment, any compound can either be chemically dissected, or else be made to yield such products as are easily identified or well known; for it is not necessary that the actual elements themselves should be obtained in a free state by the processes of analysis; all we usually require is to obtain some characteristic colour or odour or precipitate or gas, which is, without doubt, due to one particular element. There are various ways of accomplishing this result, such as the action of heat upon the substance to be examined, or its treatment with particular chemical tests. In the Lessons contained in the First Part of this book many examples of both these methods of analysing substances have been given; we may here recall a few of them.

When mercuric oxide (HgO), a compound of mercury and oxygen, is heated, it splits up into its elementary constituents, mercury (Hg) and oxygen (O), both easily identified by characteristic properties. When, on the other hand, a substance like potassium chlorate ($KClO_3$) is heated, it does not split up so completely as mercuric oxide; but while its oxygen is wholly separated, and can be recognized as in the preceding case, its other constituents, the potassium (K) and the chlorine (Cl), remain united in the form of a new *compound*, which, however, can be identified almost as readily as either of its constituent elements. But heat alone is not the chief means employed in qualitative analysis, the characteristic changes produced by the action of one substance upon another are of far greater importance. Examples of these changes or reactions may be quoted from the Lessons on Silver Coin and Carbon Dioxide. In the former case the silver was identified in several ways, one of them being the *reaction* between its nitrate and hydrochloric acid, which in this case becomes the *reagent*, while an *equation* represents the change, thus

$$\underset{\text{Silver nitrate.}}{AgNO_3} + HCl = HNO_3 + \underset{\text{White precipitate.}}{AgCl.}$$

Now this white precipitate is easily ascertained to be silver chloride, either by treating it with another substance, say ammonia, which dissolves it, and would not have dissolved any other compound similarly precipitated by hydrochloric acid, or else by actually obtaining metallic silver from it by the action of zinc. In the preparation of carbon dioxide, again, we may use the reaction between the limestone and the hydrochloric acid, in order to ascertain the substance used really to be calcium carbonate—not because we thus separate it into its three elements, but because we obtain two of them in the definite and recognizable form of carbon dioxide (CO_2), and because the other element, calcium, exists at the end of the experiment in the very convenient form of a *soluble* salt or compound, with which other reactions belonging to calcium compounds only can be at once obtained.

Before the student can apply his knowledge of chemical manipulation to the actual examination and identification of unknown substances, he must make himself thoroughly acquainted with (1) the chief elements and their most common compounds, (2) the reagents or tests which are actually employed in analysis, and (3) the reactions between these tests and the substances to which they have to be added. Some information on these subjects will have been obtained already from laboratory practice as well as from lectures and the study of a text-book of chemistry. In the three following sections of this part of the Guide, the main facts relating to the chief Elements, to Reagents, and to Reactions are presented in a compact form. Then follows the description of the Method of Analysis; and afterwards a complete series of Analytical Schemes is given. It may be well to state here that, as nearly all those elements have been excluded which are not necessary or important constituents of agricultural or common products and materials, it has been possible greatly to simplify some of the analytical processes in ordinary use.

§ ii. OF THE ELEMENTS.

All the rare elements, and all those which are of little or no importance from an agricultural point of view, have been excluded from the analytical course about to be described. Of the sixty-seven elements believed to exist, about thirty have to be considered, on one account or another, in the present work; of these the greater number are metals. It is not very often, however, that we find the metals or non-metals actually separated by a process of analysis; still a knowledge of their chief physical and chemical properties is of importance for several reasons. Especially should the analyst learn the symbol and atomic weight of every element which he will have to search for or to estimate. On this account the following condensed notes on the elements are here given. The melting- and boiling-points are given on the Centigrade thermometric scale.

Hydrogen may be regarded from a chemical, and, to some extent, from a physical stand-point, as the typical element of the class of metals. Its occlusion in a highly condensed state by iron or palladium, with which metals it seems to form alloys, and its conductivity for heat, support this view. Hydrogen also in acids occupies the place which metals take in salts, so that acids may be viewed as hydrogen salts. Hydrogen is colourless, odourless, and combustible: it is the lightest of all known gases, and the unit of comparison as to density of gases and vapours. If air, however, be taken as unity, the density of hydrogen is ·0692. Hydrogen gas has hitherto resisted all attempts to liquefy it. In its combinations this element is what is called a *monad*, having only one bond of attachment to other elements: it may be said to be *univalent*, or *univinculant*: its compounds with other monad elements show this, the formula of its compound with chlorine being, for instance, HCl. The single bond or univinculance of an element may be denoted by a dash above its symbol. Three of the other important monad metals are potassium, sodium, and silver. It will, however, be found more convenient in practice to arrange the metallic elements in accordance with their analytical relationships. Those metals which are removed together in groups during the conduct of an analysis will be classified accordingly as follows:—

Group I. Metals having insoluble chlorides:—Silver, Mercury (mercurosum), and Lead. Silver is a malleable metal of great brilliancy of lustre and showing a faint yellowish-white colour. Its atomic weight is 107·7, specific gravity 10·57, and melting-point about 1040°. Mercury is a mobile, greyish-white, lustrous liquid, of specific gravity 13·6; it becomes solid at −39°. The boiling-point of mercury is 357°, and its atomic weight 200. Lead is soft and bluish-grey, having the atomic weight 206·4. Its specific gravity is 11·36; it melts at 334°.

Group II. Metals of which the sulphides are insoluble in hydrochloric acid:—Copper, Tin, Arsenic, Antimony, Platinum, and Gold. Copper is red, and has the atomic weight 63·3. Its specific gravity is 8·95. Tin is soft, white, and crystalline. Its atomic weight is 117·4, and its specific gravity 7·3. Arsenic is a greyish-white semi-metal having the atomic weight 74·9, the specific gravity 5·9, and volatilizing at 180°. Antimony is bluish-white, brittle and lustrous, having the atomic weight 120, specific gravity 6·6 to 6·8, and melting-point 420°. Platinum is greyish-white, and has the specific gravity 21·46. There is some doubt about its true atomic weight, but the value 194·5 has been adopted in the present volume. Gold is highly lustrous, of an orange-yellow colour, has the atomic weight 196·9, the specific gravity 19·3, and the melting-point 1200°.

Group III. Metals of which the sulphides and hydrates are soluble in acids, but insoluble in water:—Iron, Manganese, Aluminium, and Zinc. Iron is white to greyish-white, of density varying, according to its method of preparation, from 7·7 to 8·1; its atomic weight is 56. Manganese is greyish-white; its atomic weight is 55, and its specific gravity 7·4: it melts at a white heat. Aluminium is bluish-white, having the atomic weight 27, and the remarkably low specific gravity 2·58. This is a pseudo-triad, being in reality quadrivinculant. Zinc is bluish-white, hard and crystalline: its atomic weight is 65, its specific gravity 6·9, and its melting-point 433°.

Group IV. Metals of which the carbonates are insoluble in water and ammonium salts:—Calcium, Strontium, and Barium. These are the metals of the alkaline earths. Calcium has the atomic weight 40, strontium 87·2, and barium 136·8.

Group V. Metals of which the carbonates are soluble in water or ammonium salts. They are Magnesium, Potassium, Sodium, and Ammonium. Magnesium is somewhat closely allied to zinc: it is hard and nearly white: its atomic weight is 24 and its specific gravity 1·75. Potassium has the atomic weight 39·1; its specific gravity is ·875, and its melting-point 62°·5. Sodium is *soft*, pinkish-white: atomic weight 23, specific gravity ·97, and melting-point 95°·6. The supposed compound metal ammonium, NH_4, has not been isolated; its atomic weight is 18. Potassium, sodium, and ammonium are the metals of the alkalies—all unite with chlorine to form chlorides of the simple formula MCl.

The non-metals may be arranged, according to their vinculance, into four groups. They are sometimes called acid elements, or stylous elements, in contradistinction to the basic elements. Arsenic, antimony, and tin, however, play the parts of metals and of non-metals: they have been termed semi-metals. Even the more distinctively metallic elements, such as iron and manganese, are capable of playing the part of some non-metals, as shown in the ferrates and manganates. In the course of the analytical operations described in the present work we meet with ten non-metals—some of them being separated during analysis in the uncombined or free state, the remainder in various forms of combination.

Group I. Acid or "chlorous" elements or non-metals, which are monads, that is, univinculant, and combine in the proportion of 1 atom or 1 gaseous vol. to 1 atom or 1 vol. of hydrogen, yielding 2 vols. of an acid gas. These are chlorine, bromine, iodine, and fluorine, all of which form with silver insoluble compounds. Chlorine is a greenish-yellow gas, 35·4 times as heavy as hydrogen; 2·5 vols. of it dissolve in 1 vol. of cold water; it may be liquefied by pressure. Its atomic weight is 35·4. It is a powerful bleaching-agent. Bromine is a red-brown liquid, boiling at 63°, and of specific gravity 3·19. Its vapour is red; its atomic weight is 79·9; it turns starch-paste orange. Iodine is a bluish-black solid, of specific gravity 4·95, melting at 114°, and boiling at 185°. Its vapour is violet. The atomic weight of iodine is 126·5; it turns starch-paste blue. Fluorine has been isolated as a colourless gas: its atomic weight is 19·1: its compound with hydrogen, hydrofluoric acid, acts upon glass, etching it rapidly.

Group II. Dyad or bivinculant acid elements, which combine in the proportion of 1 gaseous vol. to 2 vols. of hydrogen, yielding 2 vols. of a compound gas, in which the acid character is indistinct. These are Oxygen and Sulphur. Oxygen is a colourless gas, 16 times as heavy as hydrogen; its atomic weight is 16; it is very slightly soluble in water; it relights a glowing splinter of wood immersed in it. It may be condensed into a pale blue liquid of specific gravity 1·124, which boils at −181°·4 under a barometric pressure of 742 mm. Sulphur is a yellow solid, of specific gravity 2·05, melting at 115°, and boiling at 440°. It yields an orange-coloured vapour; its atomic weight is 32.

Group III. Triad or tervinculant non-metals or acid elements, which combine in the proportion of 1 gaseous vol. or 1 atom to 3 vols. or 3 atoms of hydrogen, yielding 2 vols. of a basic compound. These are Nitrogen and Phosphorus (arsenic and antimony also). Nitrogen is a colourless gas, 14 times as heavy as hydrogen; it has the atomic weight 14. It has been reduced to the liquid state, when it has the specific gravity ·885; liquid nitrogen boils at −194°·4. It is incombustible, nor does it support combustion. Phosphorus has the atomic weight 31. It is known chiefly in two forms:—a colourless wax-like solid, of specific gravity 1·82, melting under water at 44°, and boiling at 269° (this variety may be crystallized); and a chocolate-red powder, of specific gravity 2·24, which at 250° melts, and is then converted into the ordinary form of the element. Common phosphorus is very easily combustible, and burns in oxygen with a splendid white light.

Group IV. Tetrad or quadrivinculant non-metals or acid elements, which combine in the proportion of 1 gaseous vol. or 1 atom to 4 vols. or 4 atoms of hydrogen, yielding 2 vols. of a neutral compound gas. These are Carbon and Silicon. Carbon has the atomic weight 12. It occurs in three forms—diamond, graphite, lampblack. The diamond crystallizes in octahedra, of specific gravity 3·53; graphite is greyish-black, of specific gravity 2·3, while charcoal, lampblack, &c., varieties of amorphous carbon, have a still lower specific gravity. All three forms, however, yield the same quantity of carbon dioxide (CO_2) when equal weights are burnt in oxygen. Silicon occurs in a somewhat similar variety of forms; its atomic weight is 28·3.

Annexed is a list of the names, symbols, and atomic weights of 67 substances believed to be simple or elementary: until more is known of them, the bodies designated, respectively, Decipium, Philippium, Dysprosium, Samarium, Holmium, Thulium, and several other bodies which have been announced as new elements, do not demand a place in the table.

Atomic Weights and Symbols of the Elements.

(The more important elements are printed in capitals. Elements found in all animals and plants are marked with an asterisk *.)

ALUMINIUM	Al	27·
ANTIMONY	Sb	120·
ARSENIC	As	74·9
BARIUM	Ba	136·8
Beryllium	Be	9·1
Bismuth	Bi	207·5
Boron	B	10·9
BROMINE	Br	79·9
Cadmium	Cd	111·7
Cæsium	Cs	132·7
*CALCIUM	Ca	40·
*CARBON	C	12·
Cerium	Ce	140·
*CHLORINE	Cl	35·4
Chromium	Cr	52 4
Cobalt	Co	58·7
COPPER	Cu	63·3
Didymium	D	144·
Erbium	Eb	166·
*FLUORINE	F	19·1
Gallium	Ga	69·9
Germanium	Ge	72·3
GOLD (*Aurum*)	Au	196·9
*HYDROGEN	H	1·
Indium	In	113·4
IODINE	I	126·5
Iridium	Ir	192·5
*IRON (*Ferrum*)	Fe	56·
Lanthanum	La	138·2
LEAD (*Plumbum*)	Pb	206·4
Lithium	Li	7·
*MAGNESIUM	Mg	24·
*MANGANESE	Mn	55·
MERCURY (*Hydrargyrum*)	Hg	200·
Molybdenum	Mo	96·
Nickel	Ni	58·6
Niobium	Nb	94·
*NITROGEN	N	14·
Osmium	Os	190·3
*OXYGEN	O	16·
Palladium	Pd	106·4
*PHOSPHORUS	P	31·
PLATINUM	Pt	194·5
*POTASSIUM (*Kalium*)	K	39·1
Rhodium	Rh	102·7
Rubidium	Rb	85·2
Ruthenium	Ru	101·4
Scandium	Sc	44·
Selenion	Se	79·
*SILICON	Si	28·3
SILVER (*Argentum*)	Ag	107·7
*SODIUM (*Natrium*)	Na	23·
Strontium	Sr	87·2
*SULPHUR	S	32·
Tantalum	Ta	182·
Tellurium	Te	127·7
Thallium	Tl	203·6
Thorium	Th	231·9
TIN (*Stannum*)	Sn	117·4
Titanium	Ti	48·
Tungsten (*Wolframium*)	W	184·
Uranium	U	240·
Vanadium	V	51·1
Ytterbium	Yt	173·
Yttrium	Y	89·6
ZINC	Zn	65·
Zirconium	Zr	90·5

§ iii. OF REAGENTS AND TESTS.

The following is a descriptive list of the reagents and tests employed in the qualitative and quantitative processes given in the present work. The most important impurities are noted, together with the most suitable strength for each solution. In a few instances, however, solutions which are employed for special purposes and of exact strength are described under the headings of those quantitative methods in which they are used.

METALS.—*Copper* (Cu). Copper foil or fine wire may be obtained nearly pure, and may be rendered still purer by ignition to redness in a stream of hydrogen.

Iron (Fe). Some kinds of steel and soft iron wire, notably piano-wire, contain a very small percentage of impurities.

Zinc (Zn). The most usual impurities of zinc are iron, lead, and arsenic. By distillation it may be freed from lead and iron; if the distilled zinc be kept fused for some time in an earthen crucible it may often thus be freed from arsenic.

NON-METALS.—*Chlorine* (Cl) may be prepared by gently warming strong hydrochloric acid with manganese dioxide. If a solution be wanted, the gas is conducted into very cold water until the latter is saturated.

Iodine (I). A saturated aqueous solution of resublimed iodine is to be used; or the element may be dissolved in water containing 4 per cent. of alcohol.

Carbon (C). Charcoal for blowpipe experiments should be of beech or other compact wood, and should be free from bark or knots. Pieces about 1½ inch in diameter and 4 inches in length should be sawn lengthwise in two; the flat surface of the longitudinal section thus made will be found adapted for most blowpipe purposes; occasionally a cross or slant section is to be preferred.

POTASSIUM SALTS.—*Potassium Iodide* (KI). Commercial iodide often contains iodate, carbonate, and bromide. The two former impurities may be removed by digesting the powdered salt with hot strong alcohol, when they will remain undissolved. Evaporate the alcoholic solution to dryness, and make a 10 per cent. ($^0/_0$) solution of the residue.

Potassium Chlorate ($KClO_3$). The commercial salt may be used; it generally, however, contains sulphate, and occasionally a trace of lead.

Potassium Nitrate (KNO_3). Refined nitre is pure enough for ordinary use; the chloride and sulphate which it generally contains may be separated by repeated crystallizations.

Potassium Cyanide (KCN). The commercial salt, if kept dry, answers every purpose.

Potassium Sulphocyanide ($KCNS$). The commercial salt may be used: 10 $^0/_0$.

Potassium Ferrocyanide (K_4FeCy_6, 3aq.) occurs pure in commerce: 8 $^0/_0$.

Potassium Ferricyanide ($K_6Fe_2Cy_{12}$). This salt occurs in commerce of sufficient purity: dissolved in water, it suffers, after a time, a partial decomposition; the fresh solution only should be used: 10 $^0/_0$.

Potassium Sulphide (K_2S). The commercial salt may be used: 4 $^0/_0$.

Potassium Hydrate or *Hydroxide* (KHO). Commercial potash answers well for most analytical operations, but it is well to remember that it contains small quantities of potassium carbonate, chloride, silicate, and sulphate; alumina is generally and lead sometimes present. If the commercial hydrate be dissolved in alcohol, and the clear liquor evaporated (in the absence of CO_2) in a silver dish, the hydrate is obtained nearly pure: 5 $^0/_0$.

Potassium and Sodium Carbonates ($K_2CO_3+Na_2CO_3$). The dry salts are mixed in atomic proportions,—about 13 parts of the former salt to 10 of the latter.

Potassium Dichromate ($K_2Cr_2O_7$). The commercial salt may be purified readily by recrystallization.

Potassium Chromate (K_2CrO_4). It may be prepared from the dichromate. To 100 parts of this salt dissolved in water add 47 parts dry potassium carbonate (K_2CO_3): crystallize: 5 $^0/_0$.

Potassium Permanganate ($KMnO_4$). The crystallized commercial salt may be used: ·395 gram is dissolved in 1 litre of water.

Potassium Antimoniate ($K_2Sb_2O_6$, 7aq.). This salt is occasionally used as a test for sodium: it is troublesome to prepare.

Potassium Acetate ($KC_2H_3O_2$) occurs nearly pure: 25 %.

SODIUM SALTS.—*Sodium Hydrate* or *Hydroxide* ($NaHO$) is used for the same purposes as potassium hydrate. When required pure, that made from sodium should be employed: 5 %.

Sodium Carbonate (Na_2CO_3). The commercial salt generally contains sulphate and chloride, besides excess of CO_2. Pure sodium carbonate may be obtained by igniting precipitated and washed sodium oxalate,—$Na_2C_2O_4 = Na_2CO_3 + CO$; or by the ignition of the pure dicarbonate; in the case of the latter salt magnesium should be first looked for: 10 %.

Sodium Phosphate (Na_2HPO_4, 12aq.). The ordinary phosphate contains sulphate; it may be purified by recrystallization. The solution of this salt acts powerfully upon porcelain and glass, taking up impurities and losing some of its phosphoric constituent: it should generally be prepared only when required: 10 %.

Sodium Borate ($Na_2H_2B_4O_8$, 9aq.), or borax, may be employed as obtained in commerce.

Sodium Acetate ($NaC_2H_3O_2$, 3aq.). The commercial salt may contain traces of calcium salts, but for ordinary purposes may be used. It should be dissolved in five times its weight of water.

AMMONIUM SALTS.—*Ammonium Chloride* (NH_4Cl). The chief impurity of this salt is ferric chloride. To separate this, add a few drops of ammonium sulphide, filter off the iron sulphide, add slight excess of hydrochloric acid to the filtrate, evaporate till all odour of hydrosulphuric acid has ceased, neutralize with ammonia, evaporate and crystallize: 20 %.

Ammonium Sulphide ($[NH_4]_2S$). This salt is obtained in solution thus:—Take some solution of ammonia, divide it into two equal parts, saturate one with hydrosulphuric acid, and then add the other part. Ammonia is known to be saturated with the acid in question when it no longer occasions a precipitate in magnesium sulphate. *Yellow* ammonium sulphide is prepared by dissolving a little sulphur in the ordinary sulphide. The glass of the bottles in which these reagents are kept must not contain lead.

Ammonia (NH_3). Ammonia-gas dissolved in water is supposed to form ammonium hydrate (NH_4HO). Commercial liquor ammoniæ, if it leave no residue on evaporation, may be used in analysis ; it may be diluted with 4 times its volume of water.

Ammonium Carbonate ($[NH_4]_2CO_3$). The commercial "sesquicarbonate" appears to yield a solution of this salt when dissolved in hot water. The commercial salt is pure enough for most analytical purposes : 10 %. A solution saturated in the cold, of commercial sesquicarbonate, is also required in analysis.

Ammonium Acetate ($NH_4C_2H_3O_2$). Acetic acid may be saturated with ammonium carbonate, and warmed.

Ammonium Oxalate ($[NH_4]_2C_2O_4$, 2aq.). The commercial salt suffices for most purposes ; but if pure ammonium oxalate be desired, it may be obtained by saturating liquor ammoniæ with a solution of sublimed oxalic acid : 1 part of the crystals obtained by evaporating the solution should be dissolved in 25 parts of water.

Ammonium Phosphate ($[NH_4]_2HPO_4$). This salt may be obtained in commerce quite pure.

Ammonium Molybdate ($[NH_4]_2MoO_4$). Dissolve 50 grams of the commercial salt in 200 c. c. of ammonium hydrate solution (made by mixing 1 vol. of ·88 ammonia with 2 vols. of water); pour this into 800 c. c. of dilute nitric acid prepared from equal volumes of strong nitric acid and of water : keep the solution in the dark, and decant it from any precipitate which may form. This reagent may be made from molybdic acid by dissolving 1 part in 4 parts of ammonia solution of sp. gr. ·96, filtering the solution and pouring it, with constant stirring, into 15 parts of nitric acid of sp. gr. 1·2.

SILVER SALT.—*Silver Nitrate* ($AgNO_3$). This is best obtained by dissolving pure silver in nitric acid (HNO_3) which has been diluted with about its own bulk of water, evaporating the solution to dryness, and gently fusing the residue. The fused mass may be dissolved in water when cold, and then crystallized. It is thus obtained quite free from acid. If silver coin (*i. e.* silver alloyed with copper) be employed, it is necessary, after dissolving it in nitric acid, to precipitate the silver as chloride by the addition of hydrochloric acid, to filter it off, and then to wash it till it no longer contains a trace of the soluble copper salt. The silver chloride may then be reduced into metal, either by fusing it with twice its weight of dry sodium carbonate, or by placing it in a dish together with water, a drop or two of hydrochloric acid, and a strip of pure zinc. When the reduction of the silver is complete, the remaining zinc must be removed, the spongy silver warmed with a little dilute hydrochloric acid, and then thoroughly washed, dissolved in nitric acid, and the solution evaporated to dryness. The residue, if gently fused, will be nearly pure silver nitrate; it may be further purified by crystallization: 5 %.

BARIUM SALTS.—*Barium Chloride* ($BaCl_2$, 2aq.). This salt is generally found in commerce of sufficient purity for ordinary analytical operations. If it contain lead, it may be purified by recrystallization: 10 %.

Barium Oxide or *Baryta* (BaO). Introduce finely powdered barium nitrate, little by little, into a crucible maintained at a bright red heat. After cooling, the crucible is broken, and the fused mass separated from foreign matters and preserved from the air.

Barium Hydrate (BaH_2O_2, 2aq.). Boil the oxide in water, filter into a large flask, and allow the filtrate to cool. Crystals of the hydrate will separate; one or two recrystallizations of these will give a perfectly pure product. Or the commercial crystallized hydrate may be similarly purified. A cold saturated solution may be used in testing: it should be prepared and kept out of contact with the air.

Barium Nitrate ($Ba2NO_3$). The commercial salt may be used: 5 %.

Barium Carbonate ($BaCO_3$). Precipitate a warm solution of barium chloride with ammonium carbonate; wash the precipitate thoroughly. It should be kept moistened with water in a wide-mouthed stoppered bottle.

CALCIUM SALTS.—*Calcium Chloride* ($CaCl_2$). This may be prepared in the purest form by dissolving the finest white marble, or, better still, small crystals of Iceland spar, in hydrochloric acid, the acid not being in sufficient quantity to dissolve the whole of the carbonate: 5 %.

Calcium Oxide (CaO). Freshly burnt quicklime just from the kiln should be taken, the white hard pieces being selected, and preserved in a well-stoppered bottle, the stopper having been lubricated with a little vaseline.

Calcium Hydrate (CaH_2O_2), or Lime-water. A cold saturated solution of calcium hydrate is made by shaking some slaked lime with distilled water. The first water is poured away, and a second quantity of water added to the residue: this liquid, when clear, may be decanted for use: it is to be kept out of contact with the air.

Calcium Sulphate ($CaSO_4$, 2aq.). The well-washed precipitated sulphate is shaken up with distilled water. The saturated solution (1 in 420 of water) is used.

MAGNESIUM SALTS.—*Magnesium Sulphate* ($MgSO_4$, 7aq.). The commercial salt (Epsom salts) is of sufficient purity for all ordinary analytical purposes: 10 %.

Ammoniacal Magnesium Chloride (magnesia mixture). 11 grams of crystallized magnesium chloride and 14 grams of ammonium chloride are dissolved in 130 c. c. of water, and the solution made ammoniacal by the addition of 70 c. c. of ammonium hydrate. The addition of a few drops of chlorine-water, and digestion for some hours in a warm place, will separate any manganese: a little strong ammonia water is again added to the solution, which is then filtered and preserved in bottles of hard glass.

IRON SALTS.—*Ferrous Sulphate* ($FeSO_4$, 7aq.). The best commercial salt, known as copperas, green vitriol, and protosulphate of iron, is generally of sufficient purity for use, it being very carefully prepared for photographic purposes. The crystals should be dissolved in cold water. A piece of iron wire should be kept in the bottle, and an addition of a few drops of dilute sulphuric acid be now and then made to it. This reagent may thus be kept free from ferric compounds any length of time.

Ferric Chloride (Fe_2Cl_6). The salt is also termed sesquichloride and perchloride of iron. The commercial preparation may be used: or the solution may be prepared by dissolving pure iron wire in dilute hydrochloric acid and then passing chlorine through the solution till a drop of the liquid gives no precipitate with potassium ferricyanide.

Iron Sulphide (FeS) is most conveniently made by heating a bar of iron to whiteness in a blacksmith's forge and immediately applying to it a roll of sulphur. The fused iron sulphide as it drops from the bar should be received in a vessel of water.

COBALT SALT.—*Cobalt Nitrate* ($Co2NO_3$, 6aq.). This salt may be purchased fit for use: 15 %.

COPPER SALT.—*Copper Sulphate* ($CuSO_4$, 5aq.). The commercial salt is usually contaminated with iron and lead sulphates. For analytical purposes, the metallic copper obtained by electrolysis may be dissolved in hot pure sulphuric acid, or the pure hydrate, oxide, or carbonate may be taken, and heated with diluted sulphuric acid; the salt should then be crystallized from its solution: 10 %.

Sodio-cupric Tartrate, or the Sugar test. Dissolve 34·64 grams of pure crystallized copper sulphate, dried between filter-paper, in about 200 c. c. of water. In another vessel dissolve 173 grams of crystallized potassium and sodium tartrate (Rochelle salt) in 480 c. c. of solution of sodium hydrate having the sp. gr. 1·14. Add the former solution to the latter and dilute to 1 litre. Keep the solution in a well-stoppered bottle to prevent absorption of carbon dioxide, which will interfere with the accuracy of the test: the bottle should be covered with black paper soaked in melted paraffin, or else it should be kept in the dark. The stopper should be lightly smeared with vaseline.

LEAD SALT.—*Lead Acetate* ($Pb2C_2H_3O_2$, 3aq.). The commercial salt, known as sugar of lead, answers: 15 %.

MERCURY SALTS.—*Mercurous Nitrate* (Hg_22NO_3). This salt, sometimes termed the protonitrate, may be prepared by keeping pure mercury in contact with pure cold nitric acid. A saturated aqueous solution may be used, some metallic mercury being kept in the reagent-bottle.

Mercuric Chloride ($HgCl_2$), or mercury dichloride, is met with pure in commerce as corrosive sublimate : 5 %.

Potassio-mercuric Iodide, or Nessler's test. This excessively delicate test for ammonia is a solution of HgK_2I_4 in potassium or sodium hydrate. To prepare it take 3·5 grams of potassium iodide and dissolve them in 10 c. c. of water : dissolve 1·7 gram of mercuric chloride in 30 c. c. of water, and add the latter solution to the former gradually, till a permanent precipitate is produced. Then add a 20 per cent. solution of sodium hydrate till the liquid measures 100 c. c. ; add more mercuric chloride solution drop by drop until a permanent precipitate again forms ; allow the solution to rest, then pour off the clear part, and preserve it in a well-closed bottle.

MERCURIC OXIDE (HgO).—This compound should be prepared by precipitating a saturated solution of mercuric chloride with an excess of sodium hydrate solution. The yellow mercuric hydrate at first thrown down passes, after thorough washing and drying at 100° C., into the oxide.

PALLADIUM SALT.—*Palladious Chloride* ($PdCl_2$) is made by dissolving palladium in hydrochloric acid, to which a quarter of its bulk of nitric acid has been added, evaporating the solution to dryness on the water-bath, moistening the residue with hydrochloric acid, and again evaporating to dryness on the water-bath ; this process is repeated twice or thrice : the residue is then once more dissolved in water.

URANIUM SALT.—*Uranic Acetate* may be purchased in a state of purity. It should give no precipitate with hydrosulphuric acid, or excess of ammonium carbonate.

TIN SALT.—*Stannous Chloride* ($SnCl_2$), or tin dichloride, may be prepared in solution by digesting granulated tin in a mixture of equal bulks of concentrated hydrochloric acid and water with the aid of heat, the process being stopped before all the metal and acid are consumed : the presence of a strip of platinum foil aids the process of solution. Decant the clear solution into a bottle containing granulated tin, and add a little dilute hydrochloric acid.

PLATINUM SALT.—*Platinum Tetrachloride* ($PtCl_4$). This salt, which is also called platinic chloride, may be obtained tolerably pure; but it is often purposely adulterated with sodium chloride. It may be prepared from the metal in the same way as palladious chloride. It always contains 2HCl when dried at 100° C., and is frequently contaminated with Iridium chloride. Gold terchloride may also be made by the same process.

ETHYL COMPOUNDS.—*Ethyl Oxide*, or Ether ($[C_2H_5]_2O$). Commercial methylated ether answers most purposes. If required dry, it may be distilled in a water-bath from caustic lime. Ether usually contains, besides water, a considerable quantity of alcohol, from which it may be freed by contact with water in a bottle; the washed ether may then be freed from water by means of lime. The specific gravity of pure ether is ·72.

Ethyl Hydrate, or Alcohol (C_2H_5HO). Rectified methylated spirit may generally be employed: it may be obtained nearly free from water by distillation from caustic lime.

STARCH WATER ($C_6H_{10}O_5$).—Mix finely powdered white starch with a little cold water, and pour the mixture into boiling water. Allow the liquid to cool before using it. A lump of camphor will preserve starch solution from change for some time. Arrowroot starch may be advantageously employed. 2 grams of starch in 1 litre of water.

HYDROGEN SALTS OR ACIDS.—*Hydrochloric Acid* (HCl). Nitric and sulphuric acids, salts of iron, and arsenic trichloride are common impurities of commercial hydrochloric acid; it may, however, be obtained pure in commerce. One part of the strong acid, sp. gr. 1·2, diluted with 4 parts of water is used as dilute hydrochloric acid.

Nitric Acid (HNO_3). The commercial acid generally contains a little hydrochloric and sulphuric acid; it may, however, be purchased pure. One vol. of strong acid, sp. gr. 1·42, is to be mixed with 4 vols. of water to form the dilute acid.

Acetic Acid ($HC_2H_3O_2$). This acid is often contaminated with sulphuric acid. The glacial acid prepared for photographic use is pure. It has the sp. gr. 1·048: to make the dilute acid add

3 vols. of water to the strong commercial, or 9 vols. to the glacial acid.

Water (H_2O). This liquid, as it generally occurs, holds various salts in solution—sulphates, chlorides, carbonates. Rain-water collected in the open country is nearly pure. Water may be completely purified by careful distillation after having been rendered alkaline by a little sodium carbonate, the first part of the liquid which comes over being rejected so long as it gives a yellow colour with Nessler's test.

Hydrosulphuric Acid, or *Sulphuretted Hydrogen* (H_2S). Iron sulphide is to be acted on with dilute sulphuric acid; the evolved gas is washed by passing it through a wash-bottle containing a small quantity of water. A saturated solution of gas is much employed in analysis: it should be kept in well-stoppered bottles, the stoppers of which have been smeared with vaseline.

Sulphuric Acid (H_2SO_4). The commercial acid, or oil of vitriol, generally contains lead, nitric acid, and arsenic. Lead may be separated by diluting the acid. Arsenic is more difficult of removal: addition of potassium dichromate and distillation is said to yield a pure product. Nitric acid is expelled by heating with oxalic acid or ammonium sulphate. To make the dilute acid, 1 vol. of oil of vitriol is very gradually and cautiously poured, with constant stirring, into 5 vols. of water: after 24 hours decant the clear liquid from the precipitated lead sulphate.

Oxalic Acid ($H_2C_2O_4$). The commercial acid usually contains alkalies, lime, and sulphuric acid. It may be purified by sublimation. The sublimed acid has no water of crystallization; its formula is given above: 5 %.

Phenol or *Carbolic Acid* (HC_6H_5O). The white crystallized carbolic acid of commerce may be dissolved in distilled water: 4 %.

Sulphindigotic Acid. The solution of 1 part of indigo in 6 parts of fuming sulphuric acid is known by this name. The sulphuric acid must be free from nitric acid. The blue liquid is diluted before use with 20 vols. of water.

Tartaric Acid ($H_2C_4H_4O_6$). The commercial acid is sufficiently pure: 10 %.

Citric Acid ($H_3C_6H_5O_7$, aq.) may be obtained sufficiently pure in commerce: dissolve the crystals in their own weight of water: filter the solution if it be cloudy.

Hydrofluosilicic Acid (H_2SiF_6). A mixture of 1 part of sand, 1 part of calcium fluoride (fluorspar), and 6 parts of oil of vitriol is heated in a flask or in an earthenware jar placed in hot water; the gas evolved is silicon fluoride. If conducted into about 4 parts of water, silica will separate, and the liquid will contain a *combination of* hydrofluosilicic acid and silicon tetrafluoride, known as hydrofluosilicic acid. The tube which delivers the gas into the water should just dip under the surface of a little mercury, to prevent its opening becoming choked up with the separated silica. The solution is finally filtered for use through a linen cloth. If hydrofluoric acid be required, it is to be made from 1 part calcium fluoride and 6 parts of oil of vitriol, heating the mixture and absorbing the HF evolved in water. In the preparation of this acid vessels entirely made of lead or platinum must be used; its solution is generally preserved for use in bottles of gutta-percha.

TEST-PAPERS.

Vegetable blues, or at least most of them, possess the peculiar property of becoming red when moistened with an acid, *i. e.* the hydrogen salt of a simple or compound acid-radicle; while their original colour is restored by an alkaline solution—that is, by the solution of a substance whose basic properties are definite. Some of the most delicate vegetable blues or purples even assume a new colour when submitted to an alkaline liquid, becoming a brilliant green. An alcoholic tincture of dahlia-flowers or of the stems of the *Coleus verschaffelti* may be used as a sensitive test colour. Vegetable yellows, when dipped into alkaline solutions, become red-brown, but are not influenced by acids beyond the restoration of their original colour (boracic acid being an exception, for it behaves with turmeric like an alkali). These indications, although very valuable, must not be too implicitly relied on, since certain salts which are theoretically neutral produce changes of colour.

Blue Litmus Paper.—The litmus of commerce should be crushed and mixed with water, and kept, with continual stirring, at a temperature just under that of boiling water for some time. Very dilute sulphuric acid is now added to the filtered solution, until the colour has been changed to a reddish violet; the blue colour is then just restored by the addition of a small quantity of the original solution. White wove writing-paper, not highly glazed, is then to be painted with the blue liquid on one side only; and the coloured pieces, when dry, are to be cut into narrow strips for use, and preserved in a well-stoppered bottle.

Red Litmus Paper.—This may be prepared in the same way as the preceding paper, the blue liquid being in this case first slightly reddened with a drop of dilute sulphuric acid.

Turmeric Paper.—An alcoholic extract of turmeric-root is of an orange-yellow colour, and becomes reddish-brown when submitted to the action of alkaline solutions: the paper is prepared as above.

Phenol-phthalein Paper.—Smooth unglazed writing-paper is steeped in a solution of phenol-phthalein. This solution is made by dissolving 5 grams of this substance in 1 litre of proof spirit.

Lead-acetate Paper.—Strips of paper steeped in a solution of basic acid acetate are very useful for the detection of hydrosulphuric acid (H_2S).

§ iv. OF REACTIONS.

By the use of the various reagents and tests already described, it is easy to identify or to separate the several constituents of any common substance which may require examination. But before the student can thus *analyse* (ἀνάλυσις = separation) an unknown substance successfully, he must make himself acquainted, by actual experiment, with the effects of the *reagents* or tests upon each individual basic or acid radicle which the unknown substance may contain. Those basic or acid radicles alone

which are common or important are included in our course. The simplest substance, not itself elementary, contains of course at least two elements, one of these being termed the basic or metallic constituent or radicle, and the other the acid or non-metallic, or stylous constituent or radicle: common salt is a compound of this order. Its formula, NaCl, indicates that it contains, as its metallic or basic radicle, one atom of the metal sodium, and as its non-metallic or acid radicle, one atom of the non-metal chlorine. Our reagents or tests will not indeed separate these two constituents for us in a free state; but they will show us the presence of sodium and of chlorine respectively, by signs or results which no other elements could give. But many compounds which have to be analysed, themselves contain compound instead of simple radicles. Nitre or potassium nitrate, KNO_3, while it contains a simple metal as its basic radicle, includes (according to the mode of viewing its constitution which we here adopt) a certain transferable group, NO_3, called the nitric radicle, for its acid constituent: this is a compound radicle. So ammonium and magnesium phosphate, NH_4MgPO_4, contains 2 basic radicles, one compound (NH_4) and the other simple (Mg), united to a compound acid radicle (PO_4). As we limit the analytical course to the important metals, so we shall include in it only the common non-metals and compound acid radicles. The tests used for the identification of radicles are of two kinds, *general* and *special*. General tests, or general reagents, are used to separate (commonly in new forms of combination) a group of similar basic or similar acid radicles from a solution; special tests, or special reagents, are used to identify or discriminate the individual members of such groups. For the separation of basic radicles there are four general or group reagents used; by their means the basic radicles are classified in four principal divisions, a fifth division being formed to include those basic radicles which are *not* removed from solution (that is, precipitated) by any general reagent. For the student to make himself acquainted with the reactions of the basic or metallic radicles, the following method of procedure should be adopted:—Separate solutions of salts containing each metal or basic radicle are to be prepared; a small quantity of one of these solutions is to be placed in the necessary number of test-tubes, and one of the general reagents added to each portion, exactly following the order in which they are given below. The *first* group test which produces a precipitate in a solution containing a metal, shows the group to which that metal belongs. After the general or group tests have been applied, the special tests are tried in a similar manner. As an illustration of this practical study of the reactions of the metals, we will suppose that we have a solution of a salt of copper, copper sulphate ($CuSO_4$) being generally employed. Copper belongs to group 2: we shall require seven test-tubes, each containing some of its solution; a little of the dry and powdered salt should also be at hand.

1. Add hydrochloric acid (HCl); the blue colour changes to green, but no precipitate is formed; copper therefore does not belong to group 1.

2. Add hydrosulphuric acid (H_2S) and some HCl: a brownish-black precipitate of copper sulphide (CuS); copper therefore belongs to group 2.

3. Add ammonium sulphide ($[NH_4]_2S$); a brownish-black precipitate of copper sulphide.

4. Add ammonium carbonate: a greenish-blue precipitate of copper carbonate, soluble in excess of ammonium carbonate, with a deep blue colour.

a. Add ammonium hydrate (NH_4HO); a greenish-blue precipitate of copper hydrate (CuH_2O_2), which dissolves to a deep blue liquid in excess of ammonia.

b. Add sodium hydrate ($NaHO$); a greenish-blue precipitate of copper hydrate, which changes to the black oxide (CuO) on boiling.

c. Add potassium ferrocyanide (K_4FeCy_6); a chocolate-red precipitate of copper ferrocyanide (Cu_2FeCy_6).

d. Mix the copper salt with sodium carbonate (Na_2CO_3), and heat the mixture on charcoal before the blowpipe. Red scales of copper will be obtained.

e. With borax on platinum wire in the oxidizing flame, a green bead is obtained; and in the reducing flame a dull-red bead; $CuCl_2$ gives a bluish-green colour to the flame.

f. A piece of clean iron immersed in the solution becomes coated with metallic copper, at once recognized by its characteristic pink tint.

Of these tests, 1, 2, 3, and 4 are general or group reagents, while *a*, *b*, *c*, *d*, *e*, and *f* are special tests for the individual basic constituent or metal present, namely copper. Some metals or basic constituents of salts, not being separable by any of the regular group or general reagents, have always to be specially tested for.

As a general rule it will be found that when hydrochloric acid or other soluble chloride produces a precipitate in a metallic solution, that precipitate is a chloride; when hydrosulphuric acid or a soluble sulphide (as $[NH_4]_2S$) produces a precipitate, that precipitate is a sulphide; in like manner a carbonate produces a carbonate, a hydrate a hydrate or an oxide, a phosphate a phosphate, and so on with the other reagents. This interchange of acid and basic radicle is represented by an equation, such as the following, which shows the *reaction* between hydrosulphuric acid and copper sulphate:—

$CuSO_4 + H_2S = H_2SO_4 + CuS$ (*brownish-black precipitate*).

The student should express in a similar mode the action of each general and special reagent.

We here give an illustration of the mode of writing out such equations, selecting the reactions of silver, a metal of the first group, for this purpose.

Group Tests.

(1) $AgNO_3 + HCl = HNO_3 + AgCl.$ White ppt.

(2) $2AgNO_3 + H_2S = 2HNO_3 + Ag_2S.$ Black ppt.

(3) $2AgNO_3 + (NH_4)_2S = 2NH_4NO_3 + Ag_2S.$ Black ppt.

(4) $2AgNO_3 + (NH_4)_2CO_3 = 2NH_4NO_3 + Ag_2CO_3.$ White ppt. sol. in excess.

a mercurous salt gives a greenish-grey precipitate; with sodium hydrate a black; and with stannous chloride, on warming, a grey precipitate (of fine globules of mercury).

GROUP II.—*Group Reagent, Hydrosulphuric Acid*, precipitates as sulphides in presence of an acid (HCl), Lead, Mercuric, Copper, Arsenious, Arsenic, Antimonious, Antimonic, Stannous, and Stannic (tin) salts.

Special tests.—LEAD; see above, page 81.

MERCURICUM: the chloride of dyad mercury is soluble in water; the sulphide is black; potassium iodide gives with mercuric salts a yellow precipitate changing to scarlet, and soluble in excess of the reagent: sodium hydrate gives a reddish precipitate, changing to yellow when the reagent is in excess. Metallic mercury may be obtained by the same means as those described for the treatment of mercurous salts.

COPPER: the special tests for copper have been already described (see p. 78).

ARSENIOSUM: its sulphide is canary-yellow and is soluble in ammonia, in ammonium sulphide, and in the sesquicarbonate; its solutions give a yellow precipitate with silver nitrate, soluble in nitric acid. Metallic arsenic is obtained when an arsenious salt is heated with potassium cyanide in a tube, a dark brown sublimate being formed and an odour resembling garlic evolved. Arsenic may be further identified by the tests known as Marsh's and Reinsch's (see pages 25 & 102).

ARSENICUM: the reactions are similar to the above, save that the precipitate by silver nitrate is brick-red; soluble arsenic salts also afford a white crystalline precipitate with an ammoniacal solution containing a magnesium salt.

ANTIMONIOSUM: its sulphide, of an orange-brown colour, is soluble in ammonium sulphide, but not in sesquicarbonate. Heated on charcoal with sodium carbonate, brittle metallic globules are produced and a white incrustation of oxide.

ANTIMONICUM may be distinguished from antimoniosum by adding sodium hydrate to the solution till the reaction becomes slightly alkaline, and then silver nitrate. The black precipitate which forms is wholly soluble in ammonia, while the similar precipitate obtained with antimonious salts is partially insoluble. The other reactions are similar to those of antimonious salts. Sodium antimoniate is nearly insoluble in water.

STANNOSUM: its sulphide is brown; it is soluble in ammonium sulphide. Treated with mercuric chloride, a solution of a stannous salt produces a white precipitate, which (when mercuric chloride has not been added in excess) becomes grey on boiling. Heated on charcoal with potassium cyanide and sodium carbonate, malleable globules of tin are produced; the incrustation of oxide is white.

STANNICUM: its sulphide is yellow, soluble in ammonium sulphide. Mercuric chloride produces no effect in its solutions. Metallic tin may be obtained as described in the preceding paragraph.

GROUP III.—*Group Reagent, Ammonium Sulphide* (= H_2S in an alkaline liquid), precipitates as sulphides, Ferrosum, Ferricum (iron), Manganese, and Zinc, and, as hydrate, the metal Aluminium.

Special tests.—FERROSUM: its sulphide is black; solutions of ferrous salts yield a greenish-grey precipitate with sodium hydrate, also with ammonia if ammoniacal salts are not present in large quantity; a pale blue precipitate with potassium ferrocyanide; a dark blue precipitate (Turnbull's blue) with a ferricyanide.

FERRICUM: soluble ferric salts give a red-brown precipitate with ammonia and sodium hydrate, and a dark blue precipitate (Prussian blue) with potassium ferrocyanide; with potassium ferricyanide a grass or olive-green coloured liquid is produced. Potassium sulphocyanide yields a blood-red solution.

MANGANESE: its sulphide is flesh-coloured; its salts are precipitated by sodium hydrate white, changing to brown on exposure to air. Ammonia produces no precipitate if ammoniacal salts be present. Fused on platinum foil with nitre and sodium carbonate, they produce a brilliant emerald-green mass. Heated with borax on a loop of platinum wire, an amethystine bead is obtained.

ZINC: its sulphide is white; its solutions afford white precipitates with sodium hydrate and with ammonia, both readily soluble in excess of the reagent. Heated on charcoal an incrustation is produced, yellow while hot, and white when cold. Salts of zinc moistened with cobalt nitrate and ignited on charcoal before the blowpipe become of a brilliant green.

ALUMINIUM is precipitated in this group as a white gelatinous hydrate; its solutions are precipitated by sodium hydrate, the precipitate being soluble in excess; ammonia affords a permanent precipitate. Ignited before the blowpipe, moistened with cobalt nitrate and again ignited, a brilliant blue colour is produced: this reaction, taken *alone*, however, is not sufficient to determine the presence of aluminium.

GROUP IV.—*Group Reagent*, *Ammonium Carbonate*; precipitates as carbonates, the metals Barium, Strontium, and Calcium.

Special tests.—BARIUM: its carbonate is white; its solutions afford an immediate white precipitate with solution of calcium sulphate—also a yellow precipitate, soluble in acids, with potassium chromate. Barium salts colour the blowpipe-flame yellowish green; this tint is remarkably persistent.

STRONTIUM: its carbonate is white; solution of calcium sulphate produces with strontium salts a white precipitate, but not immediately; heat assists the precipitation. The blowpipe-flame is coloured by strontium salts a vivid red; the colour is evanescent.

CALCIUM: its carbonate is white; ammonium oxalate produces a white precipitate even in very dilute solutions of calcium; the precipitate is soluble in the stronger acids. Calcium salts impart a bright red tint to the blowpipe-flame.

GROUP V.—*No Group Reagent.* This group includes the remaining bases: they are, Magnesium, Potassium, Sodium, and Ammonium.

Special tests.—MAGNESIUM: its solutions are precipitated by sodium-hydrogen phosphate in the presence of free ammonia and some ammoniacal salt. Moistened with cobalt nitrate and ignited, magnesium salts assume a pale pink tint.

POTASSIUM: with tartaric acid tolerably strong solutions of potassium salts yield a white crystalline precipitate, the formation of which is aided by agitation and the addition of alcohol. With platinum tetrachloride a bright yellow crystalline precipitate is produced in strong solutions; its formation is greatly assisted by the addition of alcohol. Potassium salts colour the blowpipe-flame of a lilac tint.

SODIUM: tolerably concentrated neutral solutions of sodium salts give a crystalline precipitate with potassium antimoniate; precipitation is aided by stirring and the addition of alcohol. Sodium salts impart a brilliant yellow colour to the blowpipe-flame.

AMMONIUM: its salts give with tartaric acid, and with platinum tetrachloride, reactions precisely similar to those of potassium. Ammonium salts heated with calcium hydrate or soda evolve ammonia gas, recognized by its pungent odour and its alkaline reaction with test-paper.

The presence of *fixed* organic matter will modify some of the reactions described above: the metals of the first three groups, for instance, are, as a rule, not precipitated by alkalies in the presence of citric or tartaric acid.

The reactions employed to detect the acid radicles are to a certain extent the converse of those used for the basic; *e. g.* instead of testing for a barium salt by sulphuric acid, we test for sulphuric acid by a barium salt; but the system is, on the whole, less perfect. We have in fact to rely more upon special tests for individual radicles than upon their successive separation in groups by a series of general reagents. Concerning these special tests, the student will find all the necessary information in the next Chapter, under the heads of the Preliminary Examination and the Detection of Acids. The reactions given below are employed in analysis to separate and identify the chief acid or non-metallic radicles, and should be tried, together with the special tests described on pages 90 to 96 and 113, for nitrates, silicates, acetates, iodides, &c. In order that the metallic or basic radicle present may not interfere with the indications, it is desirable to employ for these reactions the potassium, sodium, or ammonium salt of each acid radicle to be studied. The acid radicles of the following salts are sought for in the present course :—

Chlorides.
Bromides.
*Fluorides.
*Iodides.
*Cyanides.
Sulphides.
*Sulphites.
Sulphates.
*Phosphates.
*Silicates.
*Carbonates.
Oxalates.
*Acetates.
*Tartrates.
*Citrates.
*Nitrates.

Neutral solutions, each containing a suitable salt of one of the above acid radicles, except the silicic and nitric, should be prepared and severally submitted to the following tests :—

I. *Calcium Chloride.*—This reagent precipitates from a neutral solution as calcium salts the following acid radicles :— Carbonic, Phosphoric, Sulphurous, Sulphuric, Oxalic, Tartaric, Hydrofluoric, and, on boiling, Citric. To the several precipitates thus produced, each divided into three portions, the following further tests should be applied :—

  a. *Acetic acid* will dissolve all the calcium precipitates save the calcium oxalate and fluoride (and sulphate, if much be present).

  b. *Nitric acid* (dilute) will dissolve all the calcium precipitates.

  c. *Ammonium chloride* will dissolve calcium tartrate and citrate only.

II. *Barium Chloride.*—This reagent precipitates from a neutral solution as barium salts the same acid radicles as calcium chloride. To the several precipitates thus produced apply the following further test:—

Nitric acid (dilute) dissolves all the barium salts save the sulphate.

III. *Silver Nitrate.*—This reagent precipitates from a neutral solution as silver salts the following acid radicles: Chlorine, Bromine, Iodine, Cyanogen, Fluorine, Sulphur, Sulphurous, Phosphoric, Carbonic, Oxalic, Tartaric, Citric, and (partially) Acetic. To the several precipitates thus produced, each divided into two portions, apply the following further tests:—

a. Nitric acid (dilute) will dissolve all the precipitated silver salts, save the chloride, cyanide, bromide, iodide, and sulphide.

b. Ammonia will dissolve all the precipitated silver salts, save the iodide and sulphide.

IV. *Special tests* are applied for the Nitric radicle, which is not precipitated by either calcium or barium chloride, or by silver nitrate, and for the Silicic radicle. All the other radicles marked in the list with a star give also special reactions appropriate to each radicle under examination (see pp. 90 to 96 and 113), by which they may be more exactly identified; the experiments here referred to should likewise be made by the student before proceeding to the analysis of salts.

CHAPTER II.

§ i. THE METHOD OF ANALYSIS.

When the student has familiarized himself by actual experiment with the behaviour of each metal of the first group, he should proceed to the analysis of a mixture containing two of the metals of that group, leaving out of consideration for the time the acid or non-metallic radicle present. The same plan should be pursued with the other groups, the study of the reactions of the members of each group being at once followed up by the application of the information thus gained to the actual work of analysis. When the whole series of reactions has been completed, the analysis of a simple salt for its acid as well as its basic radicle should be performed; afterwards mixtures gradually increasing in complexity, as well as insoluble substances and alloys, should be subjected to complete examination.

From the section "Of Reactions" some notion of the method of analysing unknown substances will have been gained: but it is desirable to express this notion in a very definite form. Confining our attention, then, to the common metallic or basic radicles, we take a solution to start with which contains every one, and by a regular application of General Reagents separate from it group after group of metallic radicles till none but four metals remain.

To such a solution we add in the first place hydrochloric acid. It is well to repeat, at the outset, that these General Reagents or Group tests usually act in the following way: they separate the metals in the form of compounds with the characteristic acid elements or radicle which they (the group tests) severally contain. Thus we find that *hydrochloric* acid precipitates *chlorides*, *hydrosulphuric* acid, *sulphides*, and ammonium *carbonate*, *carbonates*. Now, as the chlorides of all the metals present, save three, are soluble in water or acid, hydrochloric acid precipitates these three alone. They are silver, lead, and monad mercury. These constitute, therefore, Group I., the group of the Insoluble Chlorides.

Next we add hydrosulphuric acid in the presence of hydrochloric acid. Now, as the sulphides of all the metals remaining in the solution, save five, are soluble in water or acid, hydrosulphuric acid precipitates these five alone. They are dyad mercury, copper, arsenic, antimony, and tin. These constitute, therefore, Group II., the group of the Insoluble Sulphides.

Next we add ammonium sulphide in the presence of ammonium chloride and ammonia. Now, as the sulphides of all the metals remaining in the solution, save four, are soluble in water or ammonium salts, ammonium sulphide precipitates these four alone. They are iron, zinc, manganese, and aluminium. These constitute, therefore, Group III., the group of the Soluble Sulphides.

Next we add ammonium carbonate in the presence of ammonium chloride and ammonia. Now, as the carbonates of all the metals remaining in solution, save three, are soluble in water or ammonium salts, ammonium carbonate precipitates these three only. They are calcium, barium, and strontium. These constitute, therefore, Group IV., the group of the Carbonates.

Finally there remain in solution four metals which have to be separately and specially tested for. These are magnesium, potassium, ammonium, and sodium. They constitute Group V.

Each of the preceding group-precipitates has to be further examined in accordance with the analytical scheme laid down for the particular group to which it belongs.

The examination for the acid radicles proceeds upon a similar but less exhaustive plan.

Before, however, proceeding with the regular examination for the basic and acid radicles of a substance, it is usual to submit it to a series of simple tests, which are collectively known as the Preliminary Examination. Some of the results thus obtained not only afford much information as to the proper course of analysis afterwards to be pursued, but in some cases of simple salts furnish conclusive evidence as to the real nature of the substance under examination.

On account, then, of the several parts into which our plan of analysis is divided, we usually find it expedient to divide our material into four parts, one part being reserved for the special tests, another for the systematic search for the metals, another for the systematic search for the acid radicles, and the fourth for the Preliminary Examination. We will now direct attention to the series of testings so designated. Let it be remembered, however, that it is seldom necessary to perform *all* the XIII experiments here described, and that in some cases the results of the preliminary examination will be either negative or inconclusive.

§ ii. PRELIMINARY EXAMINATION.

Note the colour, form, odour, density, &c. of the substance; then reduce it to a fine powder and make the following experiments, recording the result in three parallel columns headed respectively "Experiment," "Observation," and "Inference." If the substance be in solution, evaporate a quarter of the liquid just to dryness, stirring, if necessary, to prevent spirting: care must be taken that the heat does not rise higher than is sufficient to get rid of the water present—indeed it is advisable to withdraw the heat before the drying up of the residue is quite complete.

Experiment.	Observation.	Inference.
I. Heat a small portion of the substance in a small tube closed at one end—at first gently, finally before the blowpipe.	*No change*	Absence of H_2O, organic and volatile matter, and readily fusible substances.
	Substance changes colour.	
	Yellow whilst hot, white when cold	Zn.
	Yellow-brown whilst hot, white or yellow when cold.	Sn.
	Reddish-brown whilst hot, yellow when cold	Pb.
	Rust-colour	Fe.
	Water condenses in tube	Hydrates and salts containing water.
	The water has an alkaline reaction to test-papers.	NH_4 salts or nitrogenous matter as gelatine.
	The water has an acid reaction to test-papers	Salts of volatile acids, as HCl, HNO_3, HF, H_2SO_4, H_2SO_3.
	Substance volatilizes, and a sublimate *forms* in cool part of tube	NH_4, As, Hg, Sb, Sn chlorides, oxalic acid, iodine.

EXPERIMENT.	OBSERVATION.	INFERENCE.
I. (*continued*).	Yellow drops of sulphur ...	S or sulphides.
	Red sublimate	HgS, HgI_2.
	Gases or fumes are evolved.	
	α. Reddish-brown acid fumes of NO_2	α. Nitrates.
	β. Pungent and acid gas, SO_2, which passed into K_2CrO_4 solution turns it green ...	β. Sulphates, sulphites, and sulphides.
	γ. Gas, CO, which burns with a blue flame, the substance not blackening......	γ. Oxalates.
	δ. Gas, CO_2, giving a white precipitate with CaH_2O_2 solution	δ. Carbonates.
	ε. Pungent odour of NH_3 ...	ε. NH_4 and CN, and other nitrogenous compounds.
	ζ. Gas of peculiar odour, and burning with peach-blossom flame	ζ. CN compounds.
	Substance blackens with animal or vegetable odour.	
	Smell of burning matter ...	Organic matter.
	Smell of burning sugar	*Tartrates* and citrates.
	Smell of acetone, C_3H_6O ...	Acetates.
	An ash is left which effervesces with HCl, *the original substance not doing so.*	
	α. The ash dissolves in water.	α. Na or K tartrates, citrates, oxalates.
	β. The ash is insoluble in water	β. Ca, Mg, Ba, or Sr salts of same acids.
Introduce a splinter of glowing wood into the tube in Experiment I.	The wood glows or bursts into flame	An oxide, chlorate, or nitrate.
If the substance prove partially or wholly volatile in I. above, then,—		
(*a*) Heat a portion with $NaHO$ in a short test-tube.	(*a*) *Strong odour* and alkaline vapour evolved	NH_4 compounds.
(*b*) Heat a portion in a bulb-tube with dried Na_2CO_3.	(*b*) *Metallic ring of small globules*, which aggregate on pressing with a glass rod.	Hg.
	Metallic dark mirror, which on heating with access of air, forms brilliant octahedra of AS_2O_3....................	As.
	White crystalline sublimate and dense fumes	Oxalic acid.

EXPERIMENT.	OBSERVATION.	INFERENCE.
II. Moisten a loop of clean Pt wire with HCl, and dip it into the substance; heat the loop in a colourless gas-flame. If a yellow colour only be seen, examine the flame through a piece of dark blue glass.	*The flame is coloured—*	
	Yellow	Na.
	Lilac	K.
	Yellowish-green	Ba.
	Crimson	Sr.
	Orange-red	Ca.
	Bluish-green	Cu.
	Blue-grey or lilac	As, Sb, Pb, Mg, $CuCl_2$.
III. Heat a portion of the substance on charcoal in the inner blowpipe-flame.	*Substance deflagrates*	Nitrates, chlorates.
	Garlic odour is evolved	As.
	White fusible residue is left	K and Na salts.
	White infusible residue	Ca, Ba, Sr, Mg, Al, Zn, SiO_2.
	Residue is highly luminous when strongly heated	Ca, Mg, Sr, Zn.
If the residue in III. be white, moisten it with a drop of cobalt nitrate and again ignite.	*Residue becomes* blue	Al or earthy phosphates and silicates.
	Residue becomes pale pink	Mg.
	Residue becomes green	Zn.
	Residue becomes bluish-green	Sn.
	A coloured residue is left... (If metallic globules appear, see experiment IV.)	Fe, Mn.
IV. Mix a portion of the substance with KCy and Na_2CO_3, and heat on charcoal in inner blowpipe-flame.	*Substance is reduced to the metallic state:—*	
	Without incrustation:	
	White malleable bead	Sn, Ag.
	Red bead or scales	Cu.
	With incrustation:	
	White brittle bead and white incrustation	Sb.
	White malleable bead and yellow incrustation	Pb.
	Substance not reduced to metal, but yellow incrustation, white when cold	Zn.
	Or garlic odour and white incrustation	As.
	Or a sulphide is left, which placed on a silver coin and wetted with HCl, blackens the silver	Sulphur compounds, sulphates, reduced.
V. Heat a small portion near, and then in, the blue cone of a clear blow-	*A sublimate is obtained—*	
	Coffee-brown	Pb.
	Pale yellow to white	Sb.
	Black to white	As.

EXPERIMENT.	OBSERVATION.	INFERENCE.
V. (*continued*).		
pipe-flame — the substance being placed on a thin slice of charcoal in the angle of a Ross aluminium plate about 4 inches long and 2 broad.	Faint and yellowish-white.	Sn.
	Black to white, in part yellow while hot	Zn.
VI. Heat a small portion with powdered sodium thiosulphate and a crystal of oxalic acid in a small tube closed at one end, and so held that the water evolved does not flow back into the heated mixture.	*The substance becomes*	
	Black...........................	Ag, Pb, Hg, Cu, Fe.
	Brown	Sn.
	Orange-red	Sb.
	Yellow	As.
	Green	Mn.
	White	Zn.
VII. Add the substance by degrees to a clear borax bead, and heat in the outer blowpipe-flame.	The bead is coloured, whilst Hot, Cold,	
	Green. Blue.	Cu.
	Brownish-red. Light orange.	Fe.
	Amethyst-red. Violet.	Mn.

The remaining experiments, VIII–XIII, are more specially designed to indicate the non-metallic or acid radicle contained in the substance to be analysed. They constitute the

PRELIMINARY EXAMINATION FOR ACIDS.

VIII. Heat gently a small portion of the substance with dilute H_2SO_4 in a test-tube.	*Gases are evolved.*	
	α. CO_2; colourless; precipitates CaH_2O_2, with which a glass rod held in the gas has been previously wetted.	α. Carbonates.
	β. SO_2; smell of burning sulphur, turns yellow solution of K_2CrO_4 green......	β. Sulphites.
	γ. H_2S; odour of rotten eggs, blackens lead-paper.	γ. Sulphides.
	δ. NO_2; red acid vapours .	δ. *Nitrates or nitrites.*
	ε. HCN; characteristic odour	ε. Cyanides.

EXPERIMENT.	OBSERVATION.	INFERENCE.
VIII. (*continued*).	ζ. Colourless gases of pungent odour	ζ. Chlorides, iodides, and bromides.
	η. $HC_2H_3O_2$; smell of vinegar	η. Acetates.
IX. Heat (but not so strongly as to volatilize the reagent) a small portion of the substance with concentrated H_2SO_4, noticing the gases or vapours evolved.	α. *Substance blackens*, owing to separation of carbon. CO is evolved and odour of burnt sugar	α. Tartrates and citrates.
	β. *No blackening*, but CO and CO_2 are evolved	β. Oxalates.
	γ. *Gases are evolved* as in experiment VII.	γ. No further notice need be taken of these, as the due inferences will have been already drawn.
	δ. *A heavy suffocating gas* is evolved, which corrodes glass	δ. Fluorides.
	ε. *Violet vapours* of iodine, turning starch-paste blue.	ε. Iodides.
	ζ. *Red vapours* of Br, turning starch-paste orange	ζ. Bromides.
	η. *Greenish-yellow fumes* of Cl, bleaching litmus or indigo sulphate	η. Chlorides, probably with a nitrate or peroxide.
	θ. *Reddish-brown fumes* of NO_2	θ. Nitrates.
X. Add a crystal of $FeSO_4$ to a solution of the substance; let a little dissolve, and then pour strong H_2SO_4 cautiously down the side of the test-tube so as to form a layer at the bottom: the mixture must not get hot.	*A pink or brown coloration* between the two liquids, which disappears on warming without giving rise to violet vapours	Nitrates or nitrites; but iodides give a similar colour.
XI. Mix a little of the substance with strong H_2SO_4 in a test-tube, add a little pure alcohol, warm.	*Fragrant apple-like odour* of acetic ether	Acetates.
	Fragrant odour like sweet spirit of nitre	Nitrates.
XII. Add a small	*An undissolved skeleton* (of	

EXPERIMENT.	OBSERVATION.	INFERENCE.
XII. (*continued*). portion of the substance to a clear bead of fused microcosmic salt; heat.	SiO_2) floating in the fused bead	Silica or silicates.
XIII. To a weak solution of the substance add dilute HCl, and then $BaCl_2$ solution.	*A fine white precipitate*, insoluble in all reagents......	Sulphates.

The experiments just described, excepting X and XIII, are made with the original substance if it is solid. Besides the preliminary examination already given, the following experiments should be tried with every liquid to be analysed:—Test it with blue and red litmus papers, and note whether any change of colour be produced: thus:—

1. *No change: the reaction is neutral.*—Only those substances are present which are soluble in water; this solution is therefore ready for examination in accordance with the analytical schemes given further on. Water is the best solvent that can be used, and entails less trouble than any other in the subsequent treatment of the material.

2. *The reaction is acid.*—It is possible that compounds soluble only in acids are present. Many salts insoluble in water dissolve in acids without apparent decomposition, and are reprecipitated in their original form when the acid is neutralized by an alkali. In the ordinary process of analysis this occurs when ammonium hydrate (with ammonium sulphide) is added to the filtrate from the second group (p. 103). In the analytical scheme for the third group the occurrence and detection of these reprecipitated salts will be found described.

Some acids in the free state are recognized by their odour.

3. *The reaction is alkaline.*—Free ammonia is recognized by its smell. The solution is acidified with nitric acid: if effervescence take place, the nature of the gas evolved is ascertained (see p. 93, "Preliminary Examination," Exp. VIII.). If neutral-

ization of the solution produce a precipitate not dissolved on boiling with excess of acid, the clear liquid is to be separated by decantation or filtration, and its examination proceeded with according to the following groups. If the insoluble matter, on heating with concentrated hydrochloric acid, does not dissolve, it must be treated according to the directions given at page 114.

The precipitate obtained on acidifying the alkaline solution with nitric acid may be:—*Silica*, which appears as a gelatinous precipitate; *Antimonic* or *Stannic oxides*, falling as a white powder, the former soluble in tartaric acid; *Iodine*, appearing as a black precipitate or brown coloration, and dissolving in carbon disulphide with a violet colour; or *Sulphur*, which yields a white finely divided precipitate; besides various salts, which, like *Silver chloride* or *Arsenious sulphide*, are soluble in alkaline but not in acid liquids.

§ iii. PREPARATION OF THE SOLUTION.

If the substance under examination be a metal, it is to be treated according to the directions given at p. 115; if a solid but not a metal, a portion of it is to be powdered and boiled with water.

1. *It does not appear to dissolve.*—A small portion of the liquid is filtered, and a few drops of the filtrate evaporated to dryness; if the stain left be very slight, the substance must be considered as practically insoluble in water; if a distinct residue be left, the fluid is to be decanted from the undissolved portion, which is then boiled with more water. This operation is repeated till all is dissolved, or till the boiled liquid ceases to leave a stain on evaporation. In the case of a finally undissolved residue, the original substance probably contained at least two bodies of different solubilities.

2. *The substance is proved to be insoluble in water.*—A small portion of the original substance (or of the undissolved residue mentioned above, in 1) is moistened with ammonium sulphide;

if no blackening ensue, the remainder is now boiled with dilute hydrochloric acid; nitric acid is used instead, if blackening occur, as silver, mercury, or lead may be present. If effervescence take place, the gas must be examined (see p. 94). Should dilute hydrochloric acid fail to effect solution, the concentrated acid must be resorted to; if this produce no effect, a little nitric acid must be mixed with it. This acid should be added in very small quantity, and then the mixture should be boiled with the substance until the greater part of the nitric acid has been expelled or destroyed. If a watery and an acid solution have been obtained in the manner just described, they may in most cases be mixed together before proceeding to add the group-tests.

3. *The substance is insoluble in acid.*—In this case, if th substance be neither carbon, phosphorus, nor sulphur (recognized by their behaviour when ignited), it must be fused with the mixed potassium and sodium carbonates according to the directions given at page 114.

§ iv. ANALYTICAL SCHEMES FOR THE METALS OR BASIC RADICLES.

Supposing the solution, as just now directed, to be properly prepared, the following Table will be found to present, in a condensed form, the general scheme for the separation from it of all the basic radicles in groups. Each group, when precipitated, must then be further separated in accordance with a special analytical scheme to which the student must refer, not only for the final separation and special testings to be adopted, but also for precise directions and peculiar cautions as to the employment of the general test by which the group itself is to be precipitated.

General Analytical Scheme for the Basic Radicles.

Add **HCl**, agitate, filter :—

<table>
<tr><td rowspan="4"><i>Precipitate of Group I.</i> :—
AgCl
$PbCl_2$
Hg_2Cl_2
Wash and examine by Scheme I. p. 99.</td><td colspan="4"><i>Filtrate</i> : add $\mathbf{H_2S}$, warm, agitate, filter :—</td></tr>
<tr><td rowspan="3"><i>Precipitate of Group II.</i> :—
PbS
HgS
CuS
SnS
SnS_2
As_2S_3
Sb_2S_3
Wash, and examine by Scheme II. p. 101.</td><td colspan="3"><i>Filtrate</i> : (see p. 103) add NH_4Cl, NH_4HO, $\mathbf{(NH_4)_2S}$, agitate, filter :</td></tr>
<tr><td rowspan="2"><i>Precipitate of Group III.</i> :—
FeS
ZnS
MnS
$Al_2H_6O_6$
(with phosphates &c.).
Wash, and examine by Scheme III. p. 105.</td><td colspan="2"><i>Filtrate</i> : add $\mathbf{(NH_4)_2CO_3}$, filter :—</td></tr>
<tr><td><i>Precipitate of Group IV.</i> :—
$BaCO_3$
$SrCO_3$
$CaCO_3$
Wash, and examine by Scheme IV. p. 107.</td><td><i>Filtrate.</i>
Mg
K
Na
NH_4
} salts.
Examine by Scheme V. p. 108.</td></tr>
</table>

GROUP I.—THE INSOLUBLE CHLORIDES.

Hydrochloric acid gives a white precipitate, of the metallic chloride, with LEAD, SILVER, and MERCUROUS salts.

SCHEME.—To the neutral, or acid, tolerably strong solution (which must be cold) add a few drops of dilute hydrochloric acid. If a precipitate be formed, agitate the liquid, adding a little more acid, to see if further precipitation take place. When the precipitation is complete, filter; and, unless you know all other groups to be absent, reserve the filtrate for examination by the next Table.

The precipitate may contain lead chloride, silver chloride, and mercurous chloride; antimonious oxychloride may also be here precipitated, but it redissolves in excess of hydrochloric acid:

silica may also come down here; it is insoluble in ammonia. If the solution be strong, barium and strontium chlorides may be precipitated here, but they are readily dissolved again on adding cold water. To distinguish between the three first-mentioned metallic chlorides, collect the precipitate on a filter, wash it twice with cold water, transfer it to a test-tube, and treat it as follows.

TABLE FOR GROUP I.

Boil the precipitate with much water; if it entirely dissolve it is lead chloride; if it partially dissolve it contains that salt. The hot-water solution is decanted off, and, if not clear, filtered.

<table>
<tr><td colspan="2">The undissolved <i>residue</i> is to be warmed with solution of ammonia; if it entirely dissolves, it is silver chloride; decant or filter the solution in ammonia:—</td><td rowspan="2">Pb. The <i>filtrate</i> or solution is divided into two parts:—
1. To one add dilute sulphuric acid and a little alcohol: a white <i>precipitate indicates</i> lead.
2. To the other add potassium chromate: <i>a yellow</i> precipitate indicates lead.</td></tr>
<tr><td>Hg. The undissolved <i>residue</i>, if black or grey, indicates monad mercury (mercurosum). Place it <i>in a test-tube with a little</i> strong hydrochloric acid and a slip of copper foil: a silvery coating on the copper indicates mercury. Or, gently dry it, mix it with dry sodium carbonate, and heat it in a bulb <i>tube; metallic mercury</i> will sublime in globules.</td><td>Ag. The <i>filtrate</i> is to be tested for silver by adding to it a slight excess of nitric acid: a white <i>precipitate indicates</i> silver.</td></tr>
</table>

GROUP II.—THE SULPHIDES INSOLUBLE IN ACID.

Hydrosulphuric acid gives a coloured precipitate, of the metallic sulphide, with LEAD (black), MERCURIC (white, passing through yellow and red into black), COPPER (brownish black), ARSENIOUS (bright yellow), ANTIMONY (orange-red), and TIN (stannous sulphide is dark brown, stannic sulphide ochre-yellow) salts. If an oxidizing substance be present (a ferric salt for instance), a white precipitate of sulphur may be produced; a sulphite produces the same effect.

SCHEME.—To the filtrate from the precipitate produced by hydrochloric acid, a strong solution of hydrosulphuric acid is to be added until no further precipitate is formed (arsenic and tin require some time for complete precipitation), and the fluid, after agitation, smells distinctly of the gas (the gas H_2S itself may be passed through the above filtrate instead of using its solution ; in this case some water must be added). The mixture is now to be warmed and agitated ; if the precipitate settles well, it may be washed by decantation ; if not, it should be thrown on a filter : the water used for washing this precipitate should have a little H_2S solution added to it. The filtrates and washings from this precipitate must be reserved for examination by Scheme III., unless the metals of the third group are known to be absent.

Before treating the precipitate of this Group, as directed below, with ammonium sulphide in order to separate it into two subgroups, it will save much time and trouble if we ascertain whether this treatment be necessary, whether, in fact, the precipitate contains metals belonging to both subgroups. If the precipitate is light-coloured, it usually can contain only the metals of subgroup B, and should be examined according to the special Table for the further analysis of that subgroup given on p. 101. If, on the other hand, the precipitate is dark-coloured or black, it may contain members of both subgroups. But, to test this point, always warm a small quantity of the precipitate with a few drops of yellow ammonium sulphide, or sodium hydrate *, and filter.

If a black residue remain, and on the addition of excess of hydrochloric acid to the filtrate any precipitate save a white one of sulphur be produced, it will be necessary to warm the whole of the precipitated sulphides with a small quantity of yellow ammonium sulphide or of sodium hydrate, to filter the mixture, and to examine the black residue which remains on the filter according to the scheme for subgroup A below.

---

* Ammonium sulphide dissolves traces of CuS, while HgS is slightly soluble in sodium hydrate.

The yellow solution, filtered from the above black residue, must then be made acid with hydrochloric acid, warmed, and filtered. The precipitate thus obtained will have to be examined according to the scheme for subgroup B.

TABLE FOR GROUP II. SUBGROUP A.

The black precipitate (insoluble in ammonium sulphide or sodium hydrate) may contain lead, copper, and mercuric sulphides. Wash it, by decantation, several times, using water containing some H_2S solution and a drop or two of nitric acid; then heat it with moderately strong nitric acid, add water, and filter:—

<table>
<tr>
<td rowspan="2">Hg''. The <i>residue</i> insoluble in nitric acid, if black, is probably mercuric sulphide. To confirm this, wash it, add to it a few drops of strong hydrochloric acid, and boil with a slip of bright copper foil: a grey or silvery coating on the copper indicates mercury.</td>
<td colspan="2">The <i>filtrate</i> may contain lead and copper. Evaporate nearly to dryness to remove excess of free acid; and then add dilute sulphuric acid and a little alcohol; filter:—</td>
</tr>
<tr>
<td>Pb. A white precipitate ($PbSO_4$) indicates lead.</td>
<td>Cu. Divide the filtrate into two parts.
1. Add ammonia in excess; a blue colour indicates copper.
2. Add sodium acetate in excess, and then a drop of potassium ferrocyanide; a purple-brown precipitate indicates copper.</td>
</tr>
</table>

TABLE FOR GROUP II. SUBGROUP B.

The light-coloured or brown precipitate (soluble in ammonium sulphide or sodium hydrate) may contain the several sulphides of arsenic, antimony, and tin. Its colour will be a valuable indication, often decisive, of its nature when one metal only is present. If it be bright yellow, for instance, heat a small portion of it on a fragment of porcelain; if it entirely disappear, arsenic only is present; specially test for this element as directed in the note to the present group, below. If it be partially volatile or non-volatile, the whole precipitate must be syringed out of the filter, transferred to a test-tube, agitated with a saturated solution of ammonium sesquicarbonate for five minutes, and then filtered.

<table>
<tr><td colspan="2">The <i>residue</i> (insoluble in ammonium sesquicarbonate) will contain the antimony and tin sulphides: wash with solution of ammonium sesquicarbonate, and then dissolve, with the aid of heat, in a small quantity of strong hydrochloric acid, transfer to a porcelain dish, and dilute. Now add a little scrap zinc, and a piece of platinum foil, and allow the action to continue <i>for some time</i>:—</td><td rowspan="2">As. The <i>filtrate</i> may contain arsenic sulphide, with, perhaps, a little tin sulphide. Add hydrosulphuric acid and slight excess of hydrochloric acid; collect and thoroughly wash any precipitate, and then dissolve it in a little strong hydrochloric acid, dilute the solution and boil it with a small piece of copper foil.
(See Note, below.)</td></tr>
<tr><td>Sn. Remove some of the zinc and dissolve it together with <i>any adherent tin in hot HCl.</i> Dilute, and add $HgCl_2$: a white or grey precipitate indicates tin.</td><td>Sb. A black stain on the platinum <i>foil</i> indicates antimony.</td></tr>
</table>

Note on the Detection of Arsenic.

One of the most important elements of this group is arsenic; the subjoined processes afford further means for its detection:—Dry arsenious oxide (As_2O_3) may be sublimed in brilliant colourless octahedra; if its vapour be passed through red-hot charcoal, it yields a dark mirror of reduced, that is, metallic arsenic. This experiment may be performed in a small tube drawn out to a stout closed capillary tube at one end, the charcoal being placed at the narrowing of the tube. If a solution of arsenious oxide or chloride be introduced into an apparatus in which pure hydrogen is being generated, hydrogen arsenide (AsH_3) will be evolved (Marsh's test). This gas, if strongly heated, deposits its arsenic as a lustrous mirror on the interior of the tube through which the gas is passing. It burns with a bluish-lilac flame and white smoke. If into this flame a fragment of white porcelain be depressed, brown stains will be formed upon it. These stains dissolve in calcium hypochlorite (the black stains of antimony do not), and they give, after solution in nitric acid and drying, a yellow or red-brown precipitate with ammonio-silver nitrate. Most arsenious compounds, when digested with hydrochloric acid, yield the volatile arsenious chloride, which may be distilled off into a small flask and boiled with a *small* slip of pure bright copper foil, or if the first slip become grey or black, two or three more slips may be similarly treated (Reinsch's test). Heated in a narrow tube in presence of air, these slips will yield a bright crystalline sublimate of arsenious oxide (As_2O_3).

Another and excellent method for the detection of arsenic, peculiarly applicable in the presence of antimony, is known as "Fleitmann's test": it is tried as follows:—

To some fragments of pure granulated Zn, in a test-tube, add some sodium hydrate, and heat nearly to boiling, add a few drops of the solution to be tested (as the sulphides dissolved in HCl with a few drops of HNO_3), place over the mouth of the test-tube a piece of filter-paper, moistened with a drop of $AgNO_3$ solution. Again heat, taking care that the solution does not spirt on to the paper. If As is present, the spot moistened with $AgNO_3$ will become purplish-black, owing to the reduction of the silver to the metallic state.

This reaction is due to the fact that whereas As unites with the hydrogen evolved from a caustic alkali and zinc to form AsH_3, antimony only so combines with the hydrogen evolved from an acid.

GROUP III.—THE SULPHIDES SOLUBLE IN ACID.

Ammonium sulphide precipitates from an alkaline solution, in the presence of ammonium chloride and ammonium hydrate, iron, manganese, and zinc as sulphides, and aluminium as hydrate; the phosphates and oxalates of the alkaline-earthy metals, as well as magnesium phosphate, may also occur in this precipitate. The iron sulphide is black, manganese sulphide flesh-coloured, and zinc sulphide white. Aluminium hydrate and the phosphates and oxalates are white.

The condition in which the iron exists in the substance under examination, whether that of a ferrous or ferric salt, must be ascertained by testing a portion of the original solution as directed on page 83.

Before proceeding with the separation and recognition of the metals of Group III., in accordance with the scheme given below, it will be necessary to remove any silicic acid, and to destroy any oxalic acid or other organic matters that may be present in the filtrate from the precipitate produced by hydrosulphuric acid. These operations are performed thus. Firstly ascertain that further additions of hydrosulphuric acid produce no further precipitate, even on standing and warming. Then if silicic acid or organic acids have been found in the Preliminary Examination, evaporate the liquid to dryness and ignite the residue. Dissolve the solid matter remaining in a little strong HNO_3 and warm; if a white residue remains it is silicic acid.

Test a small portion of the acid liquid, after slight dilution with water, and filtration if necessary, for phosphates. This is done by warming it with *ammonium molybdate*: if P_2O_5 be present a decided yellow precipitate will be produced: in this case the first of the following schemes is to be followed; but if no precipitate be formed, owing to the absence of phosphates, then the second scheme described further on (page 106).

SCHEME.—*If* P_2O_5 *be present.* To the main portion of the solution (which has been obtained as above directed, or which, in the absence of silicic acid and organic matter, will be the filtrate from Group II., boiled down to dryness to remove all H_2S, taken up with water, and the solution then filtered) add a considerable quantity of ammonium chloride solution to prevent the precipitation of magnesium hydrate on subsequently neutralizing the solution with ammonium hydrate. Now add excess of ammonium hydrate, filter, and to the filtrate add ammonium sulphide. If a precipitate be produced collect it on a separate filter: the filtrate is reserved for Groups IV. and V. The two precipitates are now to be mixed and digested with $(NH_4)_2S$, and then filtered, the filtrate being thrown away.

The reason for collecting the precipitate separately is that when metals of Group IV. or of Mg are present not as phosphates they are not precipitated in this group: but had the $(NH_4)_2S$ been added at the same time with the NH_4HO, then ammonium phosphate would have been produced (by the decomposition of the phosphates of Fe, Zn, or Mn) in the presence of metals of Group IV. or of Mg, and would have caused them to be precipitated.

The precipitate which has been digested with $(NH_4)_2S$ as previously directed is now to be washed on the filter with a little H_2S

water, and then transferred to a test-tube and treated according to the directions given in the following Table for Group III.

TABLE FOR GROUP III.

The precipitate is to be boiled with enough dilute hydrochloric acid to dissolve it until all smell of H_2S has ceased: the solution is filtered to separate suspended sulphur. If the original precipitate was black, the filtered solution must now be boiled with a small quantity of nitric acid to change ferrous into ferric salts; the completion of this oxidation is tested by the reddish precipitate produced by the addition of a little sodium hydrate to a few drops of the solution in a test-tube. Sodium hydrate is now added in decided excess to the whole solution, and the mixture boiled and filtered.

<table>
<tr><td colspan="4">The *precipitate* may contain iron, manganese, and phosphates of Ba, Sr, Ca, and Mg. Wash, dissolve *in dilute* HCl, *and add* NH_4Cl *and an excess of* NH_4HO; filter quickly.</td><td colspan="2">The *filtrate* may contain zinc, al minium and aluminium phosphat *Acidify with HCl, add* NH_4 and a slight excess of NH_4H warm and filter.</td></tr>
<tr><td colspan="3">The *precipitate* may contain iron and phosphates (1). Dissolve it in HCl (2), add some citric acid, and then an excess of NH_4HO; filter.</td><td rowspan="3">**Mn.** The *filtrate* may contain manganese: add $(NH_4)_2S$; a flesh-coloured precipitate indicates manganese. Identify it by fusing it with Na_2CO_3, and KNO_3 on platinum *foil*, when a *green* manganate will be formed.</td><td rowspan="3">**Al.** The *precipitate* may contain aluminium or its phosphate. Wash it well; *divide it into* two parts; heat one on charcoal with a drop of cobalt nitrate, a blue colour shows aluminium. Heat the other part with HNO_3 in a tube, and add *ammonium molybdate*; a yellow precipitate indicates P_2O_5.</td><td rowspan="3">**Zn.** The *fi* *trate* may co tain zinc: ac $(NH_4)_2S$; whitish prec pitateindicat zinc. Confir by blowpip test given p. 92.</td></tr>
<tr><td colspan="2">The *precipitate* is washed *and then dissolved in a* few drops of HCl. Dilute the solution and add an excess of sodium acetate and a little ferric chloride till the liquid becomes reddish; boil and filter. The precipitate consists of *basic ferric acetate and* phosphate, and may be neglected: but to the filtrate add NH_4HO in slight excess, then ammonium carbonate, and then boil and filter.</td><td rowspan="2">**Fe.** The *filtrate may* contain iron: just acidify with HCl, and add K_4FeCy_6; a blue precipitate indicates iron.</td></tr>
<tr><td>The *precipitate* is examined *for Ba, Sr, Ca, by Table for Group IV. p. 107.*</td><td>The *filtrate* is *tested for* Mg: see p. 108.</td></tr>
</table>

Notes to Table for Group III.

(1) Test this precipitate for Mn also, by fusing a small part with Na_2CO_3 and $KClO_3$ on platinum foil.

(2) If P_2O_5 be absent, this solution may be at once tested for iron by adding K_4FeCy_6, omitting the citric acid.

If P_2O_5 *be absent.* To the main portion of the solution add NH_4Cl, NH_4HO, and then an excess of $(NH_4)_2S$ without filtering off the first precipitate as in the previous Scheme. The mixture is warmed and the precipitate collected on a filter and washed (if black, with weak $(NH_4)_2S$). The filtrate is reserved for Groups IV. and V., while the precipitate is examined for Fe, Mn, Al, and Zn, according to the above Table for Group III. As phosphates are absent, the precipitate produced by NaHO contains Fe and Mn only. (See note 2 to Table.)

A portion of the original solution of the substance may be taken for this group if *no* precipitate has been obtained in the preceding groups.

Much may be learnt as to the metals present by carefully noting the changes produced on adding ammonium hydrate after ammonium chloride. If ammonium hydrate in excess produce no precipitate, *manganese* and *ferrous* salts are the only members of the group that can be present. If a white precipitate be produced soluble in excess of ammonium hydrate, *zinc* is present. If ammonium hydrate afford a permanent white precipitate, either *aluminium* or *phosphates* or *oxalates* of the alkaline earths are present. A red precipitate by ammonia indicates a *ferric* salt, a dark green a *ferrous* salt, ferrous oxide being partially precipitated by ammonia when the amount of ammoniacal salt present is small. The knowledge thus obtained will serve greatly to shorten the subsequent operations; for instance, if no black precipitate be obtained on adding ammonium sulphide, and iron is consequently absent, the precipitate by ammonium hydrate containing manganese and phosphates need not be dissolved and treated with citric acid.

GROUP IV.—THE CARBONATES INSOLUBLE IN WATER.

Ammonium carbonate gives a white precipitate of the metallic carbonate, in neutral or alkaline solutions of calcium, strontium, and barium salts.

Before adding ammonium carbonate, the filtrate from the preceding group (that is, from the precipitate produced by ammonium sulphide) is to be treated with hydrochloric acid,

and boiled till all smell of hydrosulphuric acid has ceased; it is then, if cloudy, filtered.

If none of the preceding group-tests has produced a precipitate, the *original* solution, after addition of ammonium chloride, may be treated at once as under.

SCHEME.—To the solution add ammonium hydrate in slight excess, then ammonium carbonate, warm and filter; reserve the filtrate for examination by the Table for Group V. Wash the precipitate, and then proceed thus:—

TABLE FOR GROUP IV.

The precipitate is to be dissolved on the filter in the smallest possible quantity of acetic acid; then add potassium chromate in slight excess, warm and filter:—

Ba. The *precipitate* is barium chromate. For special tests for barium and the metals of this group, refer to Preliminary Examination, p. 92.	The *filtrate* may contain strontium and calcium; divide it into two portions:—	
	Sr. I. To one portion add a considerable quantity of solution of calcium sulphate: a white precipitate coming down after a time indicates strontium. (Calcium sulphate solution produces no precipitate in solutions of calcium salts unless they are very strong.)	**Ca.** II. To the other portion, (*a*) if strontium has not been found in I., add ammonium hydrate and ammonium oxalate: a white precipitate indicates calcium. (*b*) If strontium has been found in I., evaporate portion II. with a solution of potassium sulphate and boil the dry residue with water. *Filter* the extract thus made; to the filtrate add ammonium oxalate, as above directed.

Barium chloride is insoluble in alcohol, the strontium chloride soluble: on this fact the following mode of separating barium and strontium (in the presence of calcium) is founded. Add excess of calcium sulphate solution to the hydrochloric acid solution of the Group IV. precipitate; boil, collect and well wash the precipitated barium and strontium sulphates, then boil them for some time with potassium carbonate solution. The sulphates thus converted into carbonates are washed, and then dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue, digested with a little strong alcohol, will yield a solution of strontium chloride, which may be warmed and ignited, and the crimson colour of the flame observed.

GROUP V.—THE CARBONATES SOLUBLE IN AMMONIACAL SALTS OR WATER.

The filtrate from the previous group may contain MAGNESIUM, SODIUM, and POTASSIUM salts. AMMONIUM compounds must be tested for in the original substance. See Preliminary Examination, page 91.

Concentrate the filtrate, add to it a few drops of ammonium oxalate, and filter it if necessary.

SCHEME.—The filtrate is divided into two unequal parts, and thus tested:—

Mg. I. *Smaller portion.*—Add a little ammonium chloride and ammonium hydrate and some sodium phosphate; agitate well: a white crystalline precipitate of ammonio-magnesium phosphate, which may form very slowly, indicates magnesium.

II. *Larger portion.*—The larger portion is to be evaporated to dryness in a platinum or thin porcelain vessel, and then ignited to expel salts of ammonium. If magnesium has been found in the previous experiment, moisten the residue with ammonium carbonate, evaporate and ignite again. Dissolve the residue in a little hot water and filter: use the filtrate as follows:—

K. Moisten a platinum wire with it, and ignite in the blowpipe-flame; a lilac tint indicates potassium. To another portion of the same solution add an excess of tartaric acid and some alcohol, and agitate well: if potassium be present, a white crystalline precipitate of hydrogen-potassium tartrate ($KHC_4H_4O_6$) will be formed. Platinum tetrachloride, a drop of hydrochloric acid, and some alcohol added to another portion of the filtrate will give, on standing, an orange crystalline precipitate of the double chloride of platinum and potassium (K_2PtCl_6). To obtain the precipitates here indicated, it is essential that a concentrated solution should be employed.

Na. The presence of sodium compounds is recognized by the bright yellow tint they impart to the blowpipe-flame. This is so intense as to obscure the violet potassium colour, unless the flame be viewed through dark cobalt-blue glass, which cuts off the yellow sodium rays only. Sodium in sufficient quantity to give the flame reaction distinctly is sure to be present in the filtrate from the four groups of bases. It is impossible to obtain reagents free from it, or to prevent its introduction in other ways.

§ v. ANALYTICAL SCHEMES FOR THE DETECTION OF THE NON-METALLIC OR ACID RADICLES.

In the preliminary examination (see Experiments VIII. to XIII.) much information will have been obtained in reference to the acids. The examination of basic radicles, just concluded, will also frequently throw some light on the subject. Thus, if the substance is found to be soluble in water, and to contain certain basic radicles, it is evident that only those acid radicles can be present which form soluble compounds with them: thus the presence of barium excludes that of the sulphuric radicle. With substances insoluble in water similar reasoning will apply. The student will therefore consult with advantage the Table of Solubilities given at pp. 116, 117.

The search for the acid radicles may be divided into three parts. We make first of all certain experiments on the original substance, constituting part of the preliminary examination; then we apply two or three reagents to a prepared solution and examine further the precipitates formed; and, lastly, we try the action of a few special tests upon this prepared solution.

EXAMINATION FOR ACIDS IN A PREPARED SOLUTION.

If silica in the soluble form be present, it must first of all be separated by evaporation to dryness with excess of hydrochloric acid; in this case chlorine, iodine, and cyanogen cannot be tested for in the redissolved residue, but must be specially sought for in the original substance. The carbonic, hydrosulphuric, sulphurous, nitric, and acetic radicles will have been detected already in the preliminary examination, and would likewise be lost in the preparation of the solution. The sulphuric radicle is sought for in Experiment XIII, p. 95. If no indications of any acid radicles have been obtained in the preliminary examination, the only acid radicles that need be sought for are the phosphoric and oxygen.

Before proceeding to the following groups, all basic radicles other than the alkaline metals must be separated. This may be effected by boiling with an excess of sodium carbonate. Where long-continued ebullition with a solution of sodium carbonate does not effect a transference of acid and basic radicles, fusion with the mixed sodium and potassium carbonates will be found to answer the purpose in view (see p. 114). In this case, however, organic acids are, of course, destroyed.

If organic matter be present, together with metals of the first three groups, hydrosulphuric acid or ammonium sulphide must be employed to separate these metals; and if the alkaline earths be also present, the solution, after removal of the sulphur, must be finally boiled with sodium carbonate. If hydrosulphuric acid be employed, the arsenious radicle will of course be removed from the solution.

The prepared solution (or the original solution, supposing this to contain only alkaline bases) is divided into three portions, which are examined according to the following groups; if, however, the preliminary examination has proved the absence of organic acids, examination for the third group is omitted. The solution should not be too dilute.

GROUP I.—CHLORINE AND OTHER MONAD ACID RADICLES.

SCHEME.—To one portion of the solution add dilute nitric acid till the solution is distinctly acid, and then solution of silver

nitrate till no further precipitate is formed. The precipitate may contain silver chloride, iodide, and cyanide. Wash the precipitate, and heat it gently with excess of ammonium hydrate till no more dissolves ; filter.

<table>
<tr><td rowspan="2">I. The <i>residue</i>, insoluble in ammonium hydrate, is, if yellowish, silver iodide. Confirm the presence of iodine by treating a little of the original substance with starch-paste and a drop of chlorine water : a dark blue colour indicates iodine.</td><td colspan="2">The <i>filtrate</i> may contain silver cyanide and chloride*. Add nitric acid in excess, agitate, wash the precipitate by decantation, dry and heat it to fusion on a piece of porcelain. Boil the residue on the porcelain with nitric acid, dilute, filter.</td></tr>
<tr><td>Cl. Any insoluble <i>residue</i> is silver chloride.</td><td>Cy. If the <i>filtrate</i> contain any silver, its presence indicates cyanogen, for silver cyanide is decomposed by heat ; and the residue, chiefly of silver, which it leaves, is then soluble in nitric acid.</td></tr>
</table>

Group II.—FLUORINE AND THE PHOSPHORIC AND OXALIC RADICLES.

To another portion of the solution add acetic acid in excess, and divide into two parts.

PO_4. (1) Add ferric chloride solution, drop by drop. A yellowish-white precipitate is ferric phosphate. Confirm by the molybdate test, pages 38 and 104.

F. (2) Add calcium chloride solution. A white gelatinous precipitate is calcium fluoride. Confirm by etching glass, as in Preliminary Examination, page 94.

C_2O_4. A white crystalline precipitate on the addition of calcium chloride is calcium oxalate. It may be distinguished from calcium fluoride by leaving calcium carbonate on ignition, and then dissolving with effervescence on the addition of acetic acid. If fluorine has been found by its action on glass, and the calcium precipitate after ignition partially dissolves, with evolution of carbon dioxide, in acetic acid, both hydrofluoric and oxalic acids are present.

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* If cyanogen has not been found in the preliminary examination, further treatment can, of course, be omitted, as the precipitate, on the addition of nitric acid, can then be silver chloride only.

GROUP III.—THE TARTARIC AND CITRIC RADICLES.

Another portion of the solution is made exactly neutral. This is effected by adding dilute nitric acid until the solution is very slightly acid, boiling to expel carbon dioxide, and then adding very dilute ammonium hydrate until the solution is exactly neutral to test-papers.

It is absolutely necessary that the least possible excess of either acid or alkali should be added, as the formation of ammonium salts in any quantity interferes with the subsequent reactions. If ammonia has been found present in the substance in the search for bases, it must be expelled by continued ebullition with caustic soda before proceeding to the examination for the acids of this group.

To the neutral solution add calcium chloride, shake well, and filter.

$C_4H_4O_6$. A white *precipitate*, soluble in ammonium chloride, is calcium tartrate. Calcium phosphate and oxalate, the acid radicles of which have been detected in the previous group, would also be precipitated here, but may be distinguished from the tartrate by being insoluble in ammonium chloride.	**$C_6H_5O_7$.** To the *filtrate* add a *few* drops of ammonium hydrate, and boil; a white crystalline precipitate, soluble in ammonium chloride, is calcium citrate.

Owing to the great similarity between citric and tartaric acid (which have been previously indicated, by blackening with sulphuric acid, in the Preliminary Examination), the following points of distinction, in addition to the above, should be carefully attended to.

Calcium tartrate is soluble in a cold solution of potassium hydrate, and is reprecipitated on boiling, whereas calcium citrate is insoluble in either hot or cold caustic alkali.

Silver tartrate, heated with a little ammonium hydrate, produces a metallic mirror of silver in a few minutes, whereas silver citrate requires long boiling for reduction.

This experiment is performed as follows:—Remove the precipitate of calcium tartrate or citrate (by means of a spatula) to a test-tube which has been thoroughly cleaned by means of caustic soda and washing with distilled water. Then add a few drops of silver nitrate solution, and only so much of a very weak ammonia solution as shall suffice to dissolve part of the precipitate which it first forms. If a mirror appear in the tube on gently warming it, a tartrate was present; if the mirror form only on boiling for some time, the presence of a citrate is indicated.

A solution of a tartrate, strongly alkaline with sodium or potassium hydrate, heated to boiling, and a few drops of potassium permanganate added, first turns green; and then a brown precipitate falls, the solution becoming colourless.

An alkaline solution of a citrate so treated turns green, but no precipitate is produced.

Special Tests for Acid Radicles.

Acetates.—See Preliminary Examination, Experiment XI., p. 94. Acetates in a neutral solution give, with ferric chloride, a blood-red colour, destroyed by HCl.

Cyanides.—Cyanogen is best tested for as follows:—Moisten the substance in a watch-glass with hydrochloric acid; immediately invert over it another watch-glass, having its inner surface moistened with a drop of yellow ammonium sulphide: warm gently, remove the upper watch-glass, dry it on the water-bath, add a drop of dilute hydrochloric acid and a drop of ferric chloride: a blood-red colour indicates a cyanide.

Nitrates.—See Preliminary Examination, Experiment X., p. 94.

Phosphates.—See pp. 38 and 105.

Silicates.—See pp. 92 and 95. The silicic radicle present in its soluble form may be recognized by evaporating the solution to dryness with an excess of hydrochloric acid, heating the residue for some time to a temperature of about 150° C., and then digesting it in strong hydrochloric acid. An insoluble residue, volatilizing entirely when warmed in a platinum crucible with hydrofluoric acid, is silica.

Sulphates.—See Preliminary Examination, Experiment XIII., p. 95.

All the other acid radicles not included in the three acid groups above will have been identified in the preliminary examination.

§ vi. ANALYTICAL SCHEME FOR THE EXAMINATION OF SUBSTANCES INSOLUBLE IN ACIDS.

An examination before the blowpipe will in many cases, especially if the substance be a simple salt, prove sufficient for its identification. If the presence of sulphur, carbon, or phosphorus be suspected, the substance is first to be ignited; if it continue unaltered, or a distinct residue remain, it is to be finely powdered, mixed with four times its weight of the mixed potassium and sodium carbonates, and the whole kept in fusion for a quarter of an hour, a platinum crucible being used unless the preliminary examination has shown the presence of an easily reducible metal, when one of porcelain must be employed; in this case traces of silica and alumina will be unavoidably introduced into the analysis. The crucible and its contents, when cold, are to be boiled with water, and the solution filtered.

The solution in water may contain aluminium, tin, antimony, the silicic radicle, &c. &c. Divide into two portions. To one add nitric acid in excess and boil; render the solution slightly alkaline with ammonium hydrate, and filter if necessary; the filtrate is to be examined for all acids save nitric and the organic acids. The other portion of the solution is to be evaporated to dryness with an excess of hydrochloric acid. Heat the residue to about 150° C. for some time; when cold, moisten it with strong hydrochloric acid, and allow it to stand twenty minutes; then add water, and dissolve. An insoluble residue is probably silica: confirm by special tests. Filter. Examine the filtrate for tin, antimony, arsenic, and aluminium, according to the schemes for Groups II. and III.

The residue, insoluble in water, may contain silicic acid, the alkaline-earthy metals as carbonates, lead oxide, metallic silver, and ferric oxide. Wash thoroughly, and dissolve in dilute hydrochloric acid with the aid of heat, or, if the original substance was blackened by ammonium sulphide, in nitric acid.

The solution is to be examined for basic radicles according to the plans already given.

The residue consists, probably, of silica, or of a portion of the original substance which has escaped the action of the alkaline carbonates.

If it is desired to examine insoluble silicates for the alkaline metals, the substance is to be fused with four times its weight of barium hydrate in a platinum crucible, the mass dissolved in dilute hydrochloric acid, and the barium and alkali metals separated according to the schemes given for Groups IV. and V. Or the finely powdered silicate may be treated with hydrofluoric acid in a platinum or lead vessel, then with sulphuric acid, the excess of that acid being volatilized by heat: the silica is thus entirely removed: the residue is to be examined in the ordinary way for the basic radicles.

The construction and uses of the annexed Table of Solubilities will be readily understood by the student who has followed the instructions in Qualitative Analysis which have been given.

§ vii. ANALYTICAL SCHEME FOR THE EXAMINATION OF ALLOYS.

The alloy is reduced to a fine state of division by cutting with a knife, filing, or, when brittle, by powdering in a steel mortar. The portion taken for analysis is boiled with nitric acid diluted with twice its bulk of water, till all action ceases; the solution is then diluted with water.

The *solution* will contain all metals present in the alloy, save gold, platinum, tin, and perhaps antimony. Examine it according to the foregoing schemes for the detection of basic radicles.

The *residue* may contain gold, platinum (both greyish black), stannic oxide, and antimony oxide (both white). If large quantities of tin be present, traces of other metals may occur in this residue.

After thoroughly washing the residue, fuse it with three parts of potassium cyanide in a porcelain crucible; boil the mass with water, and wash the metallic residue by decantation; then heat it with concentrated hydrochloric acid.

Sn. To a small portion of the clear solution add a drop or two of mercuric chloride; a white precipitate, becoming grey on boiling, indicates *tin*.

Add a little nitric acid to the rest of the solution and residue, and boil till complete solution is effected: divide into three portions.

Au. A small portion of the liquid is considerably diluted, and a little stannous chloride and ferric chloride added; a purplish or reddish coloration proves the presence of *gold*.

Pt. A small portion is treated with ammonium chloride, evaporated nearly to dryness and treated with alcohol; a yellow crystalline residue indicates *platinum*.

Sb. The rest of the solution is treated with excess of ammonium sesquicarbonate, and then well boiled and filtered. The filtrate is acidified with hydrochloric acid, and hydrosulphuric acid water added. An orange-red precipitate indicates *antimony*.

In order that the student of qualitative analysis may see how the methods of examination which we have just described are applied in practice, we proceed to give

AN EXAMPLE

of the QUALITATIVE EXAMINATION of an unknown mixture of

salts, this mixture occurring as a dull greenish solution with a white residue or sediment.

First of all the solution and residue (after filtration) were separately divided into four portions, the former labelled S 1, S 2, S 3, and S 4, and the latter R 1, R 2, R 3, and R 4.

1. *Preliminary Examination for Bases.*

S 1. This portion of the solution was cautiously evaporated just to dryness, and tested in accordance with the directions given in the Table of the Preliminary Examination for Bases (pp. 90, 91, 92, and 93), when changes occurred in the following experiments only:—I. *a white sublimate in tube, and, on further heating, fumes of* NO_2; II. *bluish-green flame*; III. *substance deflagrated*; V. *when hot, green*; *when cold, blue.* From these experiments we infer that the following substances are present:—NH_4, Cu, and a nitrate or chlorate. Now, in the first instance we might have argued, from Experiment I., that As and Hg were present as well as NH_4; but this could not be the case, since neither globules nor metallic mirror was obtained with the bulb-tube and Na_2CO_3, in Experiment I *b*.

R 1. This portion of the residue was tested in the same way as the solid matter obtained by the evaporation of S 1: changes occurred in the following experiments only:—I. *a gas*, CO_2, *given off*; II. *red flame*; III. *luminous residue and bluish-white malleable globules of metal*; IV. *globules as in* III. From these results we infer the presence of Ca, Ba, Sr, or Mg, and of Pb.

2. *Systematic Examination for Bases.*

S 2. The second portion of the solution was submitted to the action of the group-tests (p. 97) in order, each precipitate obtained being further examined according to the Table for the group to which it belonged. In Group II. (pp. 99–103) a brownish-black precipitate, proved by further treatment and special tests to be *copper* sulphide; in Group III. (pp. 103–106) a black precipitate was shown to be *iron* sulphide (the iron was found to exist as a ferrous salt in the original solution); while no other base was detected, save that in the Experiment I *a* of the Preliminary Examination (p. 91) *ammonia* was detected.

R 2. This portion of the original residue was found to be altered, but not dissolved completely, by dilute HCl; and so dilute HNO_3 was employed instead, when escape of CO_2 took place. The solution thus made could not be mixed with S 2 above without producing a dense precipitate; and therefore it was analysed separately (though in most analyses such admixture may be made); had it been wholly or partially insoluble in acids, it would have been requisite to treat this residue according to the scheme for the Examination of Insoluble Substances (p. 114). When the HNO_3 solution of R 2 was duly examined by the group-tests, precipitates were obtained—in Group I. of *lead* chloride, in Group II. of *lead* sulphide, in Group IV. of *calcium* carbonate; all these indications were duly confirmed by special tests.

3. *Preliminary Examination for Acids.*

S 3 and R 3. Small portions of the solution and residue were mixed and evaporated just to dryness; with the dry material thus obtained the following Experiments (pp. 93, 94, and 95) were performed: VIII. CO_2 *evolved*; X. *brown ring.*

4. *Systematic Examination for Acids.*

S 4 and R 4. With the remaining portions of the original solution and residue mixed together, a "prepared solution" was made (p. 109). With this liquid the systematic examination for acids was conducted, a small portion, however, being used for Experiment XIII. Preliminary Examination, p. 95, when *sulphuric* acid was found. In Group I. of the acids *chloride* was identified, while no indications were obtained in the other groups. Among the special tests, those for *nitric* acid gave positive results.

Thus from the results of the preliminary and systematic examinations, we conclude the unknown mixture of salts contained the metals or basic radicles Pb, Cu, Fe, Ca, and NH_4, and the acid radicles CO_3, Cl, NO_3, and SO_4. From the separate examination of the solution and residue, we conclude that the salts actually present in each were :—

Lead carbonate, Calcium carbonate,	in the residue.	Copper, ferrous, and ammonium chlorides, sulphates and nitrates,	in the solution.

PART III.

QUANTITATIVE ANALYSIS.

CHAPTER I.

§ i. INTRODUCTION.

When the student has acquired some skill in recognizing and detecting the common basic and acid radicles, the quantitative estimation of various chemical substances will engage his attention. Scrupulous care and precision, together with manipulatory adroitness, are here more than ever necessary.

The knowledge which he has gained is here applied to determine the *quantity* of the various constituents of a compound body. The course of practice under this head is necessarily limited in its variety, from the greater amount of time required for the operations of quantitative analysis. Attention is therefore at once turned to matters of agricultural importance—the analysis of manures, soils, feeding-materials, &c.

In following the schemes of analysis here described, it should always be borne in mind that they are intended only for the particular case mentioned, and may consequently fail if otherwise applied—if, for instance, other substances be present than those here supposed. To describe processes available under every contingency would demand a far larger work than the present. In cases differing somewhat from those described, the student's own knowledge of chemistry must be brought to bear, and he must endeavour to think out a modification of the process suitable to the case.

Before proceeding to operate upon the various commercial and agricultural products which have been selected as suitable subjects of quantitative analysis, the student will find it best to make estimations of the constituents of certain definite and pure chemical compounds. For the determination of water, a weighed quantity of crystallized sulphate of copper may be taken; for the sulphuric radicle and for calcium, crystallized calcium sulphate or selenite; for magnesium, Epsom salts; for potassium, the pure sulphate of that metal; for iron, crystallized green vitriol; for aluminium, ammonia-alum; and so on with the other most important metallic and acid radicles. We proceed to give full directions for the estimation of calcium, barium, magnesium, potassium, and the phosphoric and sulphuric radicles—the quantitative determination of other ingredients of soils, food, manures, &c. being duly described under the examples in which they severally first occur. It will, however, be well to introduce a word or two now concerning the names of chemical compounds, and concerning weights and measures.

Chemical Nomenclature.—The names assigned to salts and chemical compounds in this book are mainly those commonly adopted by scientific chemists. But a very rigid adherence to one system has not been observed, and is indeed a matter of minor importance, though of considerable difficulty. In the case, for instance, of the substance which is correctly termed sodium nitrate, the terms sodic nitrate and, still more commonly, nitrate of soda, are often employed indifferently. It is of real importance nevertheless to know that these three names signify the same compound ($NaNO_3$), a combination of one atom of sodium, one of nitrogen, and three of oxygen. In the case of this compound, and of many other common substances, we shall in future use the more familiar along with the accurate names, or even instead of them, on account of the special commercial or economical character of the subjects of which we treat in the third part of this volume. We shall likewise adopt the expressions ammonia, lime, magnesia, &c., and calculate our results into these forms on account of the convenience of comparing our results with published analyses. The acid constituents of salts will appear, in a similar manner, as sulphur trioxide, phosphorus pentoxide, &c., instead of as the corresponding acid radicles, for the same reason.

Weights and Measures.—The system of weights and measures now in almost universal use for scientific work is the French metrical (decimal) system, founded on the *metre* or one ten-millionth part of a quadrant of a meridian measured through the poles of the earth. This unit of length, the metre, =39·37079 inches.

The unit of weight is a *gramme*, written in English gram, which is the weight of a cube of distilled water at its maximum density, viz. 4° C. (=39°·2 F.), the edge of this cube being a centimetre. It is equivalent to 15·432349 grains.

The unit of capacity is a *litre*, or the capacity of a cube whose edge is a decimetre, and is therefore =1000 cubic centimetres. It equals 1·76133 pint.

The decimal multiples of these units are denoted by the Greek prefixes—Deka, ten; Hecto, hundred; Kilo, thousand; and the decimal subdivisions by the Latin prefixes—Deci, one tenth; Centi, one hundredth; Milli, one thousandth.

If this system be used, the following weights and measures will be required in the work of quantitative analysis:—

1. A set of gram weights, from 50 grams to 1 gram in brass, and downwards to 5 milligrams in platinum, with a centigram wire "rider" to weigh milligrams and parts of milligrams on the divided beam of the balance.

2. A litre flask, which, filled so that the lowest point of the meniscus coincides with a mark on the neck, contains 1 litre at 60° F. (15°·55 C.). A litre is 1000 cubic centimetres, *i. e.* strictly the volume occupied by (a kilogram or) 1000 grams of water at 4° C.; measurements are, however, for convenience, taken at 15°·55 C. (60° F.); the actual difference thus made is 2 thousandth parts, equal to a deficiency of 2 grams.

3. A half-litre flask, or one which, filled to a mark on the neck, will *deliver* 500 c. c.

4. A cylindrical measure graduated to 100 or 200 c. c.

5. A Mohr's burette (with Erdmann's float), graduated to 100 c. c., divided into $\frac{1}{10}$ths c. c.

6. A pipette to hold 20 c. c., either graduated or simply marked to show when it contains the desired quantity.

If, however, the English system of weights and measures be used, the student will require :—

1. A set of grain-weights, from 1000 to 10 grains in brass, thence downwards to $\frac{1}{10}$ grain in platinum or aluminium, with a $\frac{1}{10}$-grain wire rider.

2. A burette, graduated to 200 septems. A septem is the volume occupied by 7 grains of distilled water at 62° F., and barometer 30 in.; 10,000 septems therefore equal a gallon.

3. A cylindrical stoppered measure *for mixing*, graduated to 1 or 2 decigallons. A decigallon = 1000 septems.

4. A cubic-inch pipette. A cubic inch of distilled water, at standard pressure (30 in.) and temperature (62° F.), weighs 252·457 grains: 277·274 cubic inches make 1 gallon.

A Centigrade mercurial thermometer ranging from —10° to 300°, and having its graduations etched on the glass, will be of service. The conversion of Centigrade degrees into Fahrenheit and *vice versâ* may be accomplished by means of these two equations :—

$$(1)\quad (C.^\circ \times 1{\cdot}8) + 32 = F.^\circ;$$
$$(2)\quad (F.^\circ - 32) \div 1{\cdot}8 = C.^\circ$$

The balance should be kept in a place not subject to acid fumes, and free from vibration; a tall jar containing a stick of caustic potash, or else two vessels, one containing oil of vitriol, and the other a lump of quicklime, should be kept in the case to absorb the moisture of the air, and to prevent the rusting of the knife-edges and other steel parts of the balance. The balance must be levelled by means of the three adjusting screws, two spirit-levels laid on the floor of the balance-case (one parallel with, and the other at right angles to the beam) being employed for this purpose. In order that the whole case may not shift its position, the lower ends of the levelling screws may be made to rest upon solid disks of vulcanized india-rubber permanently fixed to the table; or three box-wood cups having flanges with screws may be fastened in such positions on the table that their cavities may receive the lower ends of the levelling screws. These cavities should be accurately turned and deep, though rather narrow: they may be filled up with fine graphite powder. When the balance has been made level, the perfect equilibrium of the beam must be secured. When both pans are empty and the beam is released, the pointer should coincide with the zero of the ivory scale, or else it should swing an equal number of degrees to each side. If this be not the case, the little vane over the middle of the beam must be moved towards that end of the beam which is lighter until the adjustment is complete.

The weights must next engage our attention. When supplied by a good instrument-maker, they are usually sufficiently accurate for all ordinary purposes, although when used in original researches they must be severely tested: it is also advisable to examine their condition from time to time. The large chemical weights are usually made of brass, the tenths of the gram being made in platinum, while sometimes the centigrams and lower weights are constructed of aluminium. Brass weights increase by corrosion; gilt and platinum weights slightly diminish by wear.

The following set of weights "of precision" is commonly employed in chemical laboratories:—

In Brass.	In Platinum.	In Aluminium.
50 grams.	·5 gram.	·05 gram.
20 „	·2 „	·02 „
10 „	·1 „	·01 „
10 „	·1 „	·01 „
5 „		*·005 „
2 „		*·002 „
1 gram.		*·001 „
1 „		*·001 „
1 „		*·001 „

The milligram weights (marked *) are seldom used, a "rider" of wire, weighing 1 centigram when in the pan, being employed instead. This rider is made to travel along the divided arm of the beam, gradually diminishing in effect as it approaches the fulcrum. The arm is divided into ten parts, so that when the rider is halfway it rests on division 5 and equals 5 milligrams or ·005 gram; when it has been placed three fourths of the distance from the extremity of the arm, it rests between the division 3 and 2 and is equal to a weight of 2½ milligrams, or ·0025 gram in the pan.

The following directions should be followed in weighing the vessels and substances with which one has to deal in quantitative analysis.

1. Open the balance-case without shaking or displacing the instrument.

2. Release the beam of the balance (by means of the milled head or key in front) gently and steadily, avoiding all jerking motion.

3. Always use the same pan for the weights.

4. Never weigh any crucible &c. after heating until it has cooled down, in the desiccator, to the temperature of the balance-room.

5. The weights should be tried in regular order from the heavier downwards until the object which is being weighed is exactly balanced. The weights are to be read off when the index swings an equal number of degrees on either side of the zero of the scale.

6. Keep the balance-case closed as much as possible; this precaution is particularly necessary when completing a weighing.

7. Bring the balance to rest, by supporting the beam, exactly at the moment when the index points to zero: this must always be done before adding any thing to, or taking any thing from, either pan.

8. The watch-glass or crucible in which a substance is being weighed should be removed from the pan whenever any thing is to be added to it or taken from it.

9. Read off the weights used, not only from the marks upon them, but by means of the vacant spaces in the weight-box: then restore them to their places.

10. Particular care should be taken of the smaller weights; if

one of these be lost, immediate search for it should be made, as it would be irretrievably ruined if trodden upon.

11. Weights are to be moved only by the forceps provided for this purpose: they must on no account be touched by the fingers.

In measuring liquids in the graduated vessels, the measure must be placed perfectly perpendicular, and the eye must be on a level with the surface of the liquid. The exact level can be conveniently found by means of a small mirror placed close to the vessel on the opposite side; when the surface of the fluid is in a straight line with the centre of the eye and its reflection, the eye is in the right position. The readings should be taken at the lower line of the dark zone of the surface of the fluid; this may be made more distinct by placing behind the tube a piece of white paper, on which a strip of black paper is pasted, in such a position that the border line between the black and white is just below the dark zone.

Besides the ordinary apparatus employed in qualitative analysis, and the measures, weights, and balances just described, a few instruments or special contrivances are requisite for quantitative work. Amongst the most important of these we may here describe:—

1. A platinum crucible, about 24 millimetres broad at its base, 34 millims. at top: its height may be 37 millims.; and its weight, with a flanged capsule cover (of 7 grams) to fit loosely inside the rim, need not exceed 30 grams. The capsule cover or lid is "dished" to a depth of 3 millims., while the breadth of its flange is 2 millims., except in one place, where it is formed into a broad flat expansion. The greatest care must be taken of this crucible; it must never come in contact with zinc, tin, silver, antimony, or lead; nor must any compounds of these metals be heated in it. Even alkaline salts in the presence of carbonaceous matter may injure it. For many purposes a crucible of hard Berlin porcelain may be substituted for one of platinum.

2. A platinum spatula, spud-shaped at one end and pointed at the other, of the form and size shown in fig. 10, though not quite so slender towards the pointed end, will be found very useful. The

weight of this implement (which is made from stout wire) need not exceed 4 grams.

Fig. 10.

3. A desiccator, in which the crucible, dish, or other vessel to be weighed is allowed to cool and carried from the laboratory to the balance-room. This contrivance may be made with a heavy thick finger-glass, the upper edge of which is first to be ground on a corundum and shellac hone: a greased ground-glass disk forms a convenient cover. To support the crucible in this glass an iron wire triangle, raised on three legs and with pieces of tobacco-pipe strung on its sides, is constructed: a little piece of cork fixed to the extremity of each leg prevents the triangle from slipping about. The drying or desiccating material to be used is dry calcium chloride in lumps; it is well to prevent this from touching the bottom of the crucible by means of a piece of mica interposed between them. A still more convenient mode of fitting up a desiccator is thus carried out:—The ground finger-glass named above has the upper part of a beaker cemented by means of marine-glue to its interior: within this a neck from a flask is similarly fixed. Into this a tubular support of tin-plate, surmounted by a horizontal portion, drops, this part of the arrangement being used for holding watch-glasses and such drying-tubes as that described on p. 136. A moveable iron wire triangle, mounted with pieces of tobacco-pipe, completes the desiccator. Lumps of calcium chloride are used as the drying material. The annexed diagrams (figs. 11, 12, and 13) will explain the construction of this form of portable desiccator, and illustrate its uses better than further verbal description.

A very convenient form of portable desiccator may now be obtained of the dealers in chemical apparatus. In shape it somewhat resembles an hourglass, the slightly constricted part in the middle being occupied by a horizontal perforated plate, on which the object to be kept dry is to be placed. Below this, on the floor of the lower compartment, some lumps of calcium chloride are arranged, while the upper compartment is closed with a ground-glass plate.

Fig. 11.—*Vertical section of Desiccator.*

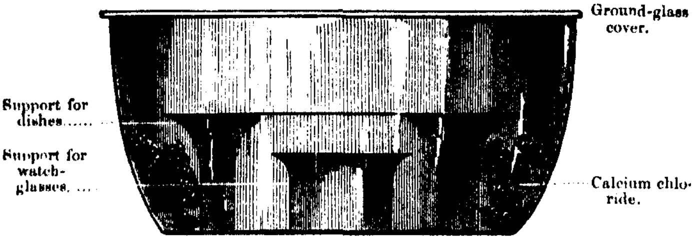


Fig. 12.—*View of Desiccator from above.*

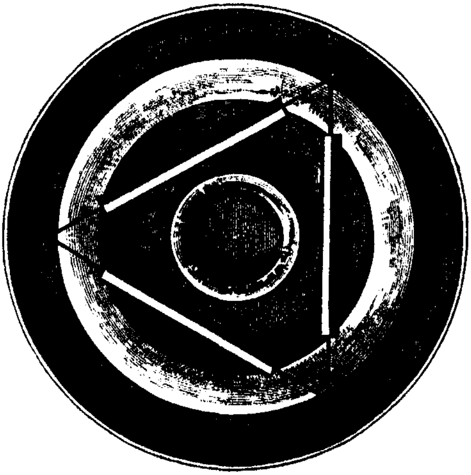
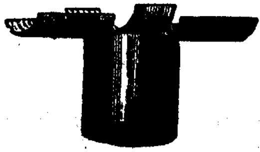


Fig. 13.—*Moveable support for watch-glasses and tubes.*



4. An iron wire triangle covered with tobacco-pipe, or a platinum triangle, or one of nickel-wire, is used to support crucibles in a ring of the retort-stand when they are being heated.

5. Besides the ordinary wash-bottle with moveable jet for cold water, a flask similarly fitted for hot water is required for washing many of the precipitates obtained in the processes of quantitative analysis. Small washing-flasks or bottles for dilute hydrochloric acid, for dilute ammonia, and for alcohol and ether should also be at hand.

6. A few funnels having four internal ribs as suggested by Messrs. Hehner and Richmond, will be found very useful for rapid filtration.

Amongst the more important general apparatus and fittings of the laboratory for quantitative analysis we may name the following:—

1. The water-oven for drying substances previously to analysis should be very capacious. It should be made of copper, and be divided into at least two cupboards. By means of sliding glass screens or shutters in these cupboards the temperature of those parts of them most distant from the doors may be maintained within two or three degrees of 100° C. The steam which serves to heat this water-oven may be advantageously condensed by means of a worm of pure tin or tin-lined pipe, and so yield an abundant supply of distilled water.

2. A hot air- or oil-bath heated by a self-acting gas-regulator.

3. A gas combustion-furnace, constructed according to one or other of the various plans in use. With due care Griffin's or Erlenmeyer's combustion-furnace answers well.

4. A table-blowpipe, fitted with double-bellows, and a Herapath blowpipe for glass-working. Fletcher's hot-blast blowpipe and his gas-furnace and muffle will also be found useful.

5. A small hand-mill for grinding samples.

6. A set of cylindrical zinc sieves of graduated fineness, and fitting into one another.

7. An apparatus for filtering under increased pressure.

For further details concerning laboratory apparatus and fittings, reference may be made to the works of Greville Williams, Thorpe, and Dittmar: but some additional contrivances will be found described further on in the present volume.

§ ii. PRELIMINARY INSTRUCTIONS IN QUANTITATIVE OPERATIONS.

The details of the quantitative estimations which have to be performed in the analysis of agricultural materials and products are best learned by practice on pure substances of known composition. For this purpose standard solutions are most convenient, for each analysis an accurately measured portion being taken. The quantity to be employed, and the strength of each solution, will be indicated further on.

Estimation of Lime.

Solution employed, $CaCO_3$ in HCl ($=CaCl_2$), containing about ½ a per cent.

The solution, about 60 c. c., is to be diluted with an equal volume of water and heated nearly to boiling, then add excess of ammonium oxalate and ammonia until the liquid, after stirring, smells strongly ammoniacal; cover the beaker, and set it aside for twelve hours in a warm place; decant off the clear liquid through German or Swedish filter-paper, add hot water to the precipitate, allow it to subside, again decant, then add more hot water, and transfer the precipitate to the filter, allowing all the liquid to run through the paper before adding a fresh portion. Remove every particle of the precipitate from the beaker with the aid of a feather, or of a rod one end of which has an inch of india-rubber tubing tightly fitted on to it. Wash the precipitate on the filter with hot water, avoiding using a rapid stream, or some of the precipitate may be driven through the pores of the paper: the precipitate should be carefully washed down from the side of the filter-paper so as to form a compact mass at the bottom of the cone. Dry, transfer the precipitate to a weighed crucible, leaving as little as possible adhering to the paper, which is to be tightly folded (in such a way as to bring the central portion of the filter into the middle of the compact folded paper), and burnt in a coil of platinum wire over a crucible standing upon a sheet of glazed black paper; add the ashes of the paper and any particles on the glazed paper to the precipitate in the crucible, and slowly heat till the bottom of the crucible is just visibly red in the dark, for about ten minutes. When cold, weigh, and then moisten the precipitate with water, and test it with turmeric paper; if an alkaline reaction be shown, it is due to caustic lime, produced by the application of too strong a heat; add a little $(NH_4)_2CO_3$ solution, and evaporate very cautiously, at a temperature below 100° C., to dryness; ignite as before, being careful not to use too high a temperature. It may be necessary to repeat this treatment.

Reactions:—

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl;$$

$$\text{by heat, } CaC_2O_4 = CaCO_3 + CO;$$

the $CaCO_3$, if heated too strongly, loses CO_2, becoming CaO, and necessitating the "carbonating" with $(NH_4)_2CO_3$.

The resulting $CaCO_3$ should have the same weight as that originally dissolved in the liquid.

Estimation of Magnesia.

Solution of magnesium sulphate ($MgSO_4 7H_2O$) employed, containing about 1½ per cent.

To the solution (50 c. c.) add ammonium chloride (NH_4Cl) and ammonia (NH_4HO); if the addition of the latter causes a precipitate, enough NH_4Cl has not been added; therefore add a further quantity, sufficient to dissolve the precipitate formed. Then add gradually sodium phosphate (Na_2HPO_4) in excess, and stir the mixture, avoiding touching the sides of the beaker with the stirring-rod; cover the beaker, and let it stand twelve hours in the cold. Collect the precipitate on a filter, and wash with water containing ammonia (NH_4HO) in solution (a mixture of 1 part of strong solution of ammonia and 7 parts of water) until a few drops of the filtrate, evaporated on a watch-glass or pla-

Preparation.—Having determined to make a certain volume of the alkali (say 2 litres), calculate the amount of hydrate required; thus, if sodium hydrate be used, and the acid contain exactly 49 grams H_2SO_4 in a litre=·98 gram in 20 c. c., then, since H_2SO_4 saturates 2NaHO,

Molecular weight. H_2SO_4		Molecular weight. 2NaHO		H_2SO_4 in 20 c. c.		NaHO in 100 c. c.
98	:	80	=	·98	:	:8.
c. c.		NaHO		c. c. taken.		NaHO required.
100	:	·8	=	a	:	x.

Weigh out the amount calculated, and add to it water to about three fourths the volume it is intended to make; dissolve and well mix, and then ascertain by experiment how many c. c. and fractions of c. c. are required to neutralize 20 c. c. of the acid, a little litmus solution being added to the portion of acid measured out in order that, by its change of colour to purple, the point of neutralization, when enough soda has been added, may be shown, duplicate determinations being made to exclude error. The alkali should be rather stronger than is required; but, its volume being known, it is easy to dilute it to the required strength; thus, if 90 c. c. neutralize the acid, and there are 1848 c. c. made,

$$90 : 100 = 1848 : 2060,$$

the number of c. c. to which the alkali must be made up. This is then done and the strength again tested, when 20 c. c. of acid should be exactly saturated by 100 c. c. of the alkali.

The solution should be kept in well-stoppered bottles in a cool place, or in a bottle through the cork of which a tube containing a mixture of equal parts of sodium sulphate and quicklime, gently ignited together, is placed; it may then be kept a long time without deteriorating.

The value of each c. c. of the alkali has now to be calculated. Since H_2SO_4 saturates $2NH_3$, if the strength of the acid and alkali be as above,—

H_2SO_4		$2NH_3$		H_2SO_4 in 20 c. c.		NH_3
98	:	34	=	·98	:	·34.

20 c. c. of the acid are neutralized by 100 c. c of the alkali; therefore each c. c. of the latter corresponds to $\frac{\cdot 34}{100} = \cdot 0034$ gram NH_3, or ·0028 gram N.

Suppose that, after a nitrogen combustion, the contents of the bulb are exactly neutralized by 65 c. c. of the alkali, it is obvious that the acid has absorbed ammonia during the combustion equal in saturating power to 35 c. c. of the alkali, since 20 c. c. of the acid were originally taken; $35 \times \cdot 0034 = \cdot 119$, the weight of NH_3 obtained, or $35 \times \cdot 0028 = \cdot 098$, the weight of N; from either of which the percentage is obtained.

If the grain, septem, and cubic inch are the weight and measures used, a cubic inch of acid should contain 8·5 to 9 grains H_2SO_4, and 200 septems of alkali should neutralize a cubic inch of acid; the calculation to find the amount of vitriol of, say, 96 per cent., required to make a certain number of cubic inches of dilute acid, 9 grains per cubic inch, will then be :—

cub. in.		grains H_2SO_4.		cub. in.		grains H_2SO_4.
1	:	9	=	a	:	x

P. c. H_2SO_4.	•	Oil of vitriol.		grains H_2SO_4.		grains oil of vitriol required.
96	:	100	=	x	:	y

Determine the exact amount of H_2SO_4 per cubic inch in the same way as above given.

The calculations for the amount of sodium hydrate required, and for the value of each septem, will be conducted in the same manner as if grams and c. c. were employed.

The litmus solution used in these experiments to ascertain when neutralization has been effected is made by digesting crushed litmus in twenty times its weight of distilled water for a few hours, decanting, filtering, and dividing the filtrate into two equal portions, adding very dilute nitric acid to one until it is faintly red, and then mixing with the other portion; the whole will then be violet, neither blue nor red. It should be mixed with alcohol and kept in a bottle, with an open bent glass tube through the cork, as if tightly corked it loses part of its colour and sensitiveness. Instead of litmus a solution of 'helianthin' ('methyl-orange') may be used. This is an orange-coloured compound which becomes purple in the presence of a trace of free acid.

Another very good example of a quantitative volumetric estimation for practice is furnished by *iron*. Full directions are given on pp. 154–156.

CHAPTER II.

§i. ANALYSIS OF MANURES.

BEFORE beginning the several operations and analyses which follow, the directions given should be carefully read over, in order that a clear idea of the whole plan to be pursued may be first obtained.

BONE-DUST, BONE-SHAVINGS, BOILED BONES, &c.

These, and all other forms of unburnt bones, consist of calcium phosphate, calcium carbonate, carbonaceous and nitrogenous matters commonly called organic matter, moisture, with sandy impurities and minute quantities of other substances. The analysis for commercial purposes may be conducted as follows. Too much care cannot be exercised in order to secure a fair average sample of the manure. Eight or ten portions from different bags are first taken: these are well mixed; and a part is then reduced, by grinding, sifting, and regrinding, to a moderately fine powder.

MOISTURE.—A convenient quantity, say 2 or 3 grams, is weighed into a watch-glass, and kept in the water-oven, at the temperature of 100° C., till it ceases to lose weight; the loss is moisture.

ORGANIC MATTER.—Weigh about 1·5 gram (or 25 grs.) into a platinum crucible, cover it loosely with the crucible-lid, and raise the temperature very gradually to low redness. When the mass appears white, and no incandescent particles are exposed on gently stirring with a platinum wire, the whole is allowed to cool, and then weighed; the loss is carbonaceous or organic matter plus combined water and moisture. The percentage of the latter constituent, having been determined in the preceding operation, is to be deducted from this loss (after its conversion into a percentage)—the remainder will then represent organic matter and combined water.

The heat employed should be as low as possible, to avoid the expulsion of carbonic acid from the calcium carbonate. If it be feared that this has occurred, moisten the whole with ammonium carbonate solution, dry on the water-bath, heat to low redness for a few seconds, and again weigh.

SAND.—The portion just calcined is removed to a beaker, and digested in dilute hydrochloric acid till nothing but the sand remains; this is collected on a filter, washed, dried, burnt, and weighed.

PHOSPHATES.—The filtrate and washings from the sand are now diluted to about 300 c. c. (or 10 ozs.), a very slight excess of ammonia added, the precipitated phosphates allowed to settle and collected on a filter. After two or three washings, the precipitate is rinsed from the filter into a beaker, the paper repeatedly moistened with hydrochloric acid and washed, the acid washings being allowed to run into the beaker containing the precipitate. The precipitate redissolves in the acid thus added (which should be as small a quantity as possible); the solution is diluted to about 300 c. c., ammonia in slight excess added, and the precipitated phosphates collected, thoroughly washed with water slightly ammoniacal, dried, burnt, and weighed.

The object of redissolving the phosphates is to separate the lime mixed with the precipitate; ordinary washing would fail to effect this: to lessen still further this source of error, precipitation is effected in a cold and dilute solution, and with the smallest possible excess of ammonia. These precautions are necessary whenever the calcium phosphate is associated with considerable amounts of other lime-salts. The ignited calcium phosphate should not effervesce with acids; if it does so, it is evidently contaminated with carbonate, and should be redissolved and again precipitated.

N.B. Calcium phosphate is not quite insoluble in water; in a careful analysis therefore it is well to concentrate the whole of the filtrates and washings to about 150 c. c., add a little acid to dissolve the calcium carbonate deposited, boil to expel carbon dioxide, and finally precipitate with ammonia, collect, and weigh. The amount thus obtained is usually about ½ per cent.

CALCIUM CARBONATE.—This may be estimated in the united filtrate from the phosphates by boiling with ammonium oxalate; but for commercial purposes this determination is frequently omitted, the amount of calcium carbonate present being sufficiently indicated by the difference between the sum of the percentage of the other ingredients and a hundred parts. The precipitation of lime by ammonium oxalate should always be effected in a *dilute* and *hot* solution. In igniting the precipitate the heat should not exceed a very low redness. When long burning has been necessary, it is advisable to moisten the residue with ammonium carbonate, and again ignite it gently before weighing; see page 133.

NITROGEN IN ORGANIC MATTER.—Make a combustion for nitrogen with about 1 to 1·5 gram (or 15 to 25 grs.) of the *finely* powdered substance.

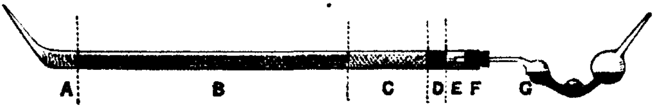
Estimation of Nitrogen.

All the more common nitrogenized substances likely to be met with, give off, when heated with soda or soda-lime, the whole, or very nearly the whole, of their nitrogen in the form of ammonia. While some of the oxygen of the soda-lime unites with the carbon of the organic matter to form carbon dioxide, the hydrogen unites with the nitrogen to yield ammonia. The nitrogen of substances like hair, wool, albumen, &c. is less completely evolved as ammonia in this way; they should be mixed with ten times their weight of pure dry starch and be burnt in a longer tube. The soda-lime used may be prepared by adding 750 grams of freshly burnt quicklime in small fragments to a litre of water in which 500 grams of good sodium hydrate and 5 grams of sodium thiosulphate have been previously dissolved. The mixture is effected in an iron pot covered with a sheet of tinned iron. Allow the lime to slake in the soda-solution, and then put the pot over a fire and evaporate the contents, constantly stirring them with an iron spatula until they are apparently dry. The dry mass is next transferred to an iron or Hessian crucible, and exposed to a dull red heat for an hour or two. When nearly cold the dry mass is to be pounded up in a warm iron mortar, and then passed through a wire-gauze sieve of 7 meshes to the linear inch. Separate the product into two grades by means of a sieve having 22 meshes to the linear inch, and preserve separately the fine part or powdery soda-lime and the coarse part or granular soda-lime in a number of well-corked phials.

Before commencing an analysis heat a sufficient quantity both of the fine and of the granular soda-lime in separate dishes till dry; then return the materials to the phials. The phials should have small necks without flanges, and of less diameter than the bore of the combustion-tube. The latter is made from hard combustion-tubing having a bore of about 14 millimetres and a length of 25 to 50 centimetres (9 to 18 inches); one end is drawn out obliquely to a strong point or tail.

The lower part of the tail of the tube is first of all loosely plugged with a little freshly-heated asbestos; then a little fine soda-lime is introduced and another dry asbestos plug. Pour in a little more soda-lime, then add about half the substance to be analysed from a previously weighed sample-tube, and introduce some more fine soda-lime. Mix the substance and the soda-lime in the tube by means of a clean brass or copper wire about 60 millimetres in length, twisted at one end like a corkscrew, and with a ring at the outer end to serve as a handle. This wire is pushed down and rapidly moved about in all directions, until no particles of unmixed substance can be detected. Some more fine soda-lime is introduced now, followed by the remainder of the substance from the weighed sample-tube—the latter is put carefully on one side, to be afterwards weighed; the difference between the original and the second weighing shows the amount taken; this should vary from ·7 to 2·7 grams, according to richness in nitrogen. More fine soda-lime is added, and the mixing process repeated. This done, another addition of fine soda-lime is made, and the wire carefully withdrawn. Place the tube in a vertical position and introduce a third plug of asbestos. Fill up the rest of the tube with granular soda-lime and a plug of asbestos; rap the tube gently on the bench. Fig. 14 shows the arrangement of the combustion-tube when ready for heating, the part of the contents marked A representing fine soda-lime, that marked B indicating the mixture containing the substance, and that marked C being the granular soda-lime; D is the last asbestos plug: a small space, E, is left free. The tube is finally closed with the cork, F, through which passes the end of the nitrogen bulbs, G.

Fig. 14.



The bulbs, containing 20 c. c. (or a cubic inch) of the standard sulphuric acid, and attached to a sound perforated cork, should be in readiness previous to the mixing of the substance with the soda-lime. It should be stated here that the amount of any nitrogenous substance taken for analysis must depend upon its richness in nitrogen; with bone-dust not more than 1 gram (or 15 grains) should be employed. Unless the substance contain ready-formed ammonia (like guano and ammonium salts) the soda-lime may be introduced warm into the tube. The bulbs are filled by measuring the acid into a beaker, inserting the point of the bulbs into the liquid, and applying suction at the other end; then wash down the point with a jet from a wash-bottle into the beaker, and set the beaker aside until the combustion is complete.

The combustion-tube is now placed in the furnace; but before being heated it should be ascertained if the apparatus is perfectly air-tight: to prove this, gently heat the bulb nearest the combustion-tube, and expel a few bubbles of air, allow it to cool; then if the acid rises to a higher level on the inside, and remains so four or five minutes, the tube is air-tight; otherwise the acid in each bulb will return to the same level.

The tube is now to be gradually heated, from end to end, commencing at the end near the bulbs, care being taken that the cork is neither scorched by too great a heat nor moistened by the condensation of liquid upon it. A moveable plate of mica enables one to regulate the temperature of the cork with exactness. Too high a temperature must be avoided, or the tube will be fused or blown out; the operation is over when the closed end has been reached, and no more gas is evolved; towards the end of the operation the heat must be considerably raised. When the process is completed, the acid in the bulbs will begin to recede towards the combustion-tube; when this occurs, and the liquid in the further bulb is at a lower level than that in the other bulb, the fine point of the tube is nipped off, and air, equal in volume to about four times the capacity of the tube, drawn through the apparatus. Or, in order to avoid this aspiration of air, about 4 centimetres in length of the combustion-tube, at the closed end, may be charged with a mixture of equal parts of zinc-dust and soda-lime. On heating this, at the conclusion of the experiment, hydrogen will be evolved, and will drive out any remaining ammonia. The bulbs are now detached, and the acid liquid is emptied into the beaker containing the residue of the measured quantity of acid, the bulbs being rinsed out repeatedly with distilled water. Some solution of litmus (or other "indicator," as methyl-orange, corallin, or cochineal) is added, and the neutralization of the acid completed with the standard alkali; from the quantity required the amount of ammonia or nitrogen in the substance burnt is calculated as before described (page 139).

When a gas-combustion furnace, consisting of a battery of 20 or 30 Bunsen burners, is employed, the flames must never touch the tube itself, which may be further protected by being placed in a trough of brass-gauze, or of sheet-iron lined with a thin layer of asbestos: perhaps asbestos-cloth affords the best protection to the tube.

It has long been known that the nitrogen of many organic and inorganic substances was not wholly and invariably obtainable in the form of ammonia by combustion with soda-lime. Nitrates and compounds in which cyanogen or oxides of nitrogen may be assumed to exist are striking examples of substances which give discordant and imperfect results by the ordinary method. But there are also some albuminoid bodies (some of the nitrogenous constituents, for example, of East-Indian linseed-cake) which do not yield quite the whole of their nitrogen in the form of ammonia when they are burnt with soda-lime. But there are two methods by which the majority of such bodies (and ammonia-salts as well) may be satisfactorily analysed. One of these, known as Kjeldahl's method, will be described further on (p. 233); the other is a modification of the soda-lime process, and was introduced by Ruffle. We now proceed to describe the latter:—

Ruffle's Thiosulphate Method.—The combustion-tube may have the form adopted in ordinary soda-lime combustions, and should be 20 inches long and of ½-inch bore. A dry, loosely-fitting asbestos-plug is first introduced, and then 1 inch of the thiosulphate mixture. This consists of equal weights of dry powdered slaked lime and of finely-powdered crystals of sodium thiosulphate. The weighed portion of the substance to be analysed is intimately mixed with an equal weight of a mixture of equal weights of pure flowers of sulphur and pure finely-powdered wood charcoal, and is then placed (in a mortar or on a sheet of glazed paper) upon enough thiosulphate mixture to fill 10 inches of the tube. Mix thoroughly and introduce by means of a funnel into the tube. Rinse the mortar or paper with a little more mixture, and add the rinsings to the tube, and then fill up the tube with granular soda-lime to within 2 inches of the open end of the tube. Place a second plug of ignited asbestos in the tube, and close the latter with a cork. Rap the tube, held horizontally, so as to form a small channel, along its whole length, above the contents. Place the charged tube in the furnace, withdraw the plain cork and attach the nitrogen-bulbs previously charged with the proper amount of standard acid. Gradually heat the portion of the tube containing the soda-lime, and then that containing the mixture—the evolved gases should come off at the rate of 2 or 3 bubbles per second. The rest of the operations are conducted as in the ordinary soda-lime process, a solution of cochineal being used as an indicator in the titration with the standard alkali. A blank analysis will serve to show whether the materials themselves are free from nitrogen.

The use of wrought-iron tubes for nitrogen determinations with soda-lime has been adopted by some analysts. The screw cap with which one end is closed is secured by moistening its thread with hydrochloric acid before screwing it on; the tube is then heated once with soda-lime alone. The absorption-tube for the evolved ammonia is a U-tube having 3 bulbs, a constriction at the base of the further limb, and a thistle-head prolongation at its summit; part of this limb is filled with glass beads, but these cannot pass the constricted bend into the nearer limb. This absorption-tube is attached directly to the open end of the iron combustion-tube by means of a cork kept from charring by means of a trickling stream of water directed on to some strands of tow which are wound round it and the contiguous extremity of the tube, and the ends of which hang down below to conduct the excess of water away.

NOTE.—*Bone-dust is not unfrequently adulterated with gypsum; it is then requisite to determine the sulphur trioxide present, from which the amount of gypsum may be calculated.*

SULPHUR TRIOXIDE.—Digest about 3 grams (or 50 grs.) of the original sample with dilute hydrochloric acid till the phosphates are dissolved; dilute to about 250 c. c., and boil for half an hour; filter, wash the residue till sulphur trioxide ceases to be found in the washings, and precipitate the filtrate with barium chloride in the usual way. The barium sulphate should, after ignition, be moistened with a drop of strong nitric acid and again ignited, in order to reconvert into sulphate any barium sulphide that may have been formed by the reducing action of the organic matter mechanically carried down with the precipitate.

Vegetable-ivory turnings have been found in bone-dust and bone-shavings; they are of no value as manure. They consist chiefly of cellulose, and may be detected by their microscopic structure or by the action of H_2SO_4 of sp. gr. 1·53, which dissolves them without blackening, and forms a solution which, on warming, diluting with water, and addition of ammonia, gives no precipitate.

BONE-BLACK, ANIMAL CHARCOAL, &c.

Partially burnt bones are to be analysed in the same way as fresh bone. They often contain a mere trace only of nitrogen. If it be required to determine the carbon present, this may be done by digesting 3 grams of the substance with dilute hydrochloric acid and collecting the residual sand and carbon on a tared filter, and weighing it after drying at 100° C. The carbon and filter-paper may then be burnt away in a crucible. The loss will represent the carbon and filter.

BONE-ASH.

The organic matter, being very small in amount, may be neglected, and the whole volatile matter estimated together by carefully heating to low redness some of the finely powdered sample; this should be done in a covered crucible, as decrepitation is apt to occur. The analysis is in other respects conducted as with bone-dust.

Not more than 1 gram (or 16 grs.) should be taken for analysis.

A nitrogen combustion is unnecessary.

APATITE,

and its numerous varieties, known as phosphorite, osteolite, staffellite, &c., contains a very large proportion of calcium phosphate associated with calcium chloride or fluoride, and minute quantities of moisture, oxide of iron and alumina, insoluble matter (which, in the case of some apatites, is partly a cerium phosphate called *cryptolite*), and occasionally calcium carbonate.

Fluorine should be first tested for. Some of the powdered mineral is placed in a platinum vessel, moistened with oil of vitriol, and the vessel covered with a plate of glass thinly coated with wax, through which a few fine lines have been traced with a point of wood or bone: the platinum vessel is then very slightly warmed. If on removing the wax the lines are found etched on the glass, fluorine is certainly present. If fluorine is found it must be expelled from the quantity taken for analysis by evaporating the hydrochloric solution with sulphuric acid; the temperature used must not be such as to volatilize the sulphuric acid. The residue is redissolved by boiling it with water and hydrochloric acid.

The CALCIUM PHOSPHATE, and the CALCIUM of the calcium chloride, fluoride, or carbonate, are determined exactly as in bone-dust; 1 gram will be sufficient for an analysis.

CHLORINE is determined in 3 grams of the substance. It is reduced to very fine powder, dissolved in dilute nitric acid, care being taken to warm the mixture, if at all, as slightly as possible; *if necessary the solution is filtered. Silver nitrate is added to* the warm solution as long as it produces a precipitate; the fluid is briskly stirred, and, if necessary, left in a warm place till the precipitate has thoroughly coagulated: the silver chloride is finally collected on a small filter, washed with cold water, dried, ignited, and weighed.

The latter operations require some care; they are effected as follows:—The precipitate is separated from the paper with a penknife, and placed in a porcelain crucible; the part of the paper to which the precipitate adhered is cut into several pieces, and carefully burnt on the lid of the crucible. When cold, the ash is moistened with strong nitric acid, and the crucible lid placed on the water-bath; when nearly dry a drop of hydrochloric acid is added, and evaporation allowed to continue: after drying, gently ignite, place the lid on the crucible and heat the silver chloride to incipient fusion, cool, and weigh.

COPROLITES.

Coprolites consist chiefly of calcium phosphate and carbonate; they contain, besides, variable and sometimes considerable amounts of silica, ferrous silicate, pyrites, ferric oxide, and alumina, also a little magnesia, carbonaceous matter, and moisture, and frequently fluorine. They are sometimes analysed for commercial purposes in the same way as bone-ash; the result, however, is not equally satisfactory, chiefly owing to the much larger amount of calcium carbonate present, and to the precipitation of calcium fluoride with the phosphate: the percentage of phosphate found is thus always excessive.

To acquire an accurate knowledge of their value, the phosphorus pentoxide present must be determined. This, with the determination of lime, silica, and volatile matter, will be sufficient for commercial purposes.

Fluorine may generally be detected according to the method for apatite; this plan, however, may possibly fail if the coprolite contain much silica: if therefore no etching is produced on the glass, a second experiment should be tried in which the glass cover is moistened on the underside in place of being waxed. If after the application of a gentle heat the wet surface becomes opalescent from the deposition of gelatinous silica, fluorine is certainly present. The presence of fluorine in small quantity is not prejudicial to the processes now to be described; if, however, simple precipitation with ammonia be resorted to, it should be previously removed (see Apatite).

If a complete analysis be desired, a determination of carbon dioxide will be necessary; for this purpose see Analysis of Soil (p. 200).

MOISTURE AND ORGANIC MATTER are determined together, as in bone-ash.

SILICIOUS MATTER.—1 gram of the powdered* coprolite is digested in a beaker with moderately strong hydrochloric acid. The fluid is finally evaporated to dryness, and the residue gently heated on a sand-bath for some time to render insoluble the whole of the silica. If the sample contains any appreciable amount of iron pyrites, the residue must now be warmed with a little nitro-hydrochloric acid and again dried at a gentle heat. The mass, when cold, is moistened with concentrated acid, and, after standing about twenty minutes, treated with a little water and warmed: more water is finally added, heat again applied, and the insoluble matter (which should appear quite free from iron) collected, washed, ignited, and weighed.

If ferric oxide and alumina are to be determined, it is best to take twice the amount of coprolite here recommended, and after removal of silica, as before directed, to divide the solution into two equal portions; this division is most accurately effected by weight. For this purpose the filtrate and washings are collected in a tared flask, diluted to 200 c. c., well mixed, and the flask with its contents weighed; it is then easy to transfer to another vessel such a portion of the contents that the remaining part shall be counterpoised by exactly half the weight of the original liquid.

The phosphorus pentoxide and lime are now determined by the following process. When, however, the greatest accuracy is desirable, and especially where the material to be analysed contains much carbonaceous matter, the "Fusion Method" described under the head of Phosphatic Guanos (p. 156) should be followed for the determination of the P_2O_5. This constituent may be very accurately estimated by means of the molybdic-acid method (p. 192).

Oxalic-Acid Method.

LIME.—A few drops of very dilute ammonia are first added to the solution, with constant stirring, till a *slight* permanent opalescence is produced. A little oxalic acid is then added, and, after a few minutes, ammonium oxalate until it ceases to produce a precipitate. The whole is then warmed for some hours, that the calcium oxalate may aggregate; the precipitate is collected on a filter, washed, dried, ignited for some time at a very low red heat, and weighed. Any lime found in excess of that necessary to form tricalcic phosphate with the phosphorus pentoxide present is calculated as calcium carbonate.

PHOSPHORUS PENTOXIDE.—The filtrate and washings from the lime precipitate are concentrated to about 60 c. c., some citric acid is added, and then ammonia in decided excess. If a precipitate be immediately produced, it is a sign of the presence of lime, iron, or alumina. But if a slight crystalline precipitate come down on standing, this is due to the presence of magnesia in the material taken for analysis, and its presence will not interfere with the subsequent operations. The next step is to add, drop by drop, some "magnesia mixture": of this 10 c. c. will be required for every decigram of P_2O_5 present in the solution. After standing twelve hours the precipitate is collected, washed with rather strong ammonia water, dried, ignited gently for some time, and afterwards at a very high temperature before the Herapath blowpipe, and finally weighed. The precipitate, as already pointed out, has the formula $Mg_2P_2O_7$ after ignition; its equivalent in Ca_32PO_4 is found by calculation, 1 part of the former salt corresponding to 1·3964 of the latter.

Determination of Alumina, Ferric Oxide, &c.

ALUMINA.—The acid solution of coprolite, freed from silica, is precipitated by sodium hydrate, a considerable excess being added and the whole warmed for some time. The solution is next diluted, the precipitate allowed to subside, and the clear liquid poured on to a filter; the precipitate is washed with hot water three or four times by decantation, the washings being passed through the filter. The filtrate is warmed, and barium chloride cautiously added till it ceases to produce a precipitate; this precipitate contains all the phosphorus pentoxide present in the solution. A little sodium carbonate is next added to throw down the excess of baryta, and finally some more sodium hydrate. After digesting a short time, the solution is filtered. The precipitate on the filter is washed with water containing a drop or two of sodium hydrate solution. The filtrate and washings are then made distinctly acid with hydrochloric acid, a crystal of potassium chlorate added, and the whole warmed for some time to destroy any trace of organic matter. Ammonium chloride is finally added, and a *slight* excess of ammonia; the precipitated alumina is allowed to subside. It is to be thoroughly washed by decantation before removal to a filter. It is finally dried, ignited, and weighed.

Should the sodium hydrate contain either alumina or silica, this will fall with the alumina of the analysis and occasion an excess. The presence of impurities of this kind may be readily detected by neutralizing the soda with acid, adding ammonium chloride with a slight excess of ammonia, and allowing the liquid to stand some hours. If the soda contain silica only, the alumina, after weighing, may be dissolved in the platinum capsule with dilute sulphuric acid, heat being applied till the excess of acid has volatilized; the residue is dissolved in water and hydrochloric acid; the insoluble matter is collected and weighed as silica. Should the soda contain both silica and alumina, the total amount of impurity must be estimated, and a known volume of soda employed in the analysis. As caustic soda and potash when kept in solution become impure from their action on glass, it is best when a pure article is at hand to use it in the *solid* state. The caustic soda made from sodium is quite pure.

FERRIC OXIDE.—This is best determined by the volumetric method presently to be described; or the following plan may be adopted. The original precipitate by soda is dissolved in hydrochloric acid, and excess of ammonia added, and, lastly, a considerable excess of acetic acid. The solution is allowed to stand for some minutes in a warm place: the precipitated iron phosphate having then subsided, the clear liquid is poured on to a filter, and the precipitate well washed with warm water by decantation; a little ammonium acetate and a drop or two of acetic acid may be added to the water used in washing. The ferric phosphate will still contain a little tricalcic phosphate; it is therefore treated as follows:—The paper-filter is moistened with dilute hydrochloric acid, and finally washed, the washings being added to the precipitate in the beaker. Should the ferric phosphate fail to redissolve in the acid thus added, a little oxalic acid is introduced; neutral potassium oxalate is lastly added, and the whole warmed to aggregate the calcium oxalate; this is finally separated by filtration. The clear solution is now treated with a considerable excess of sodium hydrate and boiled for some time; the solution is then diluted, and the precipitated ferric oxide thoroughly washed by decantation, the washings being filtered as before. The ferric oxide is, lastly, redissolved in hydrochloric acid, precipitated by ammonia, and after washing a few times by decantation, collected, washed, dried, ignited, and weighed.

If the operation has been successful, no trace of phosphorus pentoxide will be found on redissolving the weighed precipitate in nitric acid, and applying the molybdic-acid test.

The above process is the most strictly accurate; good results may, however, be obtained by simply redissolving the ferric phosphate in hydrochloric acid, adding a few drops of sodium phosphate, and treating with ammonia and acetic acid, exactly as at first. The ferric phosphate thus reprecipitated is to be washed a few times by decantation, and finally collected, dried, ignited, and weighed. Its formula is $Fe_2 2PO_4$.

LIME may, if desired, be determined in the *acetic-acid* solution in the usual way; the small precipitate of calcium oxalate obtained on redissolving the ferric phosphate is weighed with the main precipitate.

MAGNESIA.—The filtrate from the lime is concentrated to 60 or 70 c. c., sodium phosphate and excess of ammonia are then added. The precipitate, after standing 12 hours, is collected, washed with strong ammonia-water, burnt, and weighed.

Lime and magnesia need not, of course, be separated here, unless duplicate determinations are desired.

Iron, Volumetric Method.

IRON is most speedily and accurately determined by means of a standard solution of potassium permanganate. To effect this, the iron is reduced to the ferrous state, and the permanganate added till the iron is exactly peroxidized, this point being known by the purple colour of the reagent remaining undestroyed: the volume of permanganate consumed indicates the amount of iron present.

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4$$
$$= 5(Fe_2 3SO_4) + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

The reduction of the iron to the ferrous state and its subsequent estimation are performed as follows:—

The solution of iron, in which not more than one gram of metal per litre must be present, and which must contain a large excess of free sulphuric acid, is placed in a small long-necked flask, fitted with a cork and tube bent at right angles; a few fragments of pure zinc are introduced, and the flask placed in an inclined position on a retort-stand, the tube attached bending downwards; the flask is *gently* warmed to facilitate the action. As the evolution of hydrogen proceeds, the fluid will become colourless; when this is perfectly effected, and the zinc all dissolved, the operation is completed; a drop of the liquid, if withdrawn on a glass rod and mixed with a drop of potassium sulphocyanide in a porcelain dish, will give no colour if the reduction of the iron is complete. The end of the bent tube is then immersed in distilled water, and the flask allowed to cool; the water will ascend the tube and enter the flask. When perfectly cold, the clear solution is transferred to a beaker, diluted, if necessary, to *500 or 600 c. c. with recently boiled, cold, distilled water, some* sulphuric acid mixed with it, and the permanganate *slowly* added from a burette till the fluid is uniformly *slightly* reddened, the whole being *constantly* stirred during the operation. The burette used must be entirely of glass, no india-rubber or other organic matter being allowed to come into contact with the permanganate.

The absence of iron in the zinc should always be ascertained by experiment. For this purpose it is digested with sulphuric acid till entirely dissolved; the solution, when cold, is diluted, and a drop of permanganate added: if the red tint is destroyed, the zinc certainly contains iron. In this case a volumetric determination of iron must be made in a weighed quantity of zinc, and the zinc taken for each subsequent operation weighed previously to use, and the amount of iron it contains calculated and deducted from the amount found. In working with impure zinc it is very necessary, to ensure constant results, that the *whole* of it should be dissolved, as the impurities are generally the last to disappear.

Preparation of the Permanganate Solution.

A quinquenormal solution is a convenient strength for the purpose. Dissolve 3·162 grams of dry crystals of potassium permanganate in a litre of water; keep in stoppered bottle. It will be seen by the equation, p. 154, since 2 equivalents of $KMnO_4$ have 5 available atoms of O, thereby peroxidizing 10 molecules of a ferrous salt, that 1 c. c. of this solution should theoretically correspond to ·0056 Fe, ·0072 FeO, or ·0080 Fe_2O_3: in practice, as the permanganate is never quite pure, it is better to take rather more than the above quantity—say, 3·2 grams instead of 3·162.

Its exact strength may be ascertained by dissolving about

1 gram of crystals of the double sulphate of iron and ammonium ($FeSO_4$, Am_2SO_4, $6H_2O$) in water, adding dilute sulphuric acid, and titrating with the permanganate solution. The double sulphate contains exactly $\frac{1}{7}$ of its weight of metallic iron; by dividing this amount by the number of c. c. of permanganate used, the value of each c. c. in metallic iron is at once found. If septems be the measure used, 27 grains of potassium permanganate should be dissolved in each 1000 septems ($\frac{1}{10}$ gallon) of water: the value of each septem will then be about ·04 grain of metallic iron.

If a deposit should form at the bottom of the bottle containing the solution of permanganate, it should be decanted, but never filtered through paper; the strength should also be determined at intervals of a few months, as it is liable to weaken by keeping.

PHOSPHATIC GUANOS; BASIC CINDER.

Sombrero, or Rock Guano, Navassa and Rodonda Phosphate, Carolina Phosphate, and many other similar materials are rich in phosphates; but these often consist in great part of those of iron and aluminium. These substances may be analysed as coprolites, but the most satisfactory way of determining the phosphorus pentoxide is by the molybdic-acid method, see page 192, in a nitric-acid solution of about ·5 gram of the material. The substance should previously be treated with strong hydrochloric acid and evaporated to dryness to render silica insoluble. The phosphorus pentoxide may also be determined in these materials by the process given here, and entitled the

Fusion Method.

The following is a very accurate method of determining the total phosphorus pentoxide present in phosphatic guanos: it may also be successfully employed in the case of nitrogenous guanos.

Weigh out about 2·5 grams of the finely powdered and dried sample, and mix them with 10 grams of a fusion mixture containing 2 parts of dry sodium carbonate to 1 part of dry potassium chlorate (or nitrate if much carbonaceous matter is present in the phosphate to be analysed). The mixing of the sample with the alkaline salt is best performed in a capacious platinum crucible by means of a glass rod, the end of the rod being wiped afterwards with a small strip of Swedish paper, which is thrown into the crucible. A gentle heat from a small and rather distant flame is first applied to the crucible, so that the oxidation may proceed quietly and without loss. When the mixture has become white, the heat is increased and maintained at full redness, so as to keep the contents of the crucible in fusion for fifteen minutes. The crucible, when cold, is placed in a beaker, with about 150 c. c. of water, and covered with a clock-glass. Then 30 c. c. of nitric acid (sp. gr. 1·25) are cautiously poured down the side of the beaker. The mass dissolves easily and completely, unless silica and silicates be present, in which case these substances must be removed in the way described under "Coprolites," p. 149. The solution containing the phosphorus pentoxide &c. is now diluted to 500 c. c., and a portion of it analysed by some appropriate process; the volumetric uranium method (p. 170), for instance, being preferably employed if iron and aluminium be virtually absent. The bases present may be determined in the remaining portion of the solution by the processes described under "Coprolites."

The manurial value of basic cinder (Thomas powder), as also of phospho-guanos, is largely dependent on the fineness of the particles. Basic cinder should be so finely ground that about 85 per cent. of it will pass through a sieve with 100 meshes to the linear inch, *i. e.* 10,000 to the square inch.

SUPERPHOSPHATES

contain considerable quantities of three compounds not found in bone-ash or coprolites, namely, phosphoric acid (H_3PO_4), monocalcic phosphate ($CaH_4 2PO_4$) and calcium sulphate. The other constituents of a superphosphate are insoluble calcium phosphate ($Ca_3 2PO_4$), dicalcic phosphate ($CaHPO_4$), ferric and aluminium phosphates, carbonaceous or organic matter, water, with small quantities of alkaline salts and sand, and, possibly, a trace of free sulphuric acid.

If the sample is a dry one, it may be prepared for analysis by lightly rubbing it in a mortar and sifting: if moist, it must be passed through a coarse sieve and well mixed, and then a part must be beaten into a smooth paste.

MOISTURE is usually determined by drying a few grams in the water-oven for about 2 hours. But the really free water is probably more nearly estimated by desiccation over a tray of ignited calcium chloride in a fairly good vacuum. For this experiment 2 to 5 grams are taken, spread out as much as possible on a watch-glass, and allowed to remain for 18 to 24 hours under the receiver of the air-pump.

ORGANIC MATTER and COMBINED WATER.—About 1 gram is gently heated over a burner. The loss, after deduction of the 'moisture,' represents approximately, but by no means exactly, these constituents of the superphosphate.

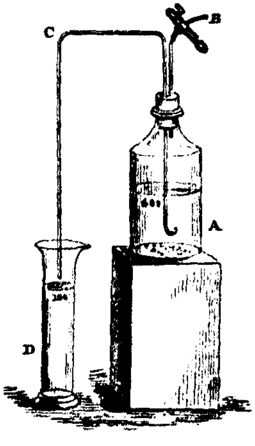
SILICIOUS MATTER.—About 1 gram gently dried over a lamp, but not ignited, is removed to a beaker, digested with hydrochloric acid and slowly evaporated just to dryness, &c. in order to render the silica insoluble. If iron pyrites be present the evaporation must be repeated with a little nitrohydrochloric acid, and again dried. The mass, when cold, is moistened with strong hydrochloric acid: after standing some time water is added, and the whole warmed until nothing but the sand remains undissolved. This is collected on a filter, thoroughly washed, dried, and weighed. In the filtrate and washings the total lime and the total phosphorus pentoxide are to be determined according to the directions on p. 151, "Oxalic-Acid Method." Ignition of the superphosphate is avoided in these directions in order to prevent any loss of the phosphoric acid.

SOLUBLE PHOSPHORUS PENTOXIDE.—Under this designation we may include the P_2O_5 existing in the monocalcic phosphate and in the free phosphoric acid of the manure. Both these compounds are produced from the tricalcium phosphate from which the superphosphate has been made by the action of the sulphuric acid, and both are freely soluble in water. The phosphoric acid is generally the more abundant of the two, and may be written

$3H_2O, P_2O_5$, or H_3PO_4; the monocalcic phosphate is expressed by the formula $2H_2O, CaO, P_2O_5$ or CaH_42PO_4. In order to determine the proportion in which these two soluble compounds, the *most important constituents of a superphosphate*, exist in a sample, they are estimated together by adopting the following method:—

5 grams of the well-mixed sample are taken; ½ a litre of water is measured into a wash-bottle; the superphosphate is then placed in a mortar and rubbed with a little of the water, grinding being avoided; more water is then added, and, after standing a few moments, the supernatant liquid is poured off into a stoppered bottle (A), a large funnel being placed in the bottle to prevent any loss. The residue in the mortar is rubbed with the pestle, and the washing continued as before, the rubbing and washing being repeated until the whole of the superphosphate taken has been transferred to the bottle. The remainder of the ½ litre of water is now added, and the bottle shaken at short intervals during three hours. The 100 c. c. required for the determination of monocalcic phosphate may now be filtered off, or the mixture may remain at rest 12 hours, and then the 100 c. c. may be, if the liquid is clear, removed from the bottle by means of a pipette or of a siphon, as shown in fig. 15. The cork, with its two tubes, having been fitted into the bottle A, the pinch-cock at B is pressed, and enough air blown through the tube to fill the siphon C. By keeping the pinch-cock open, the vessel D may be filled with the clear solution up to the mark indicating 100 c. c. If the solution be not clear, 100 c. c. must be filtered off through German or Swedish paper. The 100 c. c. are proceeded with exactly according to the directions given under Coprolite, on

Fig. 15.



page 151, and entitled the "Oxalic-Acid Method," omitting, however, the weighing of the calcium oxalate precipitate. The magnesium pyrophosphate obtained has now to be calculated into phosphorus pentoxide thus:—

(*a*) As eq. of $Mg_2P_2O_7$: eq. of P_2O_5 = ppt. : x. Now, as 100 c. c. yielding this amount of P_2O_5 contained 1 per cent. of superphosphate, x multiplied by 100 is the percentage of P_2O_5 in a soluble form existing in the original manure. It is usual to turn this into the corresponding percentage of monocalcic phosphate. This may be done by calculating the following proportion:—

(*b*) As eq. of P_2O_5 : eq. of CaH_42PO_4 = % of x : % of CaH_42PO_4. 1 part of this monocalcic phosphate corresponds to 1·33 part of "bone-phosphate rendered soluble," or to ·85 part of the so-called "biphosphate." If, therefore, a sample of superphosphate has been found to contain, *by calculation*, 20 per cent. of monocalcic phosphate, this figure may be entered in the column of percentages when the analysis is written out, but, at the same time, the quantity of tricalcic phosphate to which it corresponds, and from which it has been made, namely, 26·6 per cent., should be added. This latter figure, 26·6, should be enclosed in brackets with its proper designation "bone-phosphate made soluble," not "soluble phosphate," as it is vulgarly named. But as monocalcic phosphate constitutes a part only, and often a small part, of the soluble phosphorus pentoxide of a superphosphate, it is much to be preferred that the percentage of soluble P_2O_5 should be entered directly as such, adding in brackets the amount of "bone-phosphate made soluble" to which it corresponds: 1 part of P_2O_5 corresponds to 2·183 parts of Ca_32PO_4.

Tricalcic Phosphate.—The insoluble phosphates of a superphosphate are regarded as consisting almost entirely of unchanged bone-earth, Ca_32PO_4. In order to determine them, the filtrate and washings, obtained from one gram of the prepared sample in the estimation of the silicious matter as before described, are to be treated exactly in the manner given on p. 150 in the case of coprolites, adopting the "oxalic-acid method," and estimating both the lime and the phosphorus pentoxide as therein directed.

The $Mg_2P_2O_7$ obtained represents the *total* amount of P_2O_5 in the superphosphate. In order to learn how much of it was in the form of insoluble phosphates, calculate the $Mg_2P_2O_7$ found into P_2O_5 and then into a percentage, exactly as directed above, and then subtract from the percentage of total P_2O_5 the percentage of P_2O_5 found in the soluble part (see p. 160); then calculate the remainder into tricalcic phosphate, thus :—

As eq. of P_2O_5 : eq. of $Ca_3 2PO_4$ = residual $^0/_0$ of P_2O_5 : $Ca_3 2PO_4$. But a simpler plan may be adopted; in this the residual percentage is not converted into its equivalent of $Ca_3 2PO_4$ but directly entered in the tabulated results.

CALCIUM SULPHATE.—The whole of the calcium present in the superphosphate will now have been weighed in the form of carbonate. It really exists in the manure in the three states of monocalcic phosphate, tricalcic phosphate, and calcium sulphate. If it be desired to ascertain what amount of this last compound exists in the sample, it is best to make a direct determination of SO_3 in a small separate portion of the manure, by means of barium chloride in the presence of hydrochloric acid. The barium sulphate obtained is calculated into its equivalent of calcium sulphate. This ingredient in a superphosphate is entered in the anhydrous form, but it exists for the most part in combination with 1 molecule of water ($CaSO_4, H_2O$), and not as gypsum, $CaSO_4, 2H_2O$.

ALKALINE SALTS.—Evaporate the filtrate from the ammonio-magnesium phosphate to dryness and ignite till all fumes have ceased; let the residue cool, dissolve it in water; precipitate the magnesium present with barium hydrate, filter; then precipitate the excess of barium with ammonium carbonate and ammonia; filter, evaporate the filtrate to dryness, and heat the residue very gradually to low redness; it should be tolerably white.

The alkaline salts thus obtained are by no means pure, but their quantity is generally too small to be important. In cases where common salt and sodium nitrate have been added to the superphosphate, and the amount of alkalies is therefore comparatively large, it is necessary to treat the ignited residue with a little sulphuric acid, to ignite strongly, then to add a few drops of ammonium carbonate solution, and finally to evaporate and ignite the residue again: thus the definite composition of the substance weighed may be ensured. If qualitative testing prove that the superphosphate contain much chlorine, the sodium sulphate obtained should be calculated into sodium chloride.

Reduced or Retrograde Phosphates.—Under this name are included those phosphates which are believed to have once been in the soluble condition, but which are no longer dissolved by water. They consist chiefly of ferric and aluminium phosphates and dicalcic phosphate, and may be approximately estimated in superphosphates made from coprolites in the residue of 2 grams of superphosphate which have been exhausted with water, as in the determination of monocalcic phosphate. This residue is to be collected on a filter, care being taken to secure every particle of it. A neutral solution of ammonium citrate is used to extract the reduced phosphates. This solution is prepared by dissolving 370 grams of pure citric acid in 1050 c. c. of water; then nearly neutralize with commercial ammonium carbonate, heat to expel carbon dioxide, cool, and add ammonia to exact neutrality. Make up the volume to 2 litres, or so that the sp. gr. of the liquid is 1·09 at 20° C. Of the liquid thus prepared 100 c. c. are introduced into a 150 c. c. flask, and then the filter and contents are dropped in. The flask is corked and digested in a water-bath for 30 minutes at 65° C. with frequent shaking. Filter the warm solution quickly and wash the residue with cold water. Dry the filter and contents at 100°, ignite them till the organic matter is destroyed: add 10 to 15 c. c. of concentrated hydrochloric acid, and digest until the phosphate is dissolved, dilute to 200 c. c., mix, and pass through a dry filter. Take an aliquot part of the filtrate (usually 50 c. c.) and determine in it the P_2O_5 by the "molybdic-acid method," or by the "oxalic-acid method." Calculate the amount found into Ca_32PO_4, add this to the "bone-phosphate made soluble" and subtract the sum from the total phosphate; the remainder represents the amount of "reduced" or "citrate-soluble" phosphate expressed as $Ca_3 2PO_4$.

NITROGEN.—A combustion with soda-lime is made, using about 2 grams of the superphosphate. If the superphosphate be a moist one, the quantity weighed out must be partially dried in the water-oven before mixing it with the soda-lime. Superphosphates made entirely from bone-ash, apatite, coprolites, &c. contain no nitrogen.

A few notes on the composition of superphosphates may be found useful in arranging and appreciating the results of an analysis. We name the ingredients which have been determined in the order previously adopted.

WATER.—If a superphosphate be dried at 100° C. the loss represents not only the hygroscopic moisture of the sample, but also a portion of the water of crystallization of the calcium sulphate present. At 170° C. it appears that all the water present in any form in the superphosphate is driven off, save, indeed, the constitutional water of the monocalcic phosphate, and of the phosphoric acid.

MONOCALCIC PHOSPHATE &c.—If the superphosphate be a poor one, or if it contain much aluminium or iron, it should not remain longer than three hours in contact with the 500 c. c. of water, but should then be filtered off without waiting for the settling of the suspended matter. In fact, it is better in such cases to extract the superphosphate continuously with very small portions of cold water, filtering after each addition, and washing the residue on the filter so long as any phosphate is dissolved: the mixed filtrates may be cleared, if necessary, with a drop or two of dilute nitric acid. Hot water must on no account be used in extracting the last traces of the monocalcic phosphate and phosphoric acid. It often yields higher results, but their accuracy and constancy may be seriously impaired. Both dicalcic and tricalcic phosphates are altered by boiling water; and so an extract of a superphosphate which has been made first with cold water and then with boiling water will represent not only the amount of monocalcic phosphate and phosphoric acid, but a part of the other phosphates present, notably of those which have been called "reduced."

REDUCED PHOSPHATES.—A process for estimating these has been previously given, but the results are not quite so accurate as one would wish. It is a mistake to regard reduced phosphates as of equal value, in a manurial sense, with those which have been made (and which remain) soluble. They lack that initial diffusive power into the soil which monocalcic phosphate possesses. For, although it may be said that all soluble phosphates do ultimately become "reduced" in the ground, yet, owing to their solubility in soil-water, they will travel further and fertilize more earth before this change has been completed.

Nitrogen.—As ordinary superphosphates contain either no nitrogen or mere traces of so-called nitrogenous organic matter, we may defer any further directions, as to the determination of nitrogen in manures which have been enriched by artificial additions of ammonia-salts or nitrates, until the process for analysing phospho-guano, &c., be discussed.

Statement of Results.

There are in use two ways of stating the results of an actual analysis of a superphosphate. The simpler of these involves fewer assumptions and is sufficient for all practical purposes, the figures inserted being those which were obtained in the examination of an actual sample:—

		In 100 parts.
Moisture		18·46
Combined water and organic matter, containing nitrogen equal to ·34 ammonia		16·62
Total phosphorus pentoxide*, including—		
'Soluble' P_2O_5	13·03	
'Reduced' P_2O_5	1·06	
'Insoluble' P_2O_5	2·52	
		16·61
Calcium sulphate, $CaSO_4$		29·38
Alkaline salts, &c., undetermined		2·62
Silicious matter		3·72

The more common way of tabulating the analytical results is given below:—

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* Often described as "Phosphoric acid" or as "Phosphoric anhydride."

	In 100 parts.
MOISTURE, or loss at 100° C.	18·46
*ORGANIC MATTER AND COMBINED WATER	16·62
MONOCALCIC PHOSPHATE, $CaH_4P_2O_8$, equal to 18·18 biphosphate or 28·45 *bone-phosphate made soluble*	21·39
TRICALCIC PHOSPHATE, $Ca_3P_2O_8$, of which 2·31 was "reduced" phosphates	7·81
CALCIUM SULPHATE, $CaSO_4$	29·38
ALKALINE SALTS, &c., undetermined	2·62
SILICIOUS MATTER	3·72
	100·00

* Containing nitrogen equal to ·34 ammonia.

BEET MANURE. TURNIP MANURE. CORN AND GRASS MANURE. PHOSPHO-GUANO. SULPHATED GUANO. DISSOLVED GUANO, &c.

All manures containing soluble phosphates are analysed as a superphosphate. In some cases nitrogen and potassium compounds are present in considerable quantities and must be estimated, the nitrogen being usually determined, as before directed, by a combustion according to Ruffle's sodium thiosulphate method. In the case of superphosphates and other manures which can be easily reduced to a paste it is a good plan to grind a weighed quantity of the sample with an equal weight of sodium thiosulphate crystals, to dry the paste at 200° C., to weigh it again, and to take about 3 grams for the combustion. This is conducted as described on page 146. The potassium is determined as follows:—Make a hydrochloric solution of about 1 gram of the manure which has been previously gently ignited to char any organic matter present. Evaporate the hydrochloric-acid solution to dryness, and heat the residue slightly on a sand-bath to render insoluble the whole of the silica. The mass, when cold, is moistened with concentrated hydrochloric acid, treated with water, warmed and filtered. To the filtrate add ammonia and ammonium carbonate in excess, warm and filter. Evaporate the filtrate to dryness, and ignite the residue till all fumes cease. Dissolve the residue in the smallest possible quantity of water, filter, and add HCl and $PtCl_4$ in excess to the solution: the rest of the operations have been described under the head of the "Estimation of Potash," p. 135.

In analysing dissolved and sulphated guanos, the plan appropriate to superphosphates will answer well if the determinations of nitrogen and potassium mentioned in the preceding paragraph be also made. There is one other determination, that of sulphur trioxide, which will serve to render the analytical results more satisfactory. This estimation may be made by weighing out a convenient quantity of the manure (not more than 1 gram if dissolved Peruvian guano be under examination), and boiling it with dilute hydrochloric acid. Then the liquid is filtered off, and the residue in the beaker or flask again boiled with water and some dilute hydrochloric acid, and the liquid poured through the same filter as before. This process is repeated until a drop of the filtrate no longer gives any cloudiness with barium chloride; the sulphur trioxide is then estimated in the united filtrates by the process described on page 137. The amount of $BaSO_4$ obtained is calculated into a percentage of SO_3, which is set down in that form when the results of the analysis are tabulated. Or, if the nitrogen existing in the manure in the form of ammonia be separately determined in the manner described further on under Guano, it may be presumed to exist as ammonium sulphate; and then any surplus SO_3 may be written down as calcium sulphate. It must be remembered that, on igniting dissolved guano for the purpose of determining its volatile matter and combined water, the greater part of the sulphur trioxide is usually volatilized; a separate determination of SO_3 in the ash and residue is therefore requisite, or else some part of this constituent of the manure would be entered twice over. The difference between the total SO_3 and that found in the ash must be deducted from the total volatile matter lost on ignition, and the residue only entered as volatile matter.

PERUVIAN GUANO.

This valuable manure consists chiefly of the more or less altered excreta and carcases of sea-birds and of seals. It contains a large quantity of so-called organic matter rich in nitrogen together with ammonium carbonate, oxalate, phosphate, and urate. Calcium, magnesium, and alkaline phosphates are also present, together with moisture and a small quantity of silicious matter. *The Peruvian guanos now imported* are much poorer in nitrogen compounds and more variable in composition than the old Chincha Islands guano: occasionally cargoes damaged with sea-water are imported; this injury may be detected by the high percentage of moisture found, and by the presence of common salt, the amount of which may be determined by the process for chlorine given under apatite, p. 149. The adulteration of guano with ochre may be detected by the red colour of the ash it leaves; while the admixture of peat, clay, or sand may be ascertained by the increases in the normal percentages of volatile matter, of ash, or of silicious matter which they respectively cause.

Great care must be taken in order to secure a fair average sample of guano for analysis. Several portions should be taken, well mixed and powdered, and then preserved in a bottle having a good stopper.

MOISTURE is determined at 100° in the usual way. Occasionally, especially if the guano be damp, this determination is apt to yield results which are too high, from the volatilization of the ammonium carbonate present, along with the water.

The amount of ammonium carbonate lost in the water-bath is easily found by making a second nitrogen combustion in the guano after it has been dried. The percentage of nitrogen (calculated from the weight of the guano *before* drying) is subtracted from the total nitrogen found in the fresh guano; and the difference, calculated as $2(NH_4)_2O, 3CO_2$, gives the amount lost in the water-bath; this of course, when deducted from the actual loss, gives the true moisture.

Organic Matter is determined in about 2 grams, exactly as in bone-dust. A genuine guano gives a perfectly white ash.

Sand and Calcium and Magnesium Phosphates are determined as in bone-dust.

As calcium salts other than phosphate are seldom present in the ash of a genuine guano, it is unnecessary to make the solution dilute before precipitating by ammonia: the re-solution of the phosphates is for the same reason omitted.

Alkalies.—These are for commercial purposes determined by difference; the phosphorus pentoxide they contain should, however, be estimated, as it is of equal importance with that of the soluble monocalcic phosphate.

Phosphorus Pentoxide in Alkalies.—The filtrate from the phosphates is concentrated, and a little ammonium oxalate added. Should a decided precipitate be formed, phosphoric pentoxide can be present only as a mere trace and need not be further looked for; the calcium oxalate is in this case collected, burnt, and weighed, the amount found being placed in the analysis as calcium carbonate or sulphate, as a qualitative examination may indicate. If ammonium oxalate produces *no* precipitate, or a mere opalescence, the solution, filtered if necessary, is treated with a little magnesium sulphate and a considerable excess of ammonia; the precipitate of ammonium magnesium phosphate is collected, washed, burnt, and weighed. The $Mg_2P_2O_7$ is calculated into phosphorus pentoxide.

Total Nitrogen.—A combustion is made with about ·7 gram of the substance. The undried guano should be weighed in a small corked tube, and mixed with the soda-lime as speedily as possible, in the combustion-tube itself, by means of a wire terminating in a corkscrew twist: the bulbs filled with acid should be then at once attached. If these precautions be neglected, ammonia will be lost (see p. 143).

Nitrogen existing as Ammonia Salts.—If it be desired to ascertain what proportion of the nitrogen in a guano exists in the form of compounds of ammonia, the following plan may be adopted:—Into a small retort having its beak directed upwards, introduce about 1 gram of the guano, a little pure water, and some calcined magnesia. The beak of the retort is fitted with a cork and bent delivery-tube, which latter is connected with a nitrogen bulb containing 20 c. c. of the standard sulphuric acid used for nitrogen-determinations. After boiling for some time all the ammonia present in the guano will have been disengaged and then absorbed by the acid in the bulb, which is then titrated with standard alkali solution in the usual way (p. 139).

NITROGEN EXISTING AS NITRATES. — Some guanos contain traces of nitrates, while sodium nitrate is often added to mixed manures. In the former case the determination of total nitrogen and of that existing as ammonia will always suffice; but in the latter case we must determine the total nitrogen by means of a combustion of the manure by Ruffle's thiosulphate mixture as described on p. 146, or by a modification of Kjeldahl's process. We then proceed to the determination of the nitrogen existing as nitrate by washing out the contents of the retort (as used in the ammonia estimation described in the preceding paragraph) into a beaker, filtering the mixture, and then determining the ammonia which will be formed from it, as described further on under the head of water-analysis (p. 214), by means of a zinc-copper couple. Care must be taken to use no more of the nitrate solution than can be completely reduced to ammonia by the quantity of copper-zinc couple present: about ·05 gram of $NaNO_3$, and no more, may be employed. Before nesslerizing, the ammonia may have to be distilled off into pure water.

Gravimetric Uranium Method.

The following is a speedy and accurate method for the separation of phosphoric acid from lime, magnesia, and the alkalies. It answers well for the analysis of bone, guano, and other phosphates free from iron or aluminium. As the uranium precipitate is of great bulk, no more of the substance than will contain about ·3 gram of calcium phosphate should be taken for analysis.

PHOSPHORUS PENTOXIDE.—The clear and dilute solution of the phosphate is treated with ammonia in slight excess; dilute acetic acid is then added in small portions at a time till the precipitate is entirely redissolved. Any great excess of acetic acid is to be avoided. A residue, insoluble in acetic acid, is probably iron or aluminium phosphate, and must be removed by filtration.

Uranium acetate is now added to the solution, and the whole boiled; sufficient uranium has been employed when a fresh addition produces no further precipitate. The uranium phosphate is allowed to subside, and then washed by decantation, boiling water containing ammonium acetate being employed. The washings are carefully filtered, and the phosphate finally collected on the same paper, dried, separated from the filter as far as possible, the paper being incinerated alone first, and then the whole is ignited. Before weighing, the uranium phosphate should be moistened with strong nitric acid and again ignited. Its colour after ignition should be a bright canary-yellow. The composition of the ignited precipitate is such that one gram contains ·1991 of P_2O_5.

LIME AND MAGNESIA.—The filtrate is concentrated, and the uranium precipitated by ammonia in the cold, the vessel being kept covered. The precipitate is washed twice by decantation, then boiled with a solution of ammonium chloride and collected on a filter. The lime and magnesia are determined in the filtrate in the usual manner.

Volumetric Uranium Method.

Instead of weighing the uranic phosphate precipitated in the preceding process, a method of determining the point at which the whole of the phosphorus pentoxide present has been removed from solution has been devised. It is based upon the reaction which occurs between an uranic salt and potassium ferrocyanide—namely, the production of a reddish-brown coloration, a coloration which occurs only when no P_2O_5 remains in the liquid.

Three solutions must be made specially for this process:—1. The standard uranium solution is prepared by dissolving about 35 grams of crystallized uranium acetate in 900 c. c. of water: add 25 c. c. of glacial acetic acid. Uranium nitrate (after having been purified by solution in ether, filtration and evaporation of the ethereal solution) may be substituted for the acetate: in this case an addition of 3·5 grams of sodium acetate (instead of acetic acid) should be made to the solution. The liquid should be allowed to rest for a few days before its strength is determined, as a deposit containing uranium slowly forms. 2. A sodium acetate solution is made by dissolving 100 grams of that salt in 900 c. c. of water, and making up the bulk to 1 litre by means of strong acetic acid. 3. The third solution requisite is a standard one of calcium phosphate. To prepare this, dissolve 4·366 grams of pure calcium phosphate in the smallest quantity of nitric acid necessary to effect solution: then make up to 900 c. c. This solution must be standardized by a direct determination of the phosphorus pentoxide in it by the molybdic-acid method, not by weighing the reprecipitated phosphate. Before using this nitric-acid solution, however, the free nitric acid must be removed by adding a little sodium-hydrate solution until a slight opalescence is produced: then add 10 c. c. of the acidulated sodium-acetate solution, which will clear up the slight precipitate formed, provided no aluminium or iron (or only small quantities) be present. Finally make up the solution to 1 litre with distilled water.

Now it is necessary to dilute our uranium solution until 20 c. c. of it are exactly precipitated by 50 c. c. of the phosphate solution. To do this, pour 50 c. c. of the phosphate solution into a beaker, add 5 c. c. of the sodium-acetate solution, and then warm it on the "steamer" to about 80°, and maintain it during the process at about that temperature. Now run in, with constant stirring, about 10 c. c. of the uranium solution. Next add the uranium solution more slowly in quantities of 1 c. c. or ·5 c. c. at a time, testing the liquid as follows after each addition:—Bring a few drops of the turbid but nearly colourless liquid from the beaker on to a porcelain slab which has been previously covered with a number of annular grease marks, made by a tallowed cork ring about 1 inch in diameter. Now add a small fragment of a crystal of potassium ferrocyanide; a reddish-brown colour indicates that excess of uranium solution has been added, and the operations must be recommenced. But if no coloration occur, continue the addition of the uranium solution to the liquid in the beaker until a drop or two of the solution, when tested with ferrocyanide, just indicates excess, by the production of the characteristic colour: this testing should be repeated in five minutes to see whether the process is complete. It will now be easy to ascertain how much water must be added to the uranium solution in order that 20 c. c. of it shall be exactly equivalent to 50 c. c. of the phosphate solution. This strength corresponds to ·005 gram of P_2O_5 for 1 c. c. of the standard uranium solution.

In applying this volumetric process to the estimation of P_2O_5 in a guano, either the filtered acetic acid solution of the ash of the guano may be directly used, or the ash may be treated with hydrochloric acid, &c., in order to render any silica insoluble, and then the acid solution may be first rendered faintly alkaline with soda, and finally acid with acetic acid. In operating then upon a solution however obtained, no free acid save acetic must be present, while the rest of the treatment is conducted with 50 c. c. of the solution in question, exactly as described above. It is scarcely necessary to add that the uranium solution must be standardized by means of repeated trials, and that two or more volumetric estimations should be made in separate portions of each phosphatic solution to be tested. It is necessary that about the same quantity of sodium acetate solution be used in each experiment. Any ferric phosphate which may be precipitated on removal of the free nitric acid from the solution of the guano, &c., by means of sodium acetate may be collected on a filter, washed thrice with boiling water, dried, ignited, and weighed. The P_2O_5 in it may be calculated from its formula, which is approximately Fe_2O_3, P_2O_5. The amount thus found must be added to that obtained in the volumetric determination to represent the total.

NITRATE OF SODA OR POTASH.

The proportion of real sodium or potassium nitrate in a sample is usually determined by difference, the impurities only being estimated; these are generally moisture, sand and insoluble matter, sodium chloride, and sodium or calcium sulphate. The sample is prepared by the usual processes of powdering and mixing.

MOISTURE is determined by heating about 5 grams to 130° C. till the weight is constant.

SAND AND INSOLUBLE MATTER.—About 7 grams are dissolved in water, the residue collected on a counterpoised or weighed filter, thoroughly washed, dried, and weighed. The result is total insoluble matter. The filter may then be burnt; the inorganic residue is sand.

SULPHUR TRIOXIDE.—The filtered solution obtained from the previous operation is to be largely diluted, boiled, and precipitated with barium nitrate, nitric acid being also added. The weight of barium sulphate obtained will be calculated as calcium or as sodium sulphate, according to the amount of calcium found.

Determination of Chlorine.

The chlorine is best determined by a standard solution of silver nitrate, which is added from a graduated vessel to the filtered solution of 7 grams (or of a smaller quantity if much sodium chloride be present) with which a few drops of a solution of neutral potassium chromate have been mixed, till the orange tinge produced by each drop of the silver solution remains just perceptible *after stirring*.

Preparation of the Standard Solution of Silver Nitrate.

The most convenient strength is a decinormal solution. Dissolve 16·97 grams of pure silver nitrate in water, and make up to a litre. Preserve in a stoppered bottle. This solution now contains $\frac{1}{10}$ of the molecular weight of $AgNO_3$ in a litre: therefore 1 c. c. should correspond to $\frac{1}{10,000}$ the molecular weight of $Cl = \cdot 00354$ gram, or of $NaCl = \cdot 00584$ gram, &c. Titrate with pure sodium chloride to find the exact strength.

If septems be used, 169·7 grains of silver nitrate should be dissolved in 1000 septems of water; 1 septem will then $= \cdot 0354$ grain Cl.

The silver solution must be neutral, and the solution to be tested either neutral or very slightly alkaline with a fixed alkali; the process may also be worked in the presence of a small quantity of acetic acid. The potassium chromate must also be neutral and free from chloride; it may be conveniently made so by adding nitrate of silver till the red precipitate becomes permanent, and then filtering.

LIME is determined in the usual way, in the filtered solution from 7 grams.

N.B.—Where the necessary appliances are at hand, it is simplest to dissolve 35 grams of the nitre in water, pass the whole through the counterpoised filter, and then divide the filtrate by weight or measure into five equal parts, in which the several determinations are made.

Actual Determination of Nitrogen Pentoxide.

The amount of nitrogen pentoxide may, if desired, be found with some approach to accuracy as follows, in the absence of organic matter :—

Mix 1 gram of the finely powdered sample with six times its weight of finely ground silica or quartz ; place the mixture in a platinum capsule, and dry in the water-oven, or, preferably, at 130° C., till it ceases to lose weight ; then raise the temperature to a *low* red heat for half an hour : the whole of the N_2O_5 will be expelled, and its amount found by the loss of weight which the mixture has sustained subsequent to its desiccation in the water-oven.

The silica may be prepared by igniting flints, plunging them while red-hot into cold water, and pulverizing the residue.

Nitrogen pentoxide may be exactly determined in nitrates by means of the copper-zinc couple method or by the aluminium method as given further on (pp. 217 and 218), or by gas analysis by Schloesing's method, or with the aid of a Lunge's Nitrometer.

POTASH SALTS, KAINITE, &c.

Besides potassium salts, the articles sold under this name are likely to contain salts of sodium, calcium, and magnesium. As their value depends entirely on the amount of potash present, its determination is all that will generally be required. The methods here described are equally suited for the analysis of the commercial "sulphate" or "muriate."

The sample must be powdered and carefully mixed before analysis.

Direct Method of Determining Potash.

Weigh out 10 grams of the salt, boil for ten minutes in 200 c. c. of water, and after cooling the solution, but without filtering it, make up the bulk to 1000 c. c. and run it through a dry filter. If the sample contain 10 to 15 per cent. of K_2O (kainite), take 50 c. c. of the filtrate, but if less than 5 per cent. K_2O be present 100 c. c. must be used. In any case make up the volume to 150 c. c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride solution: without filtering, add in the same manner baryta water in slight excess. Heat, filter, and wash the precipitate until it is free from chlorides. Add to the filtrate and washings 1 c. c. of strong ammonia-water, and then a saturated solution of ammonium carbonate until the excess of barium is precipitated. Heat. Add now, in fine powder, ·5 gram of pure oxalic acid or ·75 gram of ammonium oxalate. Filter, wash free from chlorides, evaporate filtrate and washings to dryness in a thin porcelain or platinum bason. Hold the dish with crucible tongs over a naked flame, but below a red heat, until all volatile matter has been driven off. When cold, the residue is digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c. c. or more. To this filtrate, contained in a porcelain bason, two or three drops of strong hydrochloric acid are added, and then 10 c. c. of a ten per cent. solution of platinic chloride. The rest of the operations are conducted precisely as described under the heading "Estimation of Potash," p. 135. But if there be the slightest appearance of white foreign matter in the orange-coloured double chloride of potassium and platinum, it should be washed on the filter with a 20 per cent. solution of ammonium chloride which has been saturated with all the K_2PtCl_6 it will take up. 10 c. c. of this solution are first run through the filter, and then 10 c. c. more are poured on and returned 5 or 6 times: 10 c. c. more are then used in the same way. Finally, the washings with alcohol and with ether are conducted exactly as described on p. 135.

In the analysis of KAINITE the following determinations should be made:—

Moisture in 2–3 grams, in the usual way.

Loss on Ignition in 3–4 grams heated very gently and carefully over a Bunsen burner for 5 minutes, cooled and weighed.

Insoluble Matter in 10 grams dissolved in about 200 c. c. of water, and filtered through a paper which has been previously dried and tared. The residue on the paper is thoroughly washed, the filtrate being collected in a litre flask, made up to a litre and well mixed. The filter-paper with the residue is then dried, placed in a stoppered tube, and dried in the water-oven until constant in weight.

Potash is determined in 50 c. c. (=·5 gram of the mineral) of the filtrate by the method given on p. 174.

Lime is determined in 100 c. c. (=1 gram of the mineral) of the filtrate. To this about 50 c. c. of solution of ammonium chloride is added, a small quantity of ammonium hydrate, and ammonium oxalate in excess; after heating for some time the precipitate of calcium oxalate is collected, washed, dried, and ignited in the usual way. From the $CaCO_3$ weighed the percentage of CaO is calculated.

Magnesia is determined in the filtrate from the lime, which is concentrated to about 100–150 c. c., made ammoniacal, and sodium phosphate added, gradually, in excess. After standing in the cold for twelve hours, the precipitate is collected, well washed with ammonia-water, dried, ignited, at first gently and finally before the blowpipe, and weighed. The precipitate after this ignition is $Mg_2P_2O_7$, from which the percentage of MgO is calculated.

Sulphur Trioxide is estimated in 100 c. c. (= 1 gram) of the solution by adding a little hydrochloric acid, heating nearly to boiling, adding a solution of barium chloride as long as a precipitate forms, heating until the precipitate subsides, filtering and treating the barium sulphate as on p. 137. From the weight of $BaSO_4$ found the percentage of SO_3 is calculated.

Chlorine is determined in 10 c. c. (=·1 gram) of the solution by the volumetric process described on p. 173.

In calculating the results the K_2O is usually converted into K_2SO_4, the CaO into $CaSO_4$, and any residual SO_3 into $MgSO_4$. The residual MgO is calculated as $MgCl_2$, and the residual Cl as NaCl. The final results appear as follows:—

Moisture.
Combined water and organic matter.
Insoluble matter.
Potassium sulphate
  (*containing* potash, K_2O).
Calcium sulphate.
Magnesium sulphate.
Magnesium chloride.
Sodium chloride.

The oxalic acid and the ammonium oxalate used must be quite free from sulphuric acid and from potash. Potash may be tested for by igniting a portion, treating the ash (if any) with water, filtering, and examining the filtrate with platinum tetrachloride as above. Oxalic acid may be purified from sulphuric acid by means of barium chloride, and from alkaline salts by crystallization, the *first* crystals being the most impure.

Indirect Method of Determining Potash.

Not more than ·5 gram of the potassium salt is to be taken. Precipitation with barium chloride &c., and ignition with oxalic acid &c., are to be followed exactly as in the previous process. The residue left on ignition is treated with water, filtered, some ammonium chloride added, the solution evaporated to dryness in a platinum or porcelain vessel, the dry mass continuously heated till all ammoniacal salts are expelled, and the residue weighed. It consists of mixed potassium and sodium chlorides. This is next dissolved in water, and the chlorine it contains estimated by the volumetric method described at page 173. The potassium chloride present is then discovered by the following calculation:— The amount of chlorine found is multiplied by 2·1029; from the product is deducted the weight of the mixed chlorides; the difference is multiplied by 3·6562. The product is the amount of *sodium chloride* present; the remainder is potassium chloride.

Perchloric-Acid Method of Determining Potash.

Potash may be conveniently determined in the form of perchlorate. The solution to be analysed must be first freed from sulphuric acid by means of the addition of a slight excess of barium nitrate; the mixture is then evaporated nearly to dryness, and the residue moistened with nitric acid, these processes of evaporating and moistening with nitric acid being repeated until all hydrochloric acid has been removed. The mixture, having now a volume of about 5 c. c., may receive the necessary addition of pure perchloric acid and then be evaporated to dryness. To the residue a few c. c. of water are added, and the whole once more brought to dryness. Some spirit of wine is now poured on the residue: the perchlorates of barium, calcium, magnesium, and sodium are dissolved, while the barium sulphate and perchlorate remain behind. More alcohol is poured on these, and the mixture is rubbed with the end of a glass rod to break down the potassium perchlorate crystals. The alcoholic washings are poured off, and the residue once more moistened with water, evaporated to dryness, and taken up with alcohol. The whole is thrown on a filter; and when the alcohol has drained away, the residue on the filter is treated with boiling water, which dissolves the potassium perchlorate. The filtrate and washings are now evaporated to dryness, heated to 100°, and weighed. If the weight found be multiplied by ·3398, the corresponding amount of K_2O will be the product.

COMMON SALT.

The amount of real sodium chloride is determined, as in the previous analysis, by difference. The impurities present are usually moisture, insoluble matter, and calcium sulphate, with magnesium chloride and sulphate in traces; these are estimated by the processes already given: the moisture being driven off at 130°. The sulphur trioxide found is combined with the lime;

if an excess remains this is considered to be in union with soda. In waste salt which has been used for curing bacon, potassium nitrate may occur; its amount may be determined by one of the processes given on pp. 217 and 218.

AMMONIACAL SALTS. GAS-AMMONIA.

The ammonia present in these substances is usually in the form of sulphate. The impurities are very varied both in nature and amount: they may be roughly classed as water, organic and volatile matters, and iron compounds.

In preparing the sample for analysis, it should be reduced to a fine powder, and well mixed.

MOISTURE is determined by drying in the water-oven in the usual way.

ORGANIC AND VOLATILE MATTERS are estimated by loss of weight on ignition. The ferric oxide, with other inorganic matter present, remains as a dark-red powder.

AMMONIA.—A combustion is made with a quantity not exceeding ·7 gram, all possible precautions to prevent the loss of ammonia during the mixing with soda-lime being carefully attended to. The ammonia found may be calculated into sulphate $(NH_4)_2SO_4$.

As the whole value of the substance depends on the ammonia which it contains, *its* determination will be all that is generally required. But if a qualitative examination indicates the presence of sulphocyanogen, the *real* ammonia should be determined as $PtCl_4,2NH_4Cl$, the operation being conducted exactly as in the estimation of potash (p. 135), except that the precipitate is to be washed with mixed alcohol and ether.

SOOT.

Ordinary soot consists mainly of finely divided carbon; it contains, besides, a small quantity of ammonium sulphate and complex nitrogenous compounds, with various inorganic substances, such as constituents of the fuel-ash or fragments of broken masonry; its value depends on the amount of available nitrogen present.

TOTAL INORGANIC MATTERS.—An ash-determination is made in about 3 grams of the sample; the loss on ignition includes the carbonaceous and nitrogenous matters and the water.

NITROGEN.—A combustion is made with about 1 gram. The nitrogen is usually calculated as ammonium sulphate, but part of the nitrogen in soot exists in the form of nitrogenous bodies having but a low manurial value.

§ ii. ANALYSIS OF SOILS.

The constituents of soil may be looked at from a physical or from a chemical point of view.

It will conduce to the clear understanding of the problems which the analysis of soils presents if their physical or mechanical constituents be first enumerated:—

1. Water, interstitial, hygroscopic, and combined.
2. Air, both interstitial and absorbed or occluded.
3. Stones, remaining on a sieve of 5 mm.
4. Gravel, remaining on a sieve of 3 mm.
5. Gravelly sand, remaining on a sieve of ·6 mm.
6. Coarse sand.
7. Fine sand.
8. Clay.
9. Organic matter.

It should be noted that the four last-named soil-constituents, associated with much water and air or gases, make up the true soil or "fine earth" in which plants find their immediately available supplies of nourishment. The terms clay, sand, and gravel, as here used, are, however, not to be understood as implying any special chemical characters; they express simply certain mechanical conditions. On the proportions in which the several physical constituents above named are present in a soil depend many of its most important physical properties. Not only so, but as the several mechanical constituents differ from each other in chemical composition, the results of the chemical analysis of a soil will be greatly affected by the proportion in which the mechanical constituents occur. As a rule, the "fine earth" alone is submitted to minute qualitative chemical examination; but if it be desired to ascertain what reserve of plant-food be present in any soil, then the gravelly sand, the gravel, and even the stones, as separated during the mechanical analysis, may be likewise analysed.

Thus it will be seen that there are many reasons for desiring a mechanical as well as a chemical analysis of a soil. Unfortunately most of the physical constituents can never be absolutely determined, it being impossible, for instance, to define where gravel ends and sand begins: the amounts found will be much influenced by minute variations in the plans of analysis adopted, and will not be exactly comparable when soils of different origins are treated even by the same method.

MECHANICAL ANALYSIS OF SOILS.

SAMPLING.—Where the soil of a field is uniformly and distinctly marked out from the subsoil, three or four parcels of earth may be taken from different parts of an acre. The surface vegetation and accidental foreign matter are first cleared from the selected spots; then a trench is dug down to the subsoil, so as to leave a square block, 12 or 18 inches square, of the surface-soil intact; from this vertical slices are cut until 5 kilograms (or 10 lbs.) of earth have been obtained. This material is then placed on a piece of sacking on a wheelbarrow. The same operations are repeated on the other selected spots, and from the united quantities of soil thus obtained, after thorough mixing with the spade, a final sample of about 4 or 5 kilos. is taken. This should be transported to the laboratory in a wooden box, not in a closed metallic or glass vessel. A sample of the subsoil may be obtained from the spots opened in the above operations, the depth to which the subsoil is excavated being at least equal to that of the soil.

When the surface of the land shows any kind of inequality to exist in the texture, colour, or other character of the surface-soil, it will be necessary to take a number of representative specimens from places which resemble one another closely, and to mix them together. Then a second series of samples is secured from other places in the field differing from those first selected, but also resembling one another. Of course, if three sorts of soil exist alongside of one another, a third series of samples will be required.

In order to prepare the soil for most of the operations of analysis, whether mechanical or chemical, the sample should be spread out in a warm place on a board or on smooth brown paper to dry slowly; a sample of 100 grams may, however, be at once taken for the determination of moisture. This should be dried till constant at 100° C. and then at 150° C.

The main bulk of the soil, when in a fit state, neither too moist nor too dry, must be passed between the fingers, the clods and lumps being crushed from time to time as the drying proceeds. If by any chance the lumps become too dry, they may be moistened with the spray of distilled water, and then again left until they are ready for crushing. When the whole sample has been broken down and reduced to a uniform condition, so far as hand-pressure is capable of achieving this result, then the following operations are carried out.

STONES.—If large stones be present, the sample of air-dried soil is weighed, the stones (which will not pass through a sieve of 5 mm.) are picked out, weighed, then dried in the water-oven, and again weighed. The remaining soil is then well mixed, and transferred to a stoppered bottle.

MOISTURE is determined in the usual way. As the sample is sure to be somewhat rough and uneven, 50 grams should, if possible, be taken for this determination.

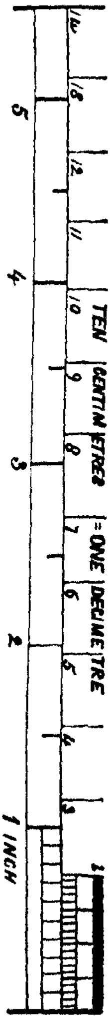
ORGANIC MATTER.—As large a portion of soil as can conveniently be taken is heated gradually to *low* redness, and thus maintained till stirring with a platinum wire fails to reveal any black particles. The residue, when cold, is moistened, with ammonium carbonate, dried, again ignited for a minute, and weighed; the loss is organic matter plus moisture.

Gravel.—About 600 grams (or 10,000 grains) are sifted through a wire sieve, the meshes of which have a diameter of 3 millims.*, the sieve being fitted with a flat circular revolving brush above, and with a drum below to receive the sifted portion. The gravel remaining in the sieve is examined; if lumps of soil are visible, these are broken, and the sifting resumed. The sieve, with its contents, is finally placed in a bason of water; and after soaking awhile, the still adhering soil is washed from the gravel, which is then dried in the water-bath and weighed. If it be mixed with roots or other organic matter, gentle ignition must precede the weighing. The matter removed by washing is to be preserved.

Gravelly Sand.—The portion of sand which passed through the first sieve is now placed in a second, the meshes of which have a diameter of 0·6 millim. The sifting and subsequent washing are conducted exactly as before. The matter removed in washing the gravel is added to the contents of the sieve before washing is commenced. The fine gravel, or gravelly sand, when quite clean, is dried, gently ignited, and weighed.

Coarse Sand.—30 grams (or 500 grains) of the soil which passed through the last sieve are perfectly dried at 100° C., and then weighed. Another similar quantity is gently ignited, and then weighed. The sample which has been dried at 100° C. is placed in a bason, four or five times its bulk of distilled

Fig. 16.



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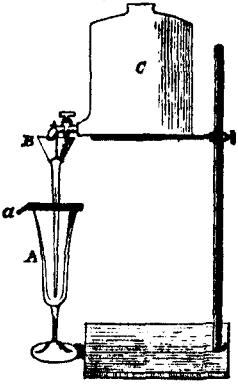
* The scale at the side of this page will enable the analyst to substitute the corresponding English measures of length for those of the metric system given in the text.

water added, and the whole boiled for half an hour, with frequent stirring. The last is especially necessary if the soil be of a clayey nature, the object in view being the perfect disintegration of the mass. The contents of the bason are then removed to the glass vessel A in fig. 17 (depth 20 centims., width at top 7 millims.), fitted at top with a narrow brass ring, provided with an exit-tube, *a*. The cistern, C, is now filled with distilled water, and the funnel-tube B (length of tube 40 centims., diameter 7 millims., drawn out at the end to a small orifice, diameter 1½ millim.) attached to the cock with a piece of twine. When all is ready, open the cock of the cistern slightly, and, while water is passing through the funnel, introduce the latter into the vessel A, the height of which is to be so arranged that the point of the funnel is about 3 millims. from the bottom of the vessel. The issue of water from the cistern is now regulated so that the height of water in the funnel is kept 20 centims. above that in the elutriating glass, A. The stream should issue steadily against the side of the funnel. The water with suspended matter overflowing from the tube *a* is collected in a large beaker or bason and preserved. The operation is completed as soon as the water from the discharge-tube runs almost clear. The funnel is then removed, the fluid in A rapidly decanted from the solid matter, which is then rinsed into a bason, dried, ignited, and weighed. The result is coarse sand.

Fig. 17.



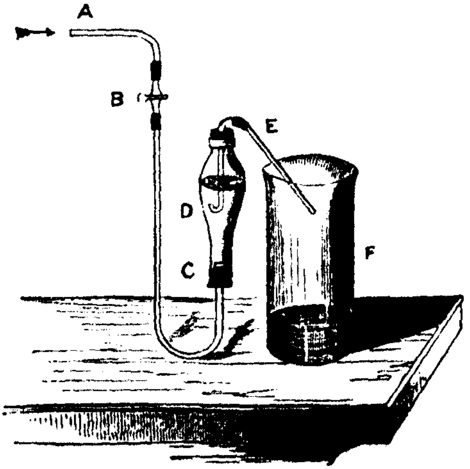
The apparatus here described admits of easy construction. An ale-glass of the required height will form a good elutriating vessel. This (in the absence of the brass ring and tube) may be placed in the midst of a large bason, which, when full, can be connected with other vessels by a small glass siphon.

Fine Sand.—The washings from the previous operations are allowed to stand an hour or two, the liquid then poured off, and the solid residue returned into the elutriating glass. The process above described is then recommenced; this time, however, the column of water in the funnel is only 3 cm. above that in the glass. The washing is continued till the water passes off clear. The residue is then collected, dried, ignited, and weighed.

CLAY.—This is found by difference, and should be entered as "clay, so-called, ignited," but it cannot be regarded, in the majority of cases, as consisting entirely of true clay.

A method of washing soils by means of the *upward flow* of a constant stream of water has been employed by several continental chemists. The essential portions of the improved form of the apparatus employed in carrying out this operation are represented in the annexed figure 18. A reservoir of water kept at a constant level by means of a large vessel and tube inverted over the reservoir, in the manner of a bird-fountain, is required: this is not shown in our illustration. The water enters the special washing-apparatus at A, passes downwards through a

Fig. 18.



small glass tube with a stopcock B, the end of which, expanded into a small funnel, and covered with fine cambric, passes first into the cork C, with which the "separator" D is closed: this separator is best made of a paraffin-lamp glass inverted. The upper end of the separator D is closed with a perforated cork through which an equal-limbed siphon, E, passes. That end of the siphon which is in the separator has a small upward bend at its extremity. The method of using this arrangement for separating clay, fine sand and coarse sand, is exactly like that just described, the boiled mixture of soil and water being poured into the vessel D and then a stream of distilled water turned on from the reservoir, so that the water flowing from the siphon shall run by drops and not in a continnous thread into the beaker F. When the difference of water-level in the reservoir and the separator is about 57 centims., and the distance between the inflow and outflow in the separator is 13 centims., the fine sand and the clay will both be found completely driven over into the receiver F after a short time and the use of a comparatively small volume of water. Then the coarse sand should be rinsed out of the separator, dried at 100° C., weighed, gently ignited, and again weighed. The fine sand and clay will have to be removed from the beaker F, placed in the separator, and washed by means of a more gentle current of water. If the difference of water-level between the reservoir and the point C be reduced to 35 centims., the clay will be washed out while the fine sand will remain in the separator, and can be removed to a dish, dried at 100° C., weighed, ignited, and again weighed. The clay is found by difference.

In using the process just described, it is a good plan to make a few preliminary trials as to level, rates of flow, and sizes of tubes and vessels; for different classes of soils demand modifications of arrangement. We may add that a lamp-glass measuring 7 centims. across its breadest part, and having an extreme length of 22 centims., forms a good separator, while the siphon should be so arranged as to admit of being lowered more or less into the liquid in this vessel, which may be $\frac{3}{4}$ full.

Calculation of Results.

If the soil is one containing large stones or pebbles, it is best to put down the amount of these separately, it being essentially a variable quantity, and to calculate the other ingredients on the soil remaining after their removal. The percentages are *all* calculated for the *dry* soil; this is easily done, the moisture present having been determined by experiment; as, however, this determination is made subsequent to the separation of the stones, the percentage of *these* must be calculated as follows: —

Subtract from the weight of sample the weight of undried stones; find the amount of dry soil the remainder is equal to; add to this the weight of dried stones, and calculate from this total the percentage of dry stones.

The percentages of organic matter, gravel, and gravelly sand are found in the usual way. The organic matter may perhaps present a difficulty. The loss in the experiment consists of organic matter plus moisture; if, however, we calculate the amount of dry soil that the quantity taken is equal to, and deduct from this the weight after ignition, the difference is organic matter only; this is then calculated on the dry soil. (Of course the term 'organic matter' here includes *combined* water.) The amounts of organic matter in the coarse sand and in the fine sand having been already determined, the quantity in the clay may be ascertained by subtracting the sum of these amounts from the total quantity.

The higher its percentage of the more finely divided ingredients, the better adapted for the growth of plants the soil will prove, taking for granted, of course, the presence in these fine earthy particles of all the necessary ingredients of plant-food in adequate proportion and in suitable condition.

Other physical characters of soil may readily be determined by experiment. Such are the amount of moisture which 70 grams of perfectly dried soil can absorb from the air, when spread out in a thin layer and shaded from the sun, on an ordinary summer day; the amount of water which the same quantity of soil can hold when made perfectly wet by dropping water upon it contained in a funnel; the rapidity with which the wet soil dries; and the power which the soil has of withdrawing such substances as ammonia, potash, phosphorus pentoxide, colouring matter, &c. from their solutions. The interstitial air of a soil may be extracted by means of a Sprengel pump, measured, and submitted to analysis.

CHEMICAL ANALYSIS OF SOILS.

Soils, as we have just seen, are really mixtures of stones, gravel, and sand of various kinds, with more perfectly disintegrated mould; each of these physical constituents will possess, to a greater or less extent, a different chemical composition; a *complete* statement of the chemical constitution of a soil will therefore include an account of the composition of each of these ingredients. An analysis in such detail, however, will seldom be required; the directions here given will therefore apply directly to the analysis of the finer portion of the soil. The processes described will nevertheless, in most cases, be equally applicable to the examination of the stony matters; occasional hints will be given having especial reference to this part of the subject.

The sample is prepared by drying, breaking the clods by the hand, and sifting to remove stones and gravel, the sieve finally employed being that mentioned above, having meshes of ·6 of a millimetre in diameter.

The prepared sample should be preserved in a tightly closed bottle.

If an analysis of the stony ingredients is desired, they are to be freed from the finer parts of the soil by washing, then dried and pulverized—the last operation being best effected, when the gravel is of a silicious nature, by first crushing in an iron mortar, and afterwards completing the pulverization in one of agate. It is particularly necessary that a very fine powder should be obtained. If the stones are evidently flint or other simple

mineral of known composition, their analysis may certainly be dispensed with, while, should they be evidently calcareous, the directions for the analysis of limestone may be made use of. It is always well to ascertain qualitatively of what the stones, gravel, and sand mainly consist, even when quantitative results are not required.

The results are best arranged so as to exhibit the composition of the perfectly dry soil. The prepared sample will generally contain a little moisture; the amount of this is to be determined by drying a small weighed quantity at 100°; it is then easy to calculate all the results as if obtained in a perfectly dry sample.

PARTIAL CHEMICAL ANALYSIS.

For most agricultural purposes a partial chemical analysis will suffice. The constituents determined quantitatively are organic matter, matters soluble in water, nitrogen, potash, lime, and phosphorus pentoxide. Qualitative testings are likewise made for sulphur trioxide, chlorine, nitrogen pentoxide, and iron in the ferrous condition.

ORGANIC MATTER.—About 4 grams are heated gradually to low redness, and thus maintained till all blackening has disappeared; the residue, when cold, is moistened with ammonium carbonate, again heated for a minute or two, in order to dry it and drive off excess of ammoniacal salt, and then weighed. The loss is organic matter and combined water.

SOLUBLE SALTS.—About 10 grams are boiled with 200 c. c. of water in a flask and kept at a boiling temperature, with occasional shaking for a quarter of an hour. The mixture may then be allowed to subside, and the supernatant liquid decanted off: this process of boiling is repeated with the residue and another portion of water. The second portion of liquid is decanted off when nearly clear; and then both it and the first portion are filtered through a carefully washed filter. The filtrate will probably still be turbid; if so it should be boiled and then again filtered. Finally the clear filtrate thus obtained is evaporated to dryness, in a weighed dish or beaker, on the water-bath, dried at 100° C. and weighed. If the dry residue amounts to more than ·2 gram (2 per cent.), it indicates a rather excessive and possibly injurious amount of saline matters in the soil. The residue should be tested qualitatively for phosphates, nitrates, sulphates, and chlorides.

NITROGEN.—The nitrogen present in soils is commonly proportionate to the amount of organic matter they contain. It is not usually convenient to burn a quantity of the soil containing more than ·8 or ·9 gram of organic matter; but within this limit the largest possible amount should be taken; if a sufficiently long tube be employed there is no difficulty in using 25 or even 30 grams of earth: the Ruffle thiosulphate method should be adopted. Determinations of nitrogen existing as ammonia and as nitrates may be made separately if desired. For this purpose a watery extract of the soil must be specially prepared as follows. A funnel 4¾ inches wide is made by cutting off the top of a Winchester quart-bottle. This is inverted and a disc of copper-gauze laid over the opening, and on this two discs of filter-paper, *the upper one slightly wider than the lower.* The filter is moistened and then the soil (previously dried at about 55° as quickly as possible) is carefully spread upon it, from 200 to 300 grams being taken according to the supposed richness of the sample in nitrates and nitrites. The neck of the Winchester has been previously fitted with an india-rubber stopper and glass tube. The latter is put into communication with a strong flask in which has been inserted an india-rubber stopper having two openings. Into the second opening of the latter is fitted a bent glass tube communicating with an exhausting syringe or a pump. Water is poured on the soil, and the air in the flask is partially exhausted. When 100 c. c. of water have passed into the flask it may be concluded that all nitrates and nitrites have been extracted from the soil. Their amount may be determined in an aliquot part of this liquid by means of the "copper-zinc method" given on page 217. If there be any ammonia-salts present they must first be removed by distillation with sodium hydrate.

The ready-formed ammonia in a soil may be determined by distilling a suitable quantity of the dried soil with pure magnesia and water (see page 169).

PHOSPHORUS PENTOXIDE.—About 10 grams of the soil are employed for the determination of the phosphorus pentoxide and the potassium. The weighed quantity is to be gently ignited for a few minutes, the heat being scarcely raised to visible redness, as the object is merely to carbonize the organic compounds, and as an intense heat is prejudicial. The soil, when cold, is removed to a beaker and digested with moderately strong hydrochloric acid (the concentrated acid diluted with its own bulk of water). The digestion should be carried on in a covered vessel, at a temperature a little below boiling, for an hour, or, in the case of a ferruginous soil, until the undissolved residue ceases to appear of a red colour. The whole is then evaporated to dryness and the residue heated for some time at a temperature above 100° C. to render the whole of the silica insoluble. The mass after cooling is to be moistened with concentrated hydrochloric acid and allowed to stand 15 minutes or longer; a little water is then added and the whole warmed. If the residue be grey or white, or black through the presence of much carbon, the liquid may be diluted with more water, boiled, and filtered. The residue on the filter, when dried and ignited, consists of silica and silicates, and may be weighed with the usual precautions. The filtrate and washings of this residue are treated as follows:—

The liquid is precipitated by a slight excess of ammonia, the precipitate washed with hot water and collected on a filter. In the filtrate the potassium is contained; in the precipitate the phosphorus pentoxide. To estimate the latter the precipitate is redissolved in a small quantity of nitric acid, and the under-mentioned process adopted for the treatment of the solution thus obtained. Should the soil contain but little ferric oxide and alumina it is preferable to use the solution of 10 grams freed as above described from silica, but without precipitating the liquid with ammonia.

Molybdic-Acid Method.

The success of this process is not interfered with by the presence of much ferric oxide or alumina; it is peculiarly applicable in cases where the amount of phosphorus pentoxide present is very small, but is the method to be generally preferred in all cases.

To the solution about 30 c. c. of an acidified solution of ammonium molybdate are added; the mixture is evaporated to a small bulk on a steamer or water-bath; the bright yellow precipitate is collected on a filter and slighly washed with a few drops of a solution of ammonium nitrate. The filtrate is then treated with a further quantity of ammonium molybdate, and submitted to a second digestion on the water-bath. Should more of the yellow precipitate be formed, it is collected on the same filter as that first obtained: digestion with ammonium molybdate is repeated until no further formation of a yellow precipitate occurs. The formation of a permanent white precipitate of molybdic acid is a proof that the solution is saturated with that body, and that, consequently, any further addition of the reagent is unnecessary, digestion in the water-bath being all that is required. The white as well as the yellow precipitates are collected on the same filter.

The precipitate is to be washed while on the filter with small quantities of the acidified solution of ammonium molybdate, or with a strong solution of ammonium nitrate. It is then treated on the filter with just enough hot dilute solution of ammonia to dissolve it completely; to the clear solution, which contains the whole of the phosphorus pentoxide, a few drops of citric acid are added, and finally some magnesia mixture. After 12 hours the precipitate of ammonium magnesium phosphate is collected and treated exactly as before described, p. 135. In all determinations of P_2O_5 by means of this salt, a small loss occurs, owing to its solubility in water and saline solutions. An approximative allowance for the error thus introduced may be made by adding to the weight of the magnesium pyrophosphate obtained ·001 gram for every 200 c. c. of washings collected. The phosphorus pentoxide is calculated from the weight of $Mg_2P_2O_7$ obtained; it is usually regarded as existing in the soil as tricalcic phosphate, although, in fact, it is much more probable that it occurs wholly, or almost wholly, in the state of aluminium and ferric phosphates.

The following modification of the molybdic-acid method may be adopted. Concentrate to a small bulk the nitric acid solution (see page 191) which contains the phosphoric acid. When cold, add excess of the acid ammonium solution and allow the mixture to stand, in the cold, for 48 hours. Decant the liquid through a small filter, wash the yellow precipitate with small quantities of dilute nitric acid by decantation, and then transfer it to the filter. Wash the precipitate on the filter with small quantities of cold water till the filtrate is free from acid. Dissolve the precipitate on the filter with ammonia, collecting the filtrate and washings in a tared platinum capsule. Evaporate just to dryness the contents of the capsule, and dry till constant in the water-oven. 1 part of the residue will contain ·035 part of P_2O_5.

LIME.—The filtrate from the ammonia precipitate (see page 191, line 30) is boiled and treated with *pure* ammonium oxalate as long as a precipitate is produced; the whole is filtered: the lime may be determined, if necessary, by washing, drying, igniting, and weighing this precipitate of calcium oxalate, the usual precautions being taken.

POTASH.—The filtrate from the calcium oxalate is evaporated to dryness, and the residue gently ignited to expel ammonium salts. The mass is then treated with *pure* oxalic acid (in such quantity as to convert all the bases present, viewed as potash, into the salt known as "quadroxalate"), some water added, and the whole once more evaporated to dryness and ignited. The residue is dissolved in a small quantity of hot water, and filtered: the filtrate, if clear, is treated with hydrochloric acid in slight excess, evaporated to dryness, and gently ignited. In a complete analysis of soil this residue is to be weighed; the weight is that of the mixed potassium and sodium chlorides. In the present case the mixed chlorides are dissolved in the smallest possible quantity of water, some platinum tetrachloride added and a drop of hydrochloric acid, and the whole evaporated nearly to dryness on the water-bath. If the *solution* lose its orange tint during evaporation, more of the platinum salt must be added. The moist residue is treated with 80 per cent. alcohol, transferred to a very small weighed or counterpoised filter, and washed with alcohol till the washings are colourless. The precipitate is dried at 100° and weighed. For its composition see p. 135. The potassium in a soil may be calculated, according to circumstances, into K_2O, KCl, or K_2SO_4.

By means of the standard silver solution employed in the estimation of chlorine (see p. 173), we may likewise determine the proportion of potassium to sodium in the dry mixed chlorides which have been weighed as above described. We merely rinse out the chlorides into a flask with water and titrate the solution with silver solution and potassium chromate in the usual manner. Thus we obtain the weight of chlorine present; and as we already know the weight of the mixed chlorides, we have now merely to calculate in what proportions the potassium and sodium must exist in the total salts in order that the quantity of chlorine found should be combined with its proper proportion of these two metals.

Let S = the weight of mixed chlorides,
and A = the weight of chlorine found;
let x stand for the potassium present, and y for the sodium.

Now as the ratio of chlorine to sodium, or $\frac{Cl}{Na}$, is expressed by the number 1·54, and the corresponding ratio, $\frac{Cl}{K}$, by ·905, we may arrive at the values of x or the potassium, and of y or the sodium present, by means of the following equations:—

$$\begin{aligned} {\cdot}905\,x + 1{\cdot}54\,y &= A, \\ x + y &= S - A, \\ 1{\cdot}54\,x - {\cdot}905\,x &= 1{\cdot}54\,(S - A) - A, \\ 1{\cdot}54\,y - {\cdot}905\,y &= A - {\cdot}905\,(S - A), \\ x &= \frac{1{\cdot}54\,(S - A) - A}{{\cdot}635}, \end{aligned}$$

$$A - {\cdot}908\,(S - A)$$

A few qualitative testings form a valuable addition to the partial quantitative analysis of a soil just described.

A small quantity of the soil is heated with a little water and stirred; a piece of blue litmus paper is then left on the top of the pasty mixture to see if the reaction of the soil is acid; carbonic acid may redden the paper, but in that case the blue tint will reappear on warming the paper. A small quantity of the soil should be gently warmed with dilute nitric acid, filtered, and nitric acid and silver nitrate added to one half the filtrate, the other half being tested for sulphates by the addition of a few drops of barium chloride.

It is of great importance to ascertain the condition in which the iron of a soil exists. This is accomplished to some extent in the following manner:—About 2 grams of the soil, which must not have been dried artificially, are shaken with moderately strong hydrochloric acid in a small flask for some minutes; water is added, and the mixture allowed to rest. The supernatant liquid is to be poured through a filter, and the clear filtrate divided into three portions. To one part add a few drops of potassium permanganate solution: an instantaneous disappearance of the violet colour indicates iron in the state of a ferrous salt, the protoxide. To another part of the solution add sodium acetate and potassium ferricyanide; a dark blue precipitate indicates a ferrous, a green colour a ferric salt. To the third part of the solution add sodium acetate and potassium ferrocyanide; a blue precipitate indicates a ferric salt.

COMPLETE CHEMICAL ANALYSIS.

The complete chemical investigation of a soil is seldom necessary, and involves, when properly conducted, a very large amount of tedious and difficult work. It would unduly extend the size of the present volume were we to attempt to give full directions for the quantitative analysis of soils. We shall therefore only describe such determinations of their usual constituents as are most easily and advantageously made. The directions already given, and those with which we now proceed to supplement them, may, however, be applied to what may be called the "fractional analysis" of a soil, as well as to that of the sample prepared as before directed. In the fractional analysis of a soil, 200 grams are taken in a finely divided state, but without artificial drying, and shaken up at intervals with two litres of a one per cent. solution of citric acid for seven days. Then the liquid is filtered and 500 c. c. evaporated to dryness, the residue being incinerated, in a platinum dish. The residue is dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue again dissolved, the solution being once more filtered. In the filtrate the potassium is determined. Another portion of 500 c. c. is similarly treated, only that nitric acid is substituted for hydrochloric acid: in this portion the phosphorus pentoxide is determined by the molybdic-acid method. When a soil contains much calcium or magnesium carbonate this process is not applicable, but in the majority of cases it may be regarded as showing how much of the potassium and phosphorus in the soil is immediately available for plant-food: the residue on the filter is then analysed exactly as directed in the case of a sample of prepared soil. But if it be desired to effect a further classification of the states in which the various kinds of plant-food exist in the soil, the above residue should be boiled in a flask for half an hour with pure hydrochloric acid of spec. grav. 1·15. The liquid is then filtered off, the residue washed, and then the united filtrate and washings are analysed as hereinafter directed.

The constituents determined in the more complete analysis of a soil are organic matter, nitrogen, soluble silica, insoluble silica, ferric oxide, alumina, lime, magnesia, potash, soda, sulphur trioxide, phosphorus pentoxide, carbon dioxide, chlorine, and also, in some cases, manganese dioxide.

Organic Matter may be determined as in a partial analysis; or that part of it which is of the greater agricultural significance may be dissolved out of 10 grams of the soil (previously deprived of $CaCO_3$ by means of dilute HCl) by the action of a solution of ordinary ammonia diluted with its own bulk of water. The liquid is filtered through glass wool after 4 hours' contact with occasional agitation. The filtrate and washings are united, evaporated to dryness in a platinum dish, and weighed. The dish is then heated strongly, and the ash of the organic matter deducted from the first weighing: the difference represents the soluble *humus* of the soil with some approach to accuracy. The ash of the organic matter always contains some phosphorus pentoxide: this may be estimated in the nitric acid extract of the ash by means of ammonium molybdate.

NITROGEN, in its several states of combination, is determined exactly as in the partial analysis.

INSOLUBLE SILICA AND SILICATES.—About 13 grams of the soil are very gently ignited, and subsequently digested in hydrochloric acid, precisely as directed in the partial analysis under the head of Phosphorus Pentoxide, p. 191. The acid solution is filtered, the insoluble matter collected, thoroughly washed, dried, ignited, and weighed: it is reserved for further examination.

SOLUBLE SILICA.—The filtrate is evaporated to dryness, the residue heated for some time, and then redissolved (see p. 191); the insoluble matter, which should be perfectly white, is collected, washed, ignited, and weighed: it generally represents a considerable part of the soluble silica of the soil.

The filtrate and washings from the above are well mixed and divided by weight or measure into two portions, one containing about twice as much as the other: the larger portion is reserved for the determination of phosphorus pentoxide and alkalies, as already described (p. 191). The smaller is employed for the determination of ferric oxide, alumina, manganese dioxide, lime, and magnesia.

SMALLER PORTION.

Method employed in the absence of Manganese.

FERRIC OXIDE.—The solution is boiled with a little nitric acid; when cold it is diluted, some ammonium chloride added, and a slight excess of ammonia: the precipitate is washed by decantation, the washings being filtered; it should then be redissolved and precipitated again, exactly as before, to free it entirely from adhering lime. The mixed ferric oxide and alumina is next dissolved in a small quantity of hydrochloric acid, brought to boiling, and precipitated by an excess of pure sodium hydrate. The solution is filtered, and the precipitate of Fe_2O_3 washed by decantation, redissolved in hydrochloric acid, reprecipitated by excess of ammonia, and finally collected, washed, dried, ignited, and weighed.

ALUMINA.—The filtrate and washings from the precipitate by sodium hydrate are treated with hydrochloric acid in slight excess, a crystal of potassium chlorate added, and the whole boiled; an excess of ammonia is next added, and the boiling continued for some time, until all but a trace of the ammonia has been volatilized: the precipitate is then allowed to subside, thoroughly washed by decantation, and finally collected, dried, ignited, and weighed.

The caustic soda or sodium hydrate used should be that made *from sodium*, and must be *free from silica and alumina*. The precipitate weighed as alumina will contain all the phosphorus pentoxide present in the "portion" operated on: its amount is to be calculated when the phosphorus pentoxide determination is finished and subtracted from the gross weight of the alumina precipitate; the difference will be the alumina itself.

N.B. The ferric oxide and alumina may also be very accurately determined by means of the volumetric iron method before described. For this purpose the ferric oxide and alumina precipitated by ammonia are collected, gently ignited, and weighed; they are then digested in concentrated hydrochloric acid till dissolved, and a determination of iron in the solution is made according to the directions previously given at page 154. The alumina will then be found by difference.

LIME and MAGNESIA are estimated in the concentrated filtrate and washings from the original precipitate produced by ammonia. The lime is precipitated by ammonium oxalate; and in the filtrate and washings from the calcium oxalate the magnesia is determined in the usual way, and with the usual precautions.

Method employed in the presence of Manganese.

The presence or absence of manganese is easily ascertained in the hydrochloric solution of a soil (prepared from a portion which has been gently ignited) by adding ammonium chloride and ammonia, filtering rapidly, and mixing some chlorine-water with the filtrate. The mixture is kept for some time in a warm place; if a brown precipitate or coloration appear, manganese is present.

FERRIC OXIDE and ALUMINA.—The solution is peroxidized by boiling with a little nitric acid; ammonium carbonate is then slowly added with constant stirring, till the liquid is neutralized as far as possible without producing a permanent precipitate; the whole is then diluted to 300 or 350 c. c., an excess of ammonium acetate added, and the solution well boiled. The precipitate, which contains all the ferric oxide and alumina, is first washed by decantation, and is best brought to the boiling-point after the addition of each washing water, to which a little ammonium acetate has been added; it is finally collected, washed with hot water, dried, ignited, and weighed. The weighed precipitate is digested in concentrated hydrochloric acid till dissolved; the ferric oxide is then determined by the volumetric method: the difference is alumina.

MANGANESE DIOXIDE.—The filtrate and washings from the above are concentrated to about 180 c. c., a considerable amount of chlorine-water or bromine-water added, and the whole digested for some hours, at a temperature of about 55° C. When the precipitate has subsided add some more chlorine-water, and observe if any further darkening takes place; if this is not the case, the precipitated manganese dioxide may be at once collected. It should be thoroughly washed, first by decantation, warm water being employed. When ignited it is converted into Mn_3O_4; for this purpose a high temperature is required. In many soils the manganese exists in the form of MnO_2.

LIME and MAGNESIA are determined in the usual manner in the filtrate from the manganese precipitate.

LARGER PORTION.

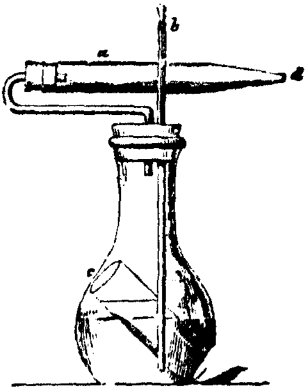
PHOSPHORUS PENTOXIDE and ALKALIES are determined, exactly as directed in the Partial Analysis, in the larger portion of the filtrate and washings (from the silica determination) reserved for that purpose. When in the estimation of the alkalies there described the amount of potassium chloride present has been ascertained, it is only necessary to subtract this amount from the total weight of the mixed alkaline chlorides to find the amount of sodium chloride: this salt may then be calculated into soda.

SULPHUR TRIOXIDE.—10 grams of the dried but unburnt soil are digested in dilute hydrochloric acid, and the whole of the silica rendered insoluble by evaporation to dryness; the residue is redissolved in a small quantity of hydrochloric acid, the solution diluted, boiled, and filtered. The clear filtrate is brought to the boiling-point, and precipitated by barium chloride. The barium sulphate, when burnt, is to be moistened with a drop of strong nitric acid, dried, again ignited, and weighed.

CHLORINE.—13 grams of the soil are gently ignited as before directed, and digested with distilled water slightly acidulated with nitric acid, the whole filtered, and the soil washed a few times on the filter. The clear solution is treated with silver nitrate, and the whole allowed to stand twelve hours in a warm place. The silver chloride is collected on a very small filter, and washed with water containing a few drops of nitric acid; the last few washings, however, should be with plain water. Its weight is determined either by having the filter counterpoised, or by ignition in a small porcelain crucible; the latter operation is conducted according to the directions given at p. 149.

CARBON DIOXIDE is determined by the loss of weight which occurs on its expulsion; the dried, unburnt soil is operated on; the quantity taken must depend on the amount of carbonates present. The soil is introduced into a small wide flask, and moistened with a little water. A short test-tube, *c*, is two thirds filled with hydrochloric acid, and carefully introduced so that its top rests against the shoulder of the flask, and that no acid escapes. A perforated cork with two tubes is then attached. One of these tubes reaches to the bottom of the flask, passes through the cork, and extends 4 or 5 centims. above it; it is closed by a small cork, *b*. The other tube, which does not extend much below the cork of the flask, is bent thrice at right angles, and is finally fitted into a wider tube, *a*, 6 or 8 centims. long and drawn to a point at its further end, *d*. This tube has a plug of cotton at either extremity, the intermediate space being filled with small fragments of neutral calcium chloride which has been well dried over a Bunsen-burner. The apparatus is now weighed. After weighing, the apparatus is slightly inclined, so that a little acid flows out of the tube; it is afterwards mixed with the soil by gentle agitation; this is repeated from time to time till the soil ceases to effervesce. The flask is then warmed, but not boiled; when nearly cold, the small cork is removed, and air slowly drawn through the apparatus, by suction applied to a piece of india-rubber tubing attached to the open end of the calcium-chloride tube; this is continued until the air no longer tastes of carbon dioxide; the little cork is then replaced, and the apparatus, when quite cold, weighed; the loss in weight is carbon dioxide. Some practice is needed to get fairly exact results with this carbon-dioxide apparatus. Other contrivances, in blown glass, may be substituted for the fitted flask shown in fig. 19; the forms devised by Schrötter and by Rohrbeck leave nothing to be desired.

Fig. 19.



ANALYSIS OF INSOLUBLE SILICATES.

N.B. The analysis of the stones and gravelly portion of the soil will fall chiefly under this head, unless, indeed, they are of a calcareous nature, in which case they will be easily decomposed by acid, and are analysed as a limestone.

The matter insoluble in hydrochloric acid is examined carefully; if it appear to be pure quartz-sand, further analysis is superfluous. To make the matter quite certain, a small portion is *very finely* powdered in an agate mortar, and treated in a platinum vessel with hydrofluoric acid; a gentle heat is applied till the whole of the fluid has evaporated. If a residue remains, it is once more treated with hydrofluoric acid; should this fail to volatilize it, the substance is not pure silica, but must be submitted to further analysis. If the insoluble silicates are apparently argillaceous, they may be analysed by the following simple process; if otherwise, the hydrofluoric-acid method, or fusion with baryta, must be resorted to.

Sulphuric-Acid Method.

The substance is reduced to an impalpable powder in an agate mortar. About 2 grams are treated with an excess of sulphuric acid (oil of vitriol plus its own bulk of water) in a platinum or porcelain capsule; heat is then applied, and continued till the acid has been almost entirely volatilized.

SILICA.—When cold, dilute with water; collect and thoroughly wash the insoluble matter; dry, ignite, and weigh. The sand and silica are left; and the mixed silica may then be partly dissolved by digestion with a strong solution of sodium carbonate. The sand when obtained should be tested for purity with hydrofluoric acid.

ALUMINA, FERRIC OXIDE, LIME, MAGNESIA, POTASH, and **SODA** are determined in the filtrate from the silica by the processes previously described; the magnesia is to be precipitated by ammonium phosphate. The excess of phosphoric acid may be removed by adding to the filtrate from the magnesia precipitate a little ferric chloride, boiling and filtering. The alkalies are obtained as sulphates on ignition.

Hydrofluoric-Acid Method.

1·3 gram of the finely powdered silicate is placed in a platinum vessel and gradually mixed with rather concentrated hydrofluoric acid till a thin paste is obtained. The whole is digested at a gentle heat for some time; oil of vitriol diluted with its own bulk of water is then added, drop by drop, in quantity sufficient to be in excess of the bases present. The vessel is then carefully heated till the whole of the acid has volatilized and a dry residue remains; this is treated with concentrated hydrochloric acid, and allowed to remain at rest one hour; water is then added, and the whole warmed. If the operation has been successful, a clear solution, devoid of solid particles, will result; should a residue remain, it must be separated by decantation, and treated again with hydrofluoric acid, exactly as before. Silica is by this method determined as loss, being volatilized as silicon tetrafluoride. Before using the hydrofluoric acid for this process its purity should be tested by evaporating in a platinum vessel the quantity required for an analysis, weighing the residue and, if necessary, submitting it to quantitative analysis.

ALUMINA, FERRIC OXIDE, LIME, MAGNESIA, POTASH, and SODA are determined as in the preceding method.

If the alkalies only should be required, the solution is precipitated with a little barium chloride, the filtrate evaporated, the residue ignited, treated with pure oxalic acid, again ignited, and the alkalies estimated as chlorides, exactly according to the directions already given.

Fusion with Baryta.

Either barium hydrate, free from water of crystallization, or barium chloride may be used for this purpose. The purity of the barium salt should always be ascertained by experiment.

3 grams, or more, are dissolved in water, the barium precipitated by sulphuric acid, the perfectly clear solution evaporated to dryness in a platinum vessel, and gently ignited: no residue should be left; if any appears, the dish may be weighed, and the amount of impurity thus found.

1·3 gram of the finely powdered substance is intimately mixed with four times its weight of the barium salt, introduced into a platinum crucible, which it should not more than one third fill, a little pure barium carbonate being spread over the surface of the mass. The crucible is covered, and its contents brought to a state of fusion, and thus maintained for a quarter of an hour: the barium chloride will require a higher temperature for fusion than the hydrate; the heat of a good gas furnace will, however, suffice; if this be not at hand, the platinum vessel is to be placed in a Hessian crucible, which it is prevented from touching by being imbedded in a little magnesium carbonate, and the whole exposed to a full red heat in any convenient fire.

The fused mass when cold is dissolved in *dilute* hydrochloric acid; solution is most conveniently effected by placing the platinum vessel in a beaker.

SILICA.—When the fused mass is completely disintegrated, the crucible is removed and washed, the whole fluid evaporated to dryness, and the residue heated to render all silica insoluble. The mass is finally redissolved, and the silica collected and weighed. It should be tested for purity with hydrofluoric acid; if found to contain other matters, the fusion has been imperfect.

ALUMINA, FERRIC OXIDE, LIME, MAGNESIA, POTASH, and SODA.—The whole of the baryta is thrown down by sulphuric acid, and the bases estimated as before directed.

ESTIMATION OF ALKALIES.—Another good method for separating the alkalies from insoluble silicates is to heat the powdered mineral with its own weight of pure ammonium chloride and eight times its weight of pure calcium carbonate, at first gently and then at a bright red heat for about three quarters of an hour; when cold the residue is digested in water, filtered, and the

lime in the filtrate separated by ammonia and ammonium carbonate. On filtering, evaporating, and igniting, the residue consists only of alkaline chlorides.

LIMESTONE, MARL, AND SHELL-SAND.

The chief constituent of limestone is calcium carbonate (carbonate of lime); in magnesian limestone or dolomite a considerable quantity of magnesium carbonate is also present. The other constituents are silica, ferric oxide, iron pyrites, alumina, with, in most cases, traces of alkalies, manganese dioxide, sulphur trioxide, phosphorus pentoxide, and organic or bituminous matter.

The sample is prepared by being finely powdered.

MOISTURE and ORGANIC MATTER are estimated by heating to low redness. If the heat, in consequence of the presence of organic matter, is necessarily prolonged, moistening with ammonium carbonate must be resorted to. The crucible should be well covered, as decrepitation is apt to occur.

SILICA.—About 1 gram is dissolved in dilute hydrochloric acid in a covered beaker, and the silica estimated by the usual process of evaporation to dryness. See Partial Analysis of Soils (p. 191). If iron pyrites be present it will remain with the silica unless nitro-hydrochloric acid be used as the solvent.

In analysing tolerably pure limestones, the best plan is to dissolve two or three times the amount here directed, and, after separating the silica and ferric oxide, to divide the solution, and determine the lime in a part only.

FERRIC OXIDE and ALUMINA are precipitated by ammonia in the filtrate from the silica; the precipitate is to be collected and washed, and must then be redissolved in acid, and again precipitated by ammonia, to free it from adhering lime. It must be remembered that the precipitated ferric oxide and alumina will generally retain all the P_2O_5 of the substance. This ingredient may be determined by the methods described below, while the ferric oxide and alumina may be separately estimated as in the analysis of soils.

greatly increases the decomposing and solvent action of the water on the rocks and soils through which it passes.

Great care must be taken in order to obtain a fair sample of the water to be analysed. Stoppered Winchester quarts which have been thoroughly cleansed may be used for collecting the water: the vessels should be first rinsed out with some of the same water. The quantity of water required will vary greatly according to the object in view: two Winchester quarts will suffice for the partial analysis which is generally requisite. When the dissolved gases of the water are to be determined, suitable arrangements should be made at the spring, where also the evaporation of large quantities of any water for the purpose of obtaining the salts should be conducted, if rare substances present in minute quantities are to be identified and estimated. The description of the processes of gas-analysis, and of the search for rare substances, does not fall within the scope of the present work.

The foreign or intruding substances usually occurring in waters may be classed as (1) Mechanical Impurities; (2) Soluble Impurities.

Mechanical Impurities, or suspended matters, if any, must be separated by filtration before proceeding to the analysis of the water. Collect them, from a measured quantity of water, on a tared filter, drying it at 100° and then weighing. The nature of the impurities may then be ascertained in the matter thus separated by submitting it to analysis, but it is usually sufficient to burn the filter and residue. The weight thus obtained represents the mineral impurities suspended in the water. Their amount is to be subtracted from the total, the remainder represents organic matter suspended.

Soluble Impurities.—These are usually calcium and magnesium salts or hardening impurities; alkaline salts or non-hardening impurities; organic matter; and inorganic matter derived from organic and especially from animal substances: among these latter impurities are ammonia, and salts of nitrous and nitric acids. The acid constituents of the salts occurring in waters are the sulphuric, carbonic, silicic, and chlorine, with occasionally the phosphoric radicle. Alumina, ferrous carbonate, and, rarely, arsenic, barium, lead, copper, manganese, zinc, &c., are found in some waters.

Arsenic, Lead, Copper, Zinc, and Manganese may be tested for qualitatively in a litre or more of the water evaporated to a small bulk. If these metals be present in more than mere traces, they ought to be separated by appropriate reagents (H_2S, &c.) before the other ingredients are estimated.

The taste and smell of a water may be best observed by warming to about 40° C. some quantity of it, about 100 c. c., in a perfectly clean covered wide-mouth bottle standing in a water-bath.

The colour of a water should be indistinguishable, or nearly so, from the faint bluish tinge of distilled water. To observe the colour of water two straight tubes of colourless glass are used. These tubes should be about 5 centims. in diameter, and 60 centims. in length. The lower ends are closed with discs of colourless plate glass, covered with white enamel on the upper surface: these discs are cemented on to the ground ends of the tube by means of marine glue or Canada balsam. The tubes are suspended side by side in a well-lighted place; one is filled with the water under examination, the other with distilled water for comparison.

In the clear water the principal matters to be quantitatively estimated are:—

1. **Total solid contents, or fixed solid residue.**
2. **Organic matter.**
3. **Oxygen taken from permanganate.**
4. **Chlorine.**
5. **Ammonia, ready-formed.**
6. **Ammonia producible from organic nitrogen compounds.**
7. **Nitrogen existing as nitrates and nitrites.**
8. **Total and permanent hardness.**

1. Total Solid Contents.

Evaporate ½ litre (or $\frac{2}{10}$ gallon) of the water to dryness in a platinum dish over the water-bath, dry the residue in an oil- or air-bath at 130° C. and weigh. It is as well to evaporate a second ½ litre, in order to obtain a residue in which qualitative testings for P_2O_5 by ammonium molybdate may be made. This second residue should be first moistened with nitric acid and evaporated to dryness to render the silica insoluble. Then it should be taken up with a little nitric acid, water being added, and lastly it should be filtered through a filter-paper which has been washed with nitric acid. The filtrate, which should measure 3 c. c., is mixed with its own bulk of the molybdic test and gently warmed for 15 minutes. A yellow colour may be regarded as indicating traces of phosphates, a yellow turbidity or actual precipitate being respectively reported as heavy traces or very heavy traces.

2. Organic Matter.

The dry residue is heated to low redness until all blackening has disappeared, a clear mica plate being placed over the dish at the commencement of the heating. The residue is treated with ammonium carbonate, dried, gently ignited, and again weighed; the loss gives approximately the amount of organic matter. The loss on ignition does not, indeed, in any case, give the exact ponderal expression of the organic matter; but it offers a valuable criterion of purity. On this point, however, much may be learnt by noting the appearance of the dry residue, and especially its changes during the progress of the heating described above. Bad signs are the deliquescent character or yellow colour of the residue, its considerable blackening when heated, or the sudden disappearance with slight deflagration of the black particles. If any sublimate appears on the mica plate, ammonia salts are indicated: the nature of the fumes and odour evolved should also be observed.

If 250 c. c. of the water, to which a few drops of sulphuric acid have been added, destroy in fifteen minutes, at 27° C., the colour of more than 2 or 3 c. c. of a solution of potassium permanganate containing ·395 gram of that salt per litre, organic matter is probably present in large quantity. Whether this organic matter is likely to be injurious to health or not is a problem that can be answered with tolerable certainty only when a large number of the indications afforded by analysis are favourable or the reverse. The decolorization of permanganate solution by a water may arise from the presence not only of oxidizable organic matter, but of ferrous carbonate and several other substances.

3. OXYGEN TAKEN FROM PERMANGANATE.

If it be desired to obtain more exact notions concerning the amount of organic matter present in a water, through the estimation of the oxygen absorbed from permanganate, the following plan may be used. The five solutions needed are:—

1. ·395 gram potassium permanganate dissolved in 1 litre of distilled water: each c. c. contains ·0001 gram of available oxygen.

2. 10 grams pure potassium iodide, recrystallized from alcohol, dissolved in 100 c. c. distilled water.

3. 100 cub. cent. pure sulphuric acid mixed with 300 c. c. of distilled water: then potassium permanganate solution is dropped in until the whole retains a very faint pink tint after warming to 27° C. for four hours.

4. 1 gram of sodium thiosulphate crystals dissolved in 1 litre of distilled water.

5. 1 gram of pure white starch, ground up into a cream with a little water, is to be poured into 500 c. c. of boiling distilled water, kept boiling for 5 minutes, and then filtered. This constitutes the "starch water" used in the recognition of free iodine in the titration of the permanganate with sodium thiosulphate, as mentioned below.

Two separate determinations have to be made, viz. the amount of oxygen absorbed during fifteen minutes, and that absorbed during four hours; both are to be made at a temperature of 27° C. It is convenient to make these determinations in 12-oz. stoppered bottles, which have been rinsed with sulphuric acid and then with water. Put 250 c. c. into each bottle, which must be stoppered and immersed in a water-bath or suitable air-bath until the temperature rises to 27° C. Now add to each bottle 10 c. c. or 100 grains of the dilute sulphuric acid, and then 10 c. c. of the standard potassium permanganate solution. Fifteen minutes after the addition of the potassium permanganate, one of the bottles must be removed from the bath, and two or three drops of the solution of potassium iodide added to remove the pink colour. At the end of four hours remove the other bottle, add potassium iodide, and titrate with sodium thiosulphate (hyposulphite). Should the pink colour of the water in the bottle diminish rapidly during the four hours, further measured quantities of the standard solution of potassium permanganate must be added from time to time so as to keep it markedly pink.

The thiosulphate solution must be standardized, not only at first, but (since it is liable to change) from time to time, in the following way:—To 250 c. c. of pure redistilled water add two or three drops of the solution of potassium iodide, and then 10 c. c. of the standardized solution of potassium permanganate. Titrate with the thiosulphate solution. The quantity used will be the amount of thiosulphate solution corresponding to 10 c. c. of the standardized potassium permanganate solution, and the factor so found must be used in calculating the results of the thiosulphate titrations to show the amount of the standard permanganate solution used, and thence the amount of oxygen absorbed.

The difference between the quantity of thiosulphate used in the blank experiment and that used in the titration of the examples of water, multiplied by the amount of available oxygen contained in the permanganate added, and the product divided by the volume of thiosulphate corresponding to the latter, is equal to the amount of oxygen absorbed by the water. After thorough admixture, run from a burette the standard solution of sodium thiosulphate, which may be made of a strength of about 1 in 1000, until the yellow colour is nearly destroyed, then add a few drops of starch water, and continue the addition of the thiosulphate until the blue colour is just discharged. If the titration has been properly conducted, the addition of one drop of potassium permanganate solution will restore the blue colour.

If it is desired to estimate the mineral matters other than chlorine and nitrogen-compounds, it may sometimes be necessary, if the water is tolerably pure, to evaporate a larger quantity than ½ a litre to dryness. When intended for the determination of other matters, the residue, after ignition, is treated as follows.

SILICA.—The residue is treated with hydrochloric acid in slight excess, loss from effervescence being guarded against; the whole is evaporated to dryness, and the silica separated in the usual way.

FERRIC OXIDE, ALUMINA, LIME, and MAGNESIA are estimated in the same way as in soils, the magnesium being precipitated by ammonium phosphate. The ferric oxide, if much be present, will require re-solution to remove adhering lime.

ALKALIES.—The filtrate from the magnesium precipitate is evaporated to dryness and the residue gently ignited; it is then dissolved in a little water, a slight excess of baryta-water added, the whole boiled and filtered: the filtrate is boiled, a little sulphuric acid added, the barium sulphate separated by filtration through Swedish paper, and the clear solution evaporated to dryness, ignited, and weighed. The alkalies are here weighed as sulphates; for their separation, see p. 193.

SULPHUR TRIOXIDE is determined by precipitation with barium chloride in ½ a litre of the water, which should be first acidified with a little HCl and then concentrated to 100 c. c.

4. CHLORINE

is determined by the volumetric method (see page 173) in from 100 c. c. to ½ a litre of the water.

Waters containing an abnormal quantity of chlorine have generally obtained it by contamination with sewage, and must therefore, if intended for domestic purposes, be looked upon with suspicion. But it must not be forgotten that two additional and perfectly innocuous sources of chlorides exist, namely:—(1) the sea spray, which is occasionally carried forty miles or more inland, finding its way ultimately to water-bearing strata; and (2) the occurrence of saliferous rocks or saline springs. But such local conditions, influencing the amount of chlorides in well-waters, are easily ascertained. The amount of chlorine in the purest waters scarcely exceeds 1 gram in 100 litres; in London sewage about 1 gram in 10 litres occurs.

5. AMMONIA, ready-formed,

is determined by distilling a measured quantity of the water rendered alkaline with sodium carbonate and testing the distillate with Nessler's solution against a solution containing a known quantity of ammonia. The comparison is made by difference in colour; but it is well to determine roughly the amount of ammonia before distillation; this may be done in the following way. Take 50 c. c. of the water and place it in a colourless glass cylinder about 18 centims. in height and capable of holding 100 c. c. Now add 2 c. c. of Nessler's solution, and mix well with a glass rod. A second cylinder of similar dimensions is to have 50 c. c. of distilled water run into it (this water should have been previously freed from ammonia by distillation from a retort with a little sodium carbonate, the distillate having been collected when no coloration was produced in it with Nessler's test: if many estimations of ammonia are being made, it will be found convenient to have a few litres of this water kept in well-stoppered bottles at hand), and then 5 c. c. of standard ammonium chloride solution. This solution, which contains ·00001 gram of ammonia (NH_3) per c. c., is to be mixed well with the pure water by stirring. Place the two cylinders upon a sheet of white paper, and compare the colour by looking down through the liquids; should the colours appear about the same in each, 500 c. c. of the water are to be taken for the estimation; but should it be more intense in the cylinder containing the sample of water, then a proportionately smaller quantity should be taken, but its bulk should be made up to 500 c. c. with pure distilled water. A measured quantity of the water, not less than ½ a litre, is now placed in a 40-oz. stoppered retort, and 1 gram, or enough to render the reaction of the water alkaline, of recently ignited sodium carbonate added. Distil rapidly, and collect the distillate in one of the glass cylinders mentioned above until it contains 50 c. c. (which may be easily known by previously marking upon them the level to which they will be filled by 50 c. c.). This cylinder is now set on one side, and another put in its place and allowed to fill to the same extent, the lamp being then removed from the retort. The second portion has 2 c. c. of Nessler's test added to it, and is then to be well mixed. A third cylinder is now taken, and as much of the standard ammonium chloride solution added as it is thought will produce about the same tint (this can be easily found with a little practice), the cylinder filled up to the mark with pure distilled water, and the Nessler test added. If it be found that the two do not agree in tint, the cylinder is to be emptied and well rinsed out with water free from ammonia, and the same operation gone through with a different quantity of ammonium chloride until the right tint has been obtained; if the quantity of ammonia does not exceed ·001 milligram, the distillation need not be continued; but should it be more than this, another 50 c. c. are to be distilled over, and so on until it does not contain more than this amount. If the amount of ammonia in the second distillate does not exceed 2 c. c. of the ammonium chloride solution, then the first quantity of 50 c. c. that was collected may have its ammonia estimated in the same way; but should the second be found to contain more than this amount, then the first must be measured and a portion only taken at a time, as it would otherwise be so strong that a very dark colour or precipitate would be produced with the Nessler's test. When the amounts of ammonia in all the distillates are known, they are to be added together, from which total the quantity in 100,000 parts is easily calculated; it should not exceed ·01 part in 100,000 in river waters; sewage may contain 1000 times as much. The standard ammonia solution is made by dissolving ·3147 gram of pure ammonium chloride in a litre of pure distilled water; from this the working solution is made by taking 100 c. c. and diluting it to 1 litre, when 1 c. c. will be equal to ·00001 gram of ammonia. The retort used in distilling the ammonia should be connected with a Liebig's condenser, both it and the retort having been thoroughly cleaned with water free from ammonia. If the neck of the retort is of such a small size that it will easily slip into the tube of the condenser, it will be easy to make the connection between them quite tight by means of a round india-rubber ring, previously cleansed in soda solution, and a band of tinfoil wrapped round the junction. The standard ammonium-chloride solution should always be added *before* the Nessler test, otherwise a turbidity will be produced; of course all the operations must be performed in a room free from ammoniacal fumes.

The presence of ammonia in any quantity is indicative of contamination of the water with decaying or refuse animal matter, such as sewage, or with the farmyard manure &c., which has been applied to the arable land in the area of country from which the water has been derived. The same origin may be assigned to a large part of the nitrates in deep-well waters.

The amount of ammonia in Thames water, as supplied to London, is about ·002 part per 100,000, and of N as nitrates and nitrites about ·2.

6. AMMONIA producible from organic nitrogen compounds in the water.

A good deal of the combined nitrogen occurring in impure waters may exist in the form of nitrogenous organic matter: about ⅔ of this nitrogen may generally be obtained in the form of what is called "albuminoid ammonia" by the following process:—

Prepare an alkaline solution of potassium permanganate by dissolving 4 grams of potassium permanganate and 100 grams of potassium hydrate in 550 c. c. of pure distilled water. Boil the solution until it has been reduced to ½ a litre, and keep it in a well-stoppered bottle.

As soon as the distillation of the water for "ready-formed ammonia" has been commenced, about 25 c. c. of this permanganate solution are to be placed in a flask diluted with 100 c. c. of distilled water and kept boiling during the whole time that the sample of water is being distilled.

To the liquid remaining in the retort, after the distillation with sodium carbonate already described, add of the above diluted permanganate solution enough to make up about 500 c. c of liquid and distil again. Collect the distillate in portions of 50 c. c., as in the estimation of ready-formed ammonia, and ascertain their strength by means of Nessler's test. Stop the distillation when the last 50 c. c. coming over contain less than ·000001 gram of NH_3. The amounts of ammonia in all these distillates are to be added together and entered as "albuminoid ammonia," a term which, though inexact, is generally understood.

The bumping or excessive violence with which alkaline liquids often boil may be mitigated by the addition to the retorts of clean pumice or of a few short pieces of capillary glass tube, each sealed at one end.

7. NITROGEN AS NITRATES AND NITRITES.

Nitrates may be detected by evaporating a few ounces nearly to dryness, and applying the indigo or sulphate-of-iron test (see p. 22); nitrites, by adding to the concentrated water a clear mixture of potassium iodide, starch-paste, and acetic acid: an indigo-blue tint indicates nitrous acid; care must, however, be taken that the iodide contains no iodate.

The nitrogen present in a water in the forms of nitrates and nitrites may be estimated quantitatively by several processes, most of these demanding a good deal of skill and patience. The mercury and oil-of-vitriol method, Warington's improved indigo method, the aluminium method, and the copper-zinc method are all in use. The last-named process is, however, so simple, easy, and exact that it is generally to be preferred.

Copper-Zinc Method.

The determination of nitrates and nitrites by this process is to be accomplished in the following way.

A wet copper-zinc couple is first of all prepared by washing a slip of clean zinc foil, about 2 inches wide and 3 inches long, with sodium-hydrate solution and then with distilled water, to remove grease, and then placing the metallic strip in a solution of copper sulphate containing 3 per cent. of the pure crystallized salt. In 3 or 4 minutes, when an adherent coating of spongy copper will have formed upon the strip, the latter is to be removed from the liquid and thoroughly washed with abundance of distilled water, and then finally with a small quantity of the water to be analysed. The couple is now to be placed in a wide-mouth stoppered bottle of 6 or 8 ounces capacity, together with a carefully measured quantity of the water under examination; about 100 to 150 c. c. will generally suffice. A small addition of pure oxalic acid to precipitate the lime and quicken the action should be made before inserting the stopper; 2 decigrams of oxalic acid will be ample. The water remains in contact with the couple all night in a warm place; on the following morning the conversion of the nitrates into ammonia will be found to be complete.

The next step in the process is the determination of the ammonia present in the liquid. A measured portion is drawn off by a siphon if clear, or, if turbid, is poured through a washed filter. If the liquid be colourless and give no precipitate with the Nessler test, then it may be Nesslerized without further treatment, exactly as described on p. 214; only it may need dilution with pure distilled ammonia-free water. But should the liquid show any decided colour in the Nessler glass, or should it become turbid on the addition of the Nessler reagent, then a measured portion must be rendered alkaline with sodium carbonate and submitted to distillation with all the precautions given on pages 214–217. The ammonia found must be calculated into its equivalent of nitrogen; from this the amount of nitrogen existing in the water as ready-formed ammonia must be subtracted; and then the remaining nitrogen should be translated into N_2O_5.

Aluminium Method.

Another method for the estimation of oxidized nitrogen consists in the conversion of the nitrogen into ammonia by the action of aluminium in an alkaline solution. For this purpose

100 c. c. of the water are introduced into a non-tubulated retort, and 50 c. c. of a 10 per cent. solution of pure sodium hydrate added; about 50 c. c. are then distilled off, or until no ammonia is found in the distillate by Nessler's test. The retort is cooled, and a piece of sheet aluminium introduced, the neck of the retort inclined upwards, and closed with a cork fitted with a small glass tube containing glass beads moistened with dilute hydrochloric acid. This is connected with a second similar tube, containing glass beads moistened with strong sulphuric acid, to prevent ammonia from the air entering the apparatus, which is now allowed to stand for a few hours. The first tube is then rinsed into the retort with pure water, the retort fitted to a purified condenser, and about half its contents distilled into pure water, the end of the retort dipping just below the surface of the water: the distillate is made up to a known volume, and the ammonia estimated by Nessler's test, as above. The soda used must be free from nitrates; it may be rendered so by dissolving a little aluminium in it and boiling. If more convenient, a litre of the water may be concentrated, and treated in the same way, except that the distillate is to be received into standard acid, and the amount of ammonia found by means of standard alkali.

The nitric acid in potassium and sodium nitrates may be conveniently estimated by this last method, the liquid being preferably first distilled into a small flask, from which it is again distilled into the standard acid, thereby retaining any trace of soda which may have first distilled over. This process is also applicable to the estimation of the nitrates existing in turnips, swedes, beets, and other vegetables. A mixture of zinc and iron filings may be substituted for the aluminium.

Nitrites.

If the nitrates and nitrites in a water have been determined together by means of one of the above-described processes, it is possible to learn by means of another analytic process the amount of nitrites present. This is done by the use of Griess's metaphenylene-diamine method. This substance gives no colour with nitric acid, but a yellow with nitrous acid.

100 c. c. of the water are poured into a glass cylinder and then 1 c. c. of dilute (1 of acid to 2 of water) pure sulphuric acid and 1 c. c. of metaphenylene-diamine solution are added. The latter reagent is made by dissolving 5 grams of this base in 1 litre of water and then acidulating the solution with sulphuric acid: the liquid must be colourless. If a red coloration be at once produced, a fresh and smaller portion of the water must be taken and diluted with pure distilled water to 100 c. c. The colour should take one or two minutes to make its appearance. It is now necessary to compare the colour produced in the water with that obtained in a precisely similar manner in a standard solution of pure potassium nitrite: this comparison must be made simultaneously, as the coloration increases on standing. The standard potassium nitrite solution contains ·00001 gram of N_2O_3 in 1 c. c. It is prepared by taking ·406 gram of pure dry crystallized silver nitrite, dissolving it in hot water and decomposing it with a slight excess of potassium chloride solution. When cold the solution is made up to 1 litre, and the silver chloride allowed to settle. The clear supernatant liquid is decanted off, and each 100 c. c. of it made up to 1 litre: this solution must be kept in well-stoppered bottles completely full.

Coloured waters, previously to being tested in the above manner for nitrites, must be decolorized by alum and sodium carbonate or by a mixture of sodium hydrate and carbonate; the precipitate formed is to be filtered off.

If the N_2O_3 found by Griess's method be translated into its equivalent of NH_3, and this amount be deducted from the amount of NH_3 *produced* from the associated nitrates and nitrites (in, say, the copper-zinc method), the remainder will represent the NH_3 due to nitrites alone, and may be converted into its equivalent of N_2O_5 or $Ca2NO_3$.

8. Total and Permanent Hardness.

The hardness of a water is determined by means of Clark's test, which is a solution of soap in weak spirit (equal parts of spirit of specific gravity ·835 and water), of which 14·25 c. c. just suffice to produce a permanent lather when shaken with 50 c. c. of water containing ·2 gram of calcium carbonate per litre (·222 gram calcium chloride).

The soap test is used as follows:—50 c. c. of the water under examination are placed in a stoppered bottle of about four times this capacity, well agitated, and the carbon dioxide given off is sucked out by means of a glass tube. A burette graduated in c. c. is then filled with the soap solution and 1 c. c. added at a time. After each addition the stopper is to be placed in the bottle, which is then to be well shaken: towards the end of the operation smaller quantities should be added, the estimation being finished when an unbroken lather remains permanently for five minutes, the bottle being placed upon its side. The number of c. c. of soap solution is now to be read off, and the hardness found by inspection of the Table on p. 222. Should the water not yield a permanent lather with 16 c. c. of soap test, a fresh experiment is commenced with a smaller portion of the water made up to 50 c. c. with fresh-boiled distilled water, and the number showing the hardness multiplied by the fraction of 50 c. c. used; thus if 25 c. c. were used, multiply by 2, &c. If magnesium salts are known to be present in considerable quantity in any water, the sample should be so diluted as to require not more than 7 c. c. of soap test for 50 c. c. of the diluted water.

The method given above shows the total hardness; the permanent hardness is determined by boiling ½ a litre of the water in a flask of rather large size, and having a long but broad neck. The ebullition is allowed to go on gently for half an hour, a little boiled distilled water being added now and then to replace in part that lost by evaporation; then the flask is rapidly cooled, the mouth being covered with a watch-glass, and the volume of water in it again made up, with boiled distilled water, to ½ a litre, filtered, and the hardness estimated in 50 c. c. as before.

Table of Hardness.

c. c. soap test used.	CaCO$_3$ in 100,000 parts.	c. c. soap test used.	CaCO$_3$ in 100,000 parts.	c. c. soap test used.	CaCO$_3$ in 100,000 parts.	c. c. soap test used.	CaCO$_3$ in 100,000 parts.
·7	·00	4·6	5·43	8·5	11·05	12·4	17·06
·8	·16	4·7	·57	8·6	·20	12·5	·22
·9	·32	4·8	·71	8·7	·35	12·6	·38
1·0	·48	4·9	·86	8·8	·50	12·7	·54
1·1	·63	5·0	6·00	8·9	·65	12·8	·70
1·2	·79	5·1	·14	9·0	·80	12·9	·86
1·3	·95	5·2	·29	9·1	·95	13·0	18·02
1·4	1·11	5·3	·43	9·2	12·11	13·1	·17
1·5	·27	5·4	·57	9·3	·26	13·2	·33
1·6	·43	5·5	·71	9·4	·41	13·3	·49
1·7	·56	5·6	·86	9·5	·56	13·4	·65
1·8	·69	5·7	7·00	9·6	·71	13·5	·81
1·9	·82	5·8	·14	9·7	·86	13·6	·97
2·0	·95	5·9	·29	9·8	13·01	13·7	19·13
2·1	2·08	6·0	·43	9·9	·16	13·8	·29
2·2	·21	6·1	·57	10·0	·31	13·9	·44
2·3	·34	6·2	·71	10·1	·46	14·0	·60
2·4	·47	6·3	·86	10·2	·61	14·1	·76
2·5	·60	6·4	8·00	10·3	·76	14·2	·92
2·6	·73	6·5	·14	10·4	·91	14·3	20·08
2·7	·86	6·6	·29	10·5	14·06	14·4	·24
2·8	·99	6·7	·43	10·6	·21	14·5	·40
2·9	3·12	6·8	·57	10·7	·37	14·6	·56
3·0	·25	6·9	·71	10·8	·52	14·7	·71
3·1	·38	7·0	·86	10·9	·68	14·8	·87
3·2	·51	7·1	9·00	11·0	·84	14·9	21·03
3·3	·64	7·2	·14	11·1	15·00	15·0	·19
3·4	·77	7·3	·29	11·2	·16	15·1	·35
3·5	·90	7·4	·43	11·3	·32	15·2	·51
3·6	4·03	7·5	·57	11·4	·48	15·3	·68
3·7	·16	7·6	·71	11·5	·63	15·4	·85
3·8	·29	7·7	·86	11·6	·79	15·5	22·02
3·9	·43	7·8	10·00	11·7	·95	15·6	·18
4·0	·57	7·9	·15	11·8	16·11	15·7	·35
4·1	·71	8·0	·30	11·9	·27	15·8	·52
4·2	·86	8·1	·45	12·0	·43	15·9	·69
4·3	5·00	8·2	·60	12·1	·59	16·0	·86
4·4	·14	8·3	·75	12·2	·75		
4·5	·29	8·4	·90	12·3	·90		

The temporary hardness is the difference between the total and permanent hardness.

It will be evident from the preceding Table that 50 c. c. of distilled water require nearly ¾ of a c. c. of soap test to produce a permanent lather.

For the determination of hardness in water two solutions are necessary—one of soap, the other of calcium chloride or sulphate. The modes of preparing these solutions may be thus conducted.

PREPARATION OF STANDARD SOAP TEST.—Take 9 grams of lead-plaster (Emplastrum Plumbi, B. P.) and 2·6 grams of dry potassium carbonate: rub these materials together in a mortar with a few drops of rectified spirits of wine of spec. grav. ·835, till a perfect mixture, having the consistence of cream, has been effected. When the mass has stood some time, exhaust it with repeated additions of spirit, filter the spirituous solution, and add more spirit till the whole liquid is of the bulk of 600 c. c.; lastly, add 400 c. c. of distilled water, which has been recently boiled to expel carbon dioxide.

The strong soap solution thus obtained will now require standardizing by means of a solution of calcium chloride, which is prepared as follows. Weigh out ·2 gram of Iceland spar into a clean porcelain or platinum dish, having a clock-glass for a cover, and add dilute hydrochloric acid, a little at a time, until the substance is dissolved. Evaporate the solution, together with the washings from the cover, carefully to dryness, and heat the residue till no more acid fumes are given off. Redissolve the residue in water and again evaporate as below. Now to the residue, which must be wholly soluble in water, add enough pure boiled water to make up the volume to 1 litre. The calcium solution may now be used to standardize that containing soap. Pour 50 c. c. of the former liquid into a bottle, and run into it from a burette a few drops of the strong soap solution previously described. This operation is repeated with the usual precautions until a permanent lather is obtained. The soap test will be found too strong and must be diluted with proof spirit until its strength has been lowered to the proper standard: this point is reached when 14·25 c. c. produce a permanent lather with 50 c. c. of the standard calcium chloride—a strength which corresponds to 20 parts of $CaCO_3$ in 100,000. The diluted soap test should be allowed to stand some time, and then filtered, before its strength is finally adjusted to the point just named.

The soap solution may be prepared with pure white curd soap; the calcium solution may be made with an equivalent weight of pure crystallized calcium sulphate, $CaSO_4$, 2aq.

STATEMENT OF RESULTS.

We have hitherto assumed that all the results of a water analysis are referred to parts in 100,000; if it be desired to convert these into grains per gallon, multiply them by ·7. To convert grams per litre into grains per gallon, multiply by 70.

The total solid residue left on evaporating a water seldom agrees closely in amount with the total amounts of the several ingredients which have been specially determined. One source of this discrepancy lies in the reactions which occur amongst the salts of a water as the liquid becomes concentrated; another in the partial loss of water of crystallization suffered by the calcium sulphate and other salts at the temperature of drying the residue.

It is impossible to ascertain the manner in which each substance is combined in the original water; the best plan therefore is to set down all the items, as deduced from the several analyses, separately, subtracting from the total an amount of oxygen equivalent to the chlorine found, that element being supposed to be combined with the sodium. The total, thus amended, will be less than the solid contents found, by the amount of carbonic acid present. The sum of the saturating power of the acid oxides should of course be equal to the sum of the saturating power of the bases, if the analysis be correct.

The most usual mode of placing the results, however, is to combine the acids and bases; this is generally done as follows:—

The sulphur trioxide is combined with lime, the remainder of the calcium being set down as carbonate: the chlorine is combined with sodium; if chlorine still remains, it is combined with potassium; if still in excess, with magnesium. Magnesia, potash, and soda (when their metals are not combined with chlorine) are united with carbon dioxide. Nitrogen pentoxide, if present, may be combined with lime or potash, ammonium with chlorine. Silica remains uncombined, while ferrous oxide is united with carbon dioxide. Some of these arrangements of acids and bases are known to be merely conventional or artificial, and in particular cases there may be found good reasons for modifying them. For instance, there are natural mineral or medicinal waters in which such compounds as magnesium sulphate, ferrous sulphate, ferric chloride, and even barium chloride are known to occur.

In order to render a water analysis more complete and instructive it is desirable to examine under the microscope the deposit which settles down from the freshly drawn sample of water when left to rest for 12 hours; a $\frac{1}{4}$ and then a $\frac{1}{8}$ objective being employed. The action of the water on strips of tarnished and untarnished lead should also be tried. This experiment is to be made in 20-ounce bottles half full, the strips rising above the level of the water. The liquid is to be poured off after 24 hours' contact with the metal and tested for lead in solution. A third experiment consists in ascertaining the number of colonies of organisms which grow in a given time on a nutritive jelly which has been mixed with 1 c. c. of the sample of water. All the apparatus used must be completely sterilized, and every precaution taken during the course of the experiment to prevent the entrance of extraneous organisms. For the details of the method reference must be made to special works in which this biological method of examining water is fully described. The precise value of the indications afforded by this process has scarcely been determined; it requires very elaborate precautions, and the most expert manipulation in order that trustworthy results may be secured. It was devised by Dr. Koch, modified and improved by Dr. P. F. Frankland.

When the whole of the above-described qualitative and quantitative results have been obtained, the figures, which have been calculated into parts per 100,000, or into grains per gallon, together with the miscellaneous observations made, should be recorded in order. The following data at least should always be given :—

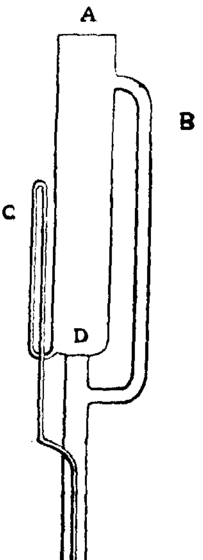
Description and origin of sample.
Date when drawn.

rendered easier and more complete. The operation is repeated eight or nine times: then, while the solvent is returning through the cake into A, the apparatus is disengaged, and a drop falling from the lower end of tube C received on a watch-glass and evaporated by a gentle warmth. If no stain be left, or if, at least, no oil-globules appear, the extraction is complete; if otherwise, the process is repeated as before. When the oil is all extracted, as much solvent as possible is distilled over into B, the oil with a little solvent remaining in the flask A. This flask, which should be short (7 centims. high), wide-mouthed, strong, and not over 18 grams in weight, is then kept for a short time in a warm place (say, on the top of the water-oven), and finally is heated to 100° until its weight is constant. The drying should be conducted without unnecessary delay, in order to avoid the oxidation of the oil and consequent increase of weight. But, on the other hand, the oil from some meals may be found to diminish seriously in weight in the water-oven. For instance, the oil from palm-nut kernel meal contains some volatile constituent, which will be lost unless the drying be conducted at the ordinary temperature of the air, *in vacuo* and over oil of vitriol. Where but a small quantity of material is available for an oil determination, it may be mixed with coarse but perfectly pure silicious sand before introduction into the oil-extractor. The whole scale of the apparatus may also be slightly reduced in such cases. The traces of chlorophyll and resin which accompany the oil and fat may generally be disregarded. Sometimes a cylinder of fine platinum gauze, fitting exactly into the tube C, may be used to contain the oily material: this enables the exhausted substance to be readily withdrawn without loss at the close of the experiment.

A very convenient form of extraction-apparatus has been introduced by Soxhlet. A vertical section of its main portion is shown in fig. 21, of one fourth the real size. To complete the apparatus, an upright glass tubular condenser, through which a current of cold water passes, is attached by means of a sound perforated cork to the digesting-tube A. The end of the inner condensing-tube should protrude a little below the entrance of the vapour-tube B. To the base of the apparatus at E a short stout flask, of about 100 c. c. capacity and not weighing more than 20 grams, is fitted by means of a good perforated cork. When the apparatus is thus completed the whole may be slung, by wire or cord, in such a way as to admit of being easily raised or lowered.

In order to commence a quantitative estimation of oil in an oilcake, about 15 c. c. (or half a fluid ounce) of the selected solvent are put into the flask (mentioned in the foregoing paragraph), which is then attached to the Soxhlet extractor. A weighed quantity of the powdered oilcake, contained in a Swedish filter-paper so folded as to loosely fit the tube, is now dropped into the extractor at D (care should be taken that no particles of the powder can escape from this paper packet). The solvent is now introduced in quantity nearly sufficient to rise to the upper curve of the siphon-tube C at the side. The vertical glass condenser above is now attached and the current of cold water permitted to flow into it. The flask below is placed in or upon a bath of warm water so as to allow the solvent to boil. The vapour will rise through E, passing into B and thence into the vertical condenser, from which it will drop into A as a liquid. The oil will be dissolved out from the cake, and the solution of it will gradually accumulate until the siphon C can act. When this occurs the extractor will be emptied, the liquid passing through the quill tube which terminates the longer limb of the siphon inside E. By the continuous warming of the receiving flask below E the solvent will repeatedly ascend as vapour through B and descend

Fig. 21.



as liquid through C, until a drop, tested as it falls from E, will no longer contain a trace of oil. The remaining operations are conducted exactly as in the case of the employment of the apparatus represented in fig. 20. The defect of the Soxhlet apparatus, as commonly made, consists in the large quantity of ether or other solvent which is required to work it. But this imperfection is remedied by making the place of exit of the siphon-tube C much lower down the extraction-tube : this change is particularly expedient when but a small bulk of material is to be employed for an oil-determination.

*FIBRE.—The terms fibre and cellulose are often used very vaguely, and include the various compounds containing carbon, hydrogen, and oxygen (other than oil), which are insoluble in cold or hot water. Pure cellulose itself may vary a good deal in its chemical deportment, according to its stage of development and its physiological *rôle*. The fundamental cellulose of plants is much altered in chemical and physical properties by those infiltrations and deposits which go on in the tissues of the plant. Thus while pure cellulose, represented by purified cotton, is soluble in oil of vitriol of sp. gr. 1·53, cuticle, cork, and lignin or lignose, the chief constituent of hard woods, are nearly insoluble in this reagent. On the other hand, these latter substances may be readily acted upon by means of a mixture of weak nitric acid and potassium chlorate, which leaves the cellulose almost untouched. The boiling of a mixed vegetable tissue with weak acid and then with weak alkali alters and dissolves some of the softer cellulose, and at the same time removes some of the lignin, &c., of which we have before made mention. As the primary object of making an analysis of an oilcake is to ascertain its feeding value, we may be content with processes which do not effect absolutely perfect separation of the constituents of the tissues known as cellulose and fibre. It might indeed have been assumed that the materials which resist the chemical treatment which has been mentioned, and which we are about to describe, cannot have much alimentary value. But this is not the case, for ruminating animals often digest half the so-called "indigestible fibre" of their food. We give two methods for determining cellulose or fibre: the first process is troublesome in manipulation, yet yields tolerably constant residues, and is that usually adopted in commercial analyses. The second process merely determines the cellulose; and so the residue in this case cannot be entered as "indigestible fibre," particularly as we know that different farm-animals are able to digest such cellulose, in some of its forms, more or less completely.

As the presence of oil in considerable quantity interferes with the determination of fibre, it is advisable to use for this purpose that portion of the sample which has been employed for the estimation of oil, or else to exhaust the dry fibre obtained by one of the processes described below with petroleum spirit or ether and again to dry it.

Acid and Alkali Method.

3 grams of the coarsely powdered sample are placed in a large beaker (or in an Erlenmeyer flask), 150 c. c. of water added, and the whole brought to a boiling heat, with frequent stirring or agitation to prevent burning: 50 c. c. of dilute sulphuric acid containing 5 per cent. of H_2SO_4 are then added, and the boiling continued for ½ an hour, the normal volume 200 c. c. (best marked by an ink line on the beaker) being maintained throughout the operation by the addition of a little boiling water. Collect the residue from the acid digestion on a fine calico or linen filter, after having siphoned off the clear supernatant liquid. The residue is to be thoroughly washed on the filter with hot water, and then syringed off the linen into the beaker with about 100 c. c. of hot water. 50 c. c. of a 5 per cent. of potassium hydrate (KHO) solution are next added, and the beaker filled up with hot water to the mark indicating 200 c. c. The mixture is boiled for ½ an hour, some cold water added, and the whole allowed to rest. When the supernatant liquid is clear it is siphoned off and the residue collected once more on the calico filter, washed with a

1 per cent. solution of ammonium hydrate until the filtrate is colourless, and then syringed out of the calico into a paper filter which has been dried and weighed previously. Now moisten the filter and its contents with dilute hydrochloric acid, and wash with hot water until a few drops of the filtrate leave no residue on evaporation. Dry the filter and weigh it. Or, when the fibre has been perfectly washed on the calico filter (the aid of an air-pump is often serviceable here), it is transferred to a platinum or porcelain dish, dried on the steamer and then at 100° till constant, and weighed. Afterwards it is ignited, and again weighed: the second weight of dish and ash having been subtracted from the first gives the weight of fibre.

Potassium-Chlorate Method.

2 grams of the dried substance (from which the oil has been extracted) are placed in a wide-mouthed stoppered bottle with 1·6 gram of finely powdered potassium chlorate, and 25 c. c. of nitric acid, having the specific gravity 1·10: the mixture is allowed to remain at a temperature not exceeding 18° C. for 14 days. Then the contents of the bottle are mixed with cold water, transferred to a filter, and thoroughly washed, at first with cold, and then with hot water. When all the soluble matters have been thus washed out, the fibre is syringed off the filter and treated with a 1 per cent. ammonium hydrate solution in a beaker, being allowed to digest in a warm place for one hour. The fibre is now transferred to a paper filter which has been previously dried and weighed: the remainder of the operations are to be conducted as in the preceding method.

Cellulose prepared as above may be rendered still purer by washing with alcohol and ether, but still retains some nitrogen compounds and ash: if it be desired to make corrections for these impurities, determinations of them must be made in the usual manner.

Albuminoids.—A nitrogen combustion is made with about ·8 gram of the *finely* powdered cake: in the case of cakes very rich in nitrogen (such as decorticated cotton cake) not more than ·5 gram should be taken; the tube used should be a tolerably long one. The percentage of nitrogen found is multiplied by 6·25; the product is regarded as representing the percentage of albuminoids in the cake; for the albuminoids of plants contain as an average about 16 per cent. of nitrogen, and 16 × 6·25 equals 100.

In the case of some cakes it has been found that the ordinary combustion with soda-lime fails to convert the whole of the nitrogen present into ammonia. East-Indian linseed cake affords an example of this peculiarity. It would seem that the use of Ruffle's thiosulphate mixture as described on page 146 affords results nearly as satisfactory as those obtained when the more troublesome and tedious absolute method of determining nitrogen devised by Dumas is employed.

But there is a more recently-invented method of determining nitrogen in organic substances easier of execution and probably quite as accurate as that of Dumas. It is known as

Kjeldahl's Method.

In this method the nitrogen present is converted into ammonia by digesting the substance with strong sulphuric acid, the ammonia formed being afterwards liberated by means of caustic soda, distilled off and estimated by a titration-process.

One gram of the substance to be analysed is brought into a flask of about 250 c.c. capacity and then 20 c.c. of the strongest sulphuric acid free from nitrogen compounds are added. The flask, placed in an inclined position, is gently heated until violent frothing has ceased, then the temperature is raised until the boiling-point of the acid is reached. When its contents, though quite black, are free from solid particles, the flask is placed in the vertical position and about 8 grams of dry powdered potassium sulphate introduced; this done, the flask is at once inclined as before. The K_2SO_4 dissolves in the acid and raises its boiling-point so considerably that, at the higher temperature which the mixture now reaches on the continued application of heat, the carbonaceous matter present is oxidized and the liquid becomes less and less dark in hue. When it has lost all or nearly all its colour, the flask is allowed to cool. During the operations above described it will be found that an Argand burner with an iron chimney affords a convenient source of heat, as the light it gives enables the operator to watch the process of the gradual clearing of the solution.

The next step to be taken consists of the liberation and condensation of the ammonia which has been formed and which is now present in the form of sulphate. These ends are accomplished by passing a current of steam through the liquid previously rendered alkaline, the ammonia being carried forward into a Liebig condenser. The steam must be generated from water which has been proved to be absolutely free from ammonia, while the condenser must be so constructed (with a small reflux adapter) that no spirting of the alkaline liquid can occur to vitiate the result.

The operations are conducted thus :—Take a glass flask of about 1750 c. c. capacity and fitted with an indiarubber stopper having three perforations. Through one of these a tube passing nearly to the bottom of the flask is inserted ; this is for the supply of steam. In the second perforation the tube of a cylindrical funnel having a glass stop-cock is adjusted, while the third receives the neck of the reflux adapter, which is itself connected with a Liebig condenser. The other end of the condenser communicates with the receiver for the ammoniacal distillate, which should be an Erlenmeyer flask of 250 c. c. capacity. In order to prevent any loss of ammonia, a wide tube should be fitted to the beak at the lower end of the condenser and should pass to the bottom of the Erlenmeyer flask. When the apparatus is quite ready, and a current of cold water is passing through the condenser,—

(1) Pour about 100 c. c. pure distilled water into the large flask, and then add the acid liquid in which the substance to be analysed has been decomposed. Rinse out the small flask thrice with water and add the rinsings to the contents of the large flask.

(2) Deliver 20 c. c. of dilute standard sulphuric acid from a pipette into the receiving flask.

(3) Run 100 c. c. of strong sodium hydrate solution (357 grams NaHO, free from nitrate, per litre) through the funnel into the large flask, and close the stop-cock.

(4) Pass steam for half-an-hour through the large flask, then light a rose-burner under it and continue the passage of the steam for five minutes longer.

(5) Detach the delivery-tube from the condenser, leaving it in the receiving flask; add a few drops of methyl-orange solution, and then titrate the unneutralized acid in the contents of the flask with standard sodium hydrate solution; exactly in the same manner as in the ordinary soda-lime process described on p. 143.

ASH is determined in about 3 grams of the sample. A good linseed cake will not leave quite 7 per cent. of ash; and of this 35 per cent. will be phosphorus pentoxide precipitable by ammonium molybdate from the nitric-acid solution of the ash. The phosphorus pentoxide in the ash may also be estimated by the process described further on under the heading "Analysis of Ashes of Plants." But determinations of the percentage of total ash and of the amount of sand and insoluble silicious matter present will suffice for most purposes.

SAND AND SILICIOUS MATTER.—The ash is digested with dilute hydrochloric (or nitric) acid, and the insoluble matter collected, washed, burnt, and weighed.

MUCILAGE, &c.—The various non-nitrogenous combustible constituents (other than oil and fibre) of cakes are usually determined by difference. They include mucilage, digestible cellulose, pectose, and other less important carbonaceous substances.

N.B. A genuine linseed cake contains no *starch*; if this be present, bran, rice-dust, or some similar substance has been mixed with the cake. Starch may be tested for by boiling some of the powdered sample in water till it forms a thin paste, filtering this through fine muslin (which has been previously cleansed by boiling with water, &c.), and adding to the filtrate

when quite cold a few drops of tincture of iodine; the formation of a blue colour indicates the presence of starch. Sugar, likewise, does not occur in genuine cakes; its presence may be ascertained thus:—boil ·2 or ·3 of a gram of the powdered cake in water, filter the solution, and add to the clear filtrate a small quantity of the sugar test and a few drops of a solution of sodium hydrate. On boiling the mixture, cuprous oxide (Cu_2O) will be more or less rapidly deposited, in greater or less quantity, and with a colour varying from yellow to red, according to the nature and proportion of the sugar present.

A very small trace of starch or of sugar may sometimes be due to amylaceous or saccharine weed seeds, which, in the proportion of a few per cent., occur in all samples of linseed, however good; indeed, linseed-sellers reckon upon the presence of 4 % of seeds other than linseed, regarding such admixture as representing the standard of commercial purity. The various kinds of cereal refuse, such as bran, rice shudes, oat husks, which are found in adulterated linseed cakes, lower the normal percentages of oil and albuminoids, and increase the proportion of indigestible fibre; on the other hand, the addition of saccharine substances like locust beans, largely increases the soluble non-nitrogenous matters. But it must be recollected that the range of variation as to oil and albuminoids in unmixed cakes is considerable, and that the quantities of the adulterating materials added may be so adjusted as to imitate very closely, even as to albuminoids and oil, the composition of the pressed linseed itself. The analyst who wishes thoroughly to master this intricate subject, must not rest content with the indications afforded by chemical analysis. He should learn to identify, by the use of the microscope, the surface markings, colours, &c. of the various vegetable products which are introduced, through accident or by design, into oilcakes. Such observations should be made first of all with the several adulterating and foreign substances themselves; it becomes then easy to recognize the fragments of the same substances when present in oilcakes. There are also special experiments which may be made with different species of cakes in order to discover some particular material likely to render them hurtful to animals. One may search by appropriate methods in any particular instance for poisonous alkaloids and for purgative substances, and for essential oil of mustard in the case of rapeseed and Indian linseed. The thick black husks of the castor-oil bean, the curcas bean, and croton seeds can be readily detected after treating the cake with solution of bleaching-powder and dilute hydrochloric acid, which bleach all the integuments of ordinary seeds. There is also one test for the goodness of linseed-cake which affords fair indications of quality: it is thus performed:—Pour 180 cubic centimetres of boiling water upon 10 grams of finely ground linseed-cake contained in a tall beaker, and stir the mixture. In one hour the whole will have set into a kind of jelly, pleasant in odour and taste, of a straw-colour, and neutral to test-papers.

GRAIN, STRAW, HAY.

Most kinds of grain, flour, bran, and meal, as well as straw, hay, and other dry fodder, may be analysed as an oilcake. Further on a hint or two as to the case of green fodder will be found. If it be desirable to determine separately the starch contained in any of the above products, one of the following plans may be adopted.

STARCH.—A quantity of the material is taken for the analysis, so that about 1 gram of starch is present in it: it must be finely ground or in a fine state of division. 100 c. c. of water and 1 c. c. of pure hydrochloric acid (of 1·125 sp. gr.) are placed in a flask and the weighed substance introduced. The mixture is kept on the water-bath at a temperature of 70° C. until a drop of the liquid no longer shows a blue tint when tested with iodine solution. The whole is then thrown on to a filter (previously freed from starch) and the filtrate and washings made up to 150 c. c. This liquid must now be further treated with rather stronger acid to convert any dextrin present into glucose. For this purpose add 20 c. c. of strong hydrochloric acid, and heat the mixture on a boiling water-bath for three hours: an upright condenser should be attached to the flask in which the digestion is carried on. At the expiry of the three hours the flask is allowed to cool, and its contents exactly neutralized with sodium hydrate solution. Finally, the liquid is made up to an exact volume, say 200 c. c., and the glucose in it determined by means of the copper test for sugar, as described further on under the heading—Analysis of Roots—*Estimation of Sugar*. It must be recollected that ·05 gram of glucose corresponds to ·045 gram of starch. The defects of this process with acids are two—the sugars already existing ready-formed in the vegetable matter analysed are not discriminated from the sugar which the starch is made to produce, but the whole are determined together; and any dextrin or other bodies capable under the circumstances of yielding sugar will be reckoned also as starch. The former of these defects is obviated by first making a determination of ready-formed sugar in the cold-water extract of the material to be analysed, previously inverting the sugar in this extract by means of acid. Of course in this case the dextrin and any other bodies soluble in cold water and capable of yielding sugar will be reckoned as starch in the second extract.

Another method of determining starch involves the conversion of starch into sugar by means of malt extract: in this process also the dextrin will accompany the starch and be converted with it into sugar. The operations are conducted thus:—The weighed substance, containing about 1 gram of starch, is boiled with 50 c. c. of water until all starch is dissolved; the action is more easily completed in half an hour in a closed vessel heated to 115° C. The extract of ground malt has been previously prepared with 100 grams in 1 litre of water, the mixture being shaken at intervals for two hours, and then thrown on a double filter. 50 c. c. of the filtrate (which must be perfectly clear) are now added to the prepared starch solution, and the liquid maintained at 65° C. for one hour, or until no starch can be detected in a drop of the solution by means of the iodine test. The contents of the flask are to be filtered and then made up to 250 c. c. *50 c. c. are taken and heated with 20 c. c. of 5 %* sulphuric acid for five hours in a closed vessel at a temperature of 110° to 120° C. Then 50 c. c. of the clear malt extract, diluted with 50 c. c. of water, are similarly treated with sulphuric acid. Nothing remains but to neutralize the two inverted solutions with sodium hydrate, dilute them to the desired volume, and titrate 10 c. c. of the sugar test with each of them. It then remains to subtract the sugar due to the malt extract only from the larger amount due to the mixture containing the starch also.

A third method of determining starch has been devised by Asbóth. The starch is dissolved by boiling with water, and then precipitated as a baryta-compound (along with any dextrin present) by a measured quantity of standard baryta-water. Some proof spirit is then added, and then the excess of free baryta is titrated by means of decinormal hydrochloric acid, using phenolphthalein as indicator, in an aliquot part of the clear liquor from the baryta-starch precipitate. This precipitate, when dry, contains about 20 per cent. of BaO, so that each milligram of BaO withdrawn from the baryta-solution used corresponds to 4 milligrams of starch and dextrin. A second experiment, in which the *cold-water* extract of the material is used, will give the dextrin. In employing this method for the examination of roots and tubers the material should be dried at 50° C., the amount of water retained at this temperature being ascertained by experiment. (See, for details of the method and of the special apparatus needed, the *Analyst* of 1887, p. 138; also *Chem. Zeit.* xvii. p. 725.)

A fourth method for estimating starch in tubers and certain roots will be found on page 243.

Brewers' grains require great care in the determination of the water, which often constitutes more than 75 per cent. of their weight, and which escapes rapidly; a sample for analysis should always be secured at the place and time of delivery. In analysing them such amounts for the various estimations must be taken as have reference to the small quantities of solid and nutritive matters they contain.

Turnips, Mangolds, Sugar-beets, &c.

The chief constituents of these plants are water, cellulose, pectose, gum, sugar, albuminoids, and mineral matters; there are also present small quantities of fatty, colouring, and other substances.

A separate analysis should be made of leaf and root.

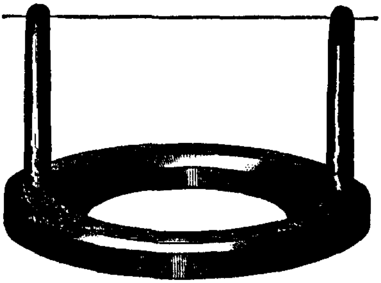
If it is wished to ascertain the composition of a *crop*, plants must be taken from several parts of the field, and all the determinations in the analysis made from a mixed sample. The analysis of a single plant will be here described, with occasional hints for the management of a larger quantity.

Analysis of Root.

After the removal of the leaves, and washing to separate adhering soil, and wiping, the root is cut through the middle, from top to bottom, into quarters or other convenient parts.

Water-determination.—A segment obtained as above, and representing therefore (if cut as directed) the average composition of the root, is weighed (a piece of 130 grams will answer well), cut into thin slices, and then strung on a wire and suspended in a warm place; the whole is dried finally in the water-oven till it ceases to lose weight. The dry matter is reduced to a fine powder and preserved in a well-closed bottle. As the complete drying of these slices is a tedious business, it is better to operate upon two separate portions: a small one of 20 grams being dried, preferably in a hot air-oven at 100° or 105°, till fairly constant, for the water determination; while a larger quantity of 100 grams is partially dried and used for the other determinations. Of course a calculation must be made to show what relation subsists between the partially dried and wholly dried samples. It must, moreover, be remembered that powdered dry residues of roots are extremely absorbent of water, so that even the partially dried sample used for the several determinations is sure to gain water after a time.

Fig. 22.



A very convenient arrangement for drying slices of roots and tubers, and also succulent leaves, is shown in fig. 22. This apparatus consists of a turned open base of mahogany, having two short pillars screwed into it opposite one another. Each of these pillars has a narrow slit at its summit to receive a platinum wire on which the materials to be dried are strung. It is best to have all the platinum wires for this purpose of such stoutness as to remain unbent with the weight of the slices. They should be pointed at each end, and all of the same weight; a convenient counterpoise is thus always at hand. The whole apparatus may be introduced into the water-oven during the last stages of the drying process. A clock-glass of suitable size placed below the wire will receive any fragments which may fall during the drying. As the dried substance is very hygroscopic it will be found a good plan to weigh it, still on the wire, in a beaker, which is allowed to cool in a desiccator of suitable form. In operating on many roots at a time, an eighth or other like part of each may be taken, the whole weighed, cut into thin slices, the slices threaded on a piece of twine, and hung up in a warm place, the drying being finished in the water-oven.

ALBUMINOIDS.—A nitrogen combustion is made in about ·8 gram, and the percentage of nitrogen multiplied by 6·25; the product, though usually regarded as the percentage of albuminoids, requires a correction for that portion of the nitrogen which exists as nitrates, amides, ammonia salts, and other non-albuminoid forms in the root. The nitrates may be estimated in the duly prepared watery extract of the root, by converting their nitrogen into ammonia by the copper-zinc couple (see p. 217).

Other plans of obtaining a fairly accurate approximation to the amount of nitrogen really existing as albuminoid or flesh-forming substances in roots, &c. are the two that follow.

Phenol Method.

The root is dried in the usual manner; a weighed quantity, about 2 grams, being then reduced to a moderately fine powder, is covered with a warm 4 per cent. aqueous solution of phenol (carbolic acid), to which a few drops of a freshly-made watery solution of metaphosphoric acid have been added. After 15 minutes a little boiling carbolic solution is added, the mixture being stirred and allowed to cool. The whole is then poured on to a small filter, which is washed with more of the same liquid but cold. The filter and its contents are then thoroughly dried, the dried material being afterwards mixed with soda-lime, and a nitrogen combustion made with the whole of it, the filter-paper itself being cut up into fine shreds and introduced into the combustion-tube.

In this process the albuminoids, being coagulated and rendered insoluble, remain on the filter, while the nitrates, alkaloids, and other nitrogenous matters, which cannot be regarded as possessed of the characters of true flesh-formers, pass into the filtrate. In the case of starchy meals, &c., an alcoholic solution of carbolic acid may be advantageously substituted for an aqueous one in the first instance.

A solution of tannic acid yields similar but less satisfactory results.

Copper-Hydrate Method.

Moist copper hydrate unites with albuminoid substances to form insoluble compounds: it unites also with a part of some nitrogenous acids, but it permits nitrates, ammonia salts, and amides to be washed away. The action of copper hydrate upon peptones seems somewhat variable. The copper hydrate to be used is prepared by dissolving 100 grams of crystallized copper sulphate in 5 litres of water to which 3 c. c. of glycerin have been added. To this solution 1½ litre of very dilute sodium hydrate solution is added, so that the resulting mixture has a faint alkaline reaction. The resulting precipitate is thrown upon a filter, allowed to drain, transferred to a dish or beaker, and washed by decantation with distilled water, containing 5 c. c. glycerin per litre, until the wash-waters are free from the least trace of alkali. The moist mass is now to be transferred to a well-stoppered bottle, syringing it out of the containing vessel by means of a 10 % solution of glycerin: this liquid helps to preserve the copper hydrate from change for a few weeks. When a nitrogen-determination is about to be made, a sufficient quantity of the moist copper hydrate is withdrawn from the store, washed by decantation to free it from the glycerin, and added to the weighed-out substance, which has been just heated to 100° C., with 100 c. c. of water. About ·8 gram, or, roughly, one teaspoonful of the copper-hydrate paste, suffices for 1 gram of dried and powdered residue of a root. A very brief further warming of the mixture will usually suffice to render the whole of the albuminoids insoluble; the mass is then thrown on to a filter, which, after washing and drying, is cut up and burnt with soda-lime, exactly as in the phenol method just described: or the Kjeldahl method may be used. In the case of seeds or other substances rich in alkaline phosphates a few c. c. of a strong solution of potash-alum should be mixed with the material taken previous to the addition of the copper hydrate.

If the total nitrogen in a sample of a tuber like the potato, or a root like the mangold, be determined by the Ruffle method, and then the nitrogen actually existing in the albuminoids, the latter will often amount to no more than half, or even but one third of the former.

MINERAL MATTER.—An ash-determination is made in 2 grams of the dry powder. Some ashes containing much alkaline salt are difficult to prepare. In such cases, char the substance at low redness, extract with boiling water, and separately ignite the black residue and the evaporated extract. Add their weight together for total ash.

CELLULOSE.—A segment of the root, precisely similar to that taken for the water-determination, but of about 65 to 100 grams, is reduced to the condition of pulp by rubbing (best from *end* to *end*) on a clean grater. The pulp is transferred to a beaker, and weighed; it is then treated with its own volume of tepid water, well stirred, and poured on to a calico filter. The cellulose left on the filter is folded in the cloth and well squeezed; it is then returned to the beaker and treated with boiling water; after a short time it is again transferred to the filter, and squeezed as before: the operation is once more repeated. The cellulose is pressed together on the filter, removed to a capsule, and dried till it ceases to lose weight; the result is *crude cellulose*, from which the greater part of the albuminoids, the pectose, and the salts of the root have been removed. This should be carefully powdered, and nitrogen and ash-determinations made in it. The amounts of albuminoid and mineral matters present being thus known, are subtracted from the weight of crude cellulose; the difference is regarded as cellulose, but does not represent a pure and definite substance. It is better to regard it as a mixture of most of the innutritious ingredients of the root which are insoluble in water, and in the several reagents used.

If a number of roots are operated on, the pulp from all might be mixed, and any convenient quantity taken for analysis.

Estimation of Sugar.

The "sugar test," made as described at page 71 is used. It should contain ·3464 gram of copper sulphate in 10 c. c., corresponding to ·05 gram of grape-sugar, $C_6H_{12}O_6$; ·0475 of cane-sugar, $C_{12}H_{22}O_{11}$; or ·045 of starch, $C_6H_{10}O_5$.

Previously to use the exact strength of the solution must be found by titration, with a solution of pure sugar diluted to about ½ $^{o}/_{o}$. The analytical process is conducted as follows:— 10 c. c. of the copper solution are measured into a white porcelain bason of about 300 c. c. or 10 oz. capacity, diluted with about 40 c. c. of water, and brought nearly to boiling. The sugar solution, previously *inverted* by boiling with sulphuric acid, made alkaline with caustic soda, and diluted to a known volume, so as to contain between ½ and 1 $^{o}/_{o}$ of sugar, is then delivered from a burette, the heat being continued, and the whole stirred well with a glass rod; when the precipitated cuprous oxide appears of a bright red colour, remove the flame, and allow the precipitate to settle as much as possible in one part of the dish; hold the dish on one side, and if any bluish-green tinge remains some more sugar solution must be added; if not, filter a few drops of the hot mixture through a very small wetted Swedish paper; make one portion acid with acetic acid, and add a drop of potassium ferrocyanide; a brown colour shows that the copper has not been all precipitated, therefore some more sugar solution must be added; if no brown colour is produced, test a few drops of the filtered liquid with a drop of the copper solution, and boil, to see if excess of sugar has been added. It is difficult to arrive at the exact point on the first trial; but it affords a good guide to exact titration the second time. From the amount of the sugar solution required to precipitate exactly the copper in the 10 c. c. of sugar test taken, the total amount of sugar and its percentage are easily calculated.

Before using the copper solution, 10 c. c. of it should be diluted and boiled alone; if any precipitate occur, it may generally be remedied by adding more sodium hydrate.

In order to maintain the copper solution in good condition, it is better to keep it in the form of two liquids, one containing the copper sulphate, the other the Rochelle salt and the sodium hydrate. The solutions are mixed in due proportions when wanted, diluted to the proper point, and titrated against a pure sample of the sugar to be sought for.

A caution is needed as to the conditions for securing constant results with Fehling's copper solution. If the copper solution or the saccharine liquid be decidedly weaker or decidedly stronger than those here recommended, strictly comparable results will not be obtained. If the Fehling solution be diluted with 4 volumes of water, and the sugar solution do not contain more than 1 per cent. of sugar, while the mode of operating is, in all cases, as far as possible identical, then fairly accurate and constant results are secured.

It may be mentioned here that a series of experiments by Soxhlet as to the reducing power of different kinds of sugar upon 10 c. c. of Fehling's solution has given figures which do not exactly correspond with those named above. The differences are not large; their importance is moreover diminished by the ease with which the results of any given mode of working with the Fehling solution may be checked by direct appeal to special titrations against solutions of pure sugars of known strength. In the experiments just referred to, Soxhlet found, with 1 °/₀ sugar solutions, and with Fehling diluted with 4 vols. of water, that 10 c. c. of the latter corresponded to:—

(*a*) ·04950 gram *dextrose*.
(*b*) ·05155 „ *invert sugar*, from cane-sugar.
(*c*) ·05376 „ *levulose*, calculated from *a* and *b*.
(*d*) ·06757 „ *milk-sugar*.
(*e*) ·07353 „ *maltose*.

It will be seen, on glancing at these figures, that 10 c. c. of Fehling's solution required ·00155 gram more (about 1½ milligram) of the grape-sugar or invert sugar to effect complete reduction than is usually assumed to be needed. This grape-sugar is made up of equal parts of dextrose and levulose, and is the sugar with which, in the estimations described in this manual, we have to deal. If the correction which this difference involves be accepted, it will correspond to a gain of 3 per cent., that is, 20 c. c. of Fehling equal 103 milligrams of grape-sugar, glucose, or invert sugar, and not 100 only as is commonly stated. When, however, a ½ per cent. solution of invert sugar is employed, and the Fehling liquid is not diluted at all, 20 c. c. of the latter do really correspond almost exactly to 100 milligrams of invert sugar, or 10 c. c. to ·05 gram.

A few words may here be said as to the method of preparing the extract of a root, so as to obtain the whole of the sugar present in a convenient form for estimation.

The selected and weighed average slices, cut as before directed, may be rasped on a grater, and the juice squeezed from the pulp in a cloth: the residual pulp is then repeatedly exhausted with hot water. The juice and washings are then heated to the boiling-point for a few minutes and filtered. The filtrate is treated as above directed.

A more exact method involves the use of a Sprengel pump filter, or other contrivance, by which the atmospheric pressure or the weight of a column of liquid is taken advantage of to hasten the otherwise tedious process of filtration. This more effective method is thus conducted:—The selected and weighed segments of root are cut into very small and thin pieces, or pulped on a grater and placed in a long funnel which may conveniently be made out of the neck and beak of a large retort; or an ordinary small paraffin lamp-glass may be used. The narrow lower end of this funnel is fitted with a perforated india-rubber cork; upon it is placed a piece of muslin and 12 millims. of clean sand; through the perforation a glass tube passes into a receiver below. This receiver (which may be a wide-mouth Winchester quart, with ground neck and having an india-rubber stopper) is kept partially exhausted of air by being placed in suitable connexion with an exhausting syringe. The funnel is kept supplied with hot water till all the sugar has been thus extracted from the root; by this means a litre of water will extract the whole of the sugar from 100 grams of beet-root. The whole filtrate is then boiled, when a coagulum is formed, and many impurities with colouring-matters thus rendered separable by filtration. About 15 c. c. of dilute sulphuric acid are then added, the whole evaporated to a small bulk, boiled for a short time to complete the inversion of the sugar, filtered if necessary, sodium hydrate in excess added, and the solution diluted to a known volume.

A convenient weight of beet-root to take is 120 grams, one half the evaporated extract from which can then be diluted to a litre; this will give a solution containing the sugar from 6 parts of beet in 100 of water, and generally the right strength for titration. The remainder of the operations have been already described.

The starch in potato tubers, parsnips, &c. may be estimated by rasping a weighed portion of the fresh materials and then washing and squeezing the pulp in a piece of fine cambric. When the water flows through clear, a little sodium hydrate solution may be added, and then the starch be allowed to settle, washed by decantation, collected, and dried *in vacuo* first, then at 100°.

In the case of the potato it is possible to obtain an approximation to the percentage of starch present in any sample of this tuber by first determining the specific gravity of an average well-grown sample free from disease, and then referring to a previously constructed table in which the relation between certain specific gravities and the corresponding starch-percentages is shown. The specific gravity is easily ascertained for this purpose by selecting 20 average tubers washed clean and wiped dry, and placing them in a solution of common salt containing about 350 grams per litre at a temperature of 16° C. Water is added with thorough agitation until half the tubers float, and then the specific gravity of the liquid is ascertained by means of a hydrometer.

The following table gives the mean results of a large number of experiments with several different varieties of potato. But these figures cannot be accepted as more than rough approximations to the truth, since the same specific gravity, so far from corresponding in all cases to the same starch-percentage, does not by any means always involve even the same percentage of total dry residue.

Starch in Potatoes.

Specific Gravity.	Percentage of Starch.	Specific Gravity.	Percentage of Starch.
1·075	12·9	1·105	19·2
1·080	13·9	1·110	20·3
1·085	14·9	1·115	21·4
1·090	16·0	1·120	22·5
1·095	17·1	1·125	23·5
1·100	18·2	1·130	24·6

In many roots there occur considerable quantities of the substances known as pectose, pectin, and pectic acid. It is rarely necessary to determine them separately; but they may be converted into pectic acid and precipitated as calcium pectate. The operations to be carried out for this purpose are these:—A convenient quantity of the material to be analysed is cut up and immersed in strong methylated spirit for 12 hours. Then it is thrown on to a cambric filter, dried partially, and ground. The ground substance (from 5 to 10 grams in weight) is treated with methylated spirit to which one fourth its volume of strong hydrochloric acid has been added. When all calcium has been dissolved out of it, it is washed with methylated spirit to remove every trace of HCl. The next step consists in a treatment with 150 c. c. of spirit containing 1 gram of potassium carbonate dissolved in a little water, the digestion being prolonged with constant agitation for half an hour at a temperature of 75° C.: the flask used should be fitted with a condensing-tube. The next step consists in throwing the contents of the flask on to a filter and washing the matter on the filter with alcohol. The whole of the solid substance is then syringed out of the filter with about 700 c. c. water into a litre flask. The addition of 2 grams of ammonium oxalate for each gram of pectic acid presumed to be present in the substance taken is now made, and the mixture is digested for 2 hours at 35° C. Then the whole is filtered and the residue on the filter washed. The filtrate and washings are made up to 1 litre, and 100 to 300 c. c. taken for the purpose of analysis. The pectose, pectin, and pectic acid are now all in the form of alkaline pectate dissolved in water; this salt is precipitated along with the oxalate by the addition of a solution of calcium acetate in slight excess. The calcium pectate and oxalate thus thrown down are collected on a weighed filter, washed with water, then with alcohol, dried at 100°, weighed, burnt, and the lime weighed as carbonate. As the quantity of pure ammonium oxalate used per 100 c. c. is known, the amount of calcium oxalate which it will yield can be ascertained. Call this *a*; let the residual CaO, in excess of that required for the oxalate, be called b; let A be the total weight of the mixed precipitate of calcium oxalate and pectate from 100 c. c. and dried at 100° C. Then x, or the weight of the pectic acid, may be found by the equation

$$A-(a+b)=x.$$

Note that calcium oxalate, after treatment with alcohol and drying at 100°, is expressed by the formula C_2CaO_4, H_2O; and that the pectic acid represented by x is calcium pectate minus lime, and not the true acid or hydrogen pectate. A simpler process for getting at the weight of the pectic acid in the mixed precipitate is to dissolve out all but the pectic acid by means of alcohol rendered strongly acid with hydrochloric acid, and then to wash, dry, and weigh the residue.

ANALYSIS OF LEAVES, GREEN FODDER, SILAGE, &c.

The constituents of the leaf will be for the most part the same as those of the root; the sugar, however, will be less in amount, while the matters soluble in ether, including fatty and waxy substances with leaf-green, may prove by no means an insignificant quantity. Oxalates, though not absent from the root, sometimes exist in the leaf to the extent of ¼ to ½ a per cent.; they are accompanied in all plants by salts of other organic acids—acetic, citric, malic, or tartaric—sometimes in considerable quantity. Tannic acid is another constituent occurring in important amount in certain leaves, while organic bases or alkaloids (such as nicotine) are found in others. It does not fall within the scope of this elementary manual to describe processes for the quantitative estimation of organic acids and bases: the instances given below refer to the more easily determined constituents only. But an outline of what may be called the "fractional" analysis of plants may be here given. In this method of treatment, which has been elaborated more particularly by Dragendorff, a weighed quantity of the substance to be analysed is exhausted with a number of solvents applied successively in the following order:—

1. *Petroleum-spirit*, boiling at 45° or under. This extracts

9·19 per cent. When a sample of spirit
er proof, it is meant that 100 measures
with water, would measure 130 of proof
under proof contains in 100 measures
res of proof spirit. The last column of
ble serves to show the volumes of proof spirit to
e several percentages of alcohol correspond.

The *detection* of the higher alcohols (or fusel oil) of potato and grain spirit is easy by the simple test of the odour produced when a few drops of the distilled spirit are allowed to evaporate on the hand or in a 3-foot length of wide combustion-tube; their *estimation* is a difficult matter.

TOTAL NON-VOLATILE MATTER.—By evaporating a given weight of the sample of wine, &c., the water, alcohol, acetic acid, and traces of ethers present are volatilized, while the sugars, the glycerin, albuminoids, colouring-matters, gums, pectin, &c., with all the organic and inorganic salts, remain behind. The processes already given in this volume may be easily adapted to the estimation of the sugar, the potash, and the albuminoids in such a residue: of course the *total* mineral matter or ash may be ascertained by mere incineration. Any free acid (save carbonic) in wine, beer, or vinegar, provided it be unmixed with any other acid or acid salt, may be estimated by the standard soda solution used in nitrogen-combustions, and litmus (or methyl-orange, or phenolphthalein, or cochineal, or alizarin). Vinegar, for instance, should always be tested for sulphuric acid before an estimation is attempted of its acetic acid. The following data will be useful in showing the quantities of various acid substances which 1 c. c. of the standard soda solution previously referred to will neutralize:—

·00766	gram	H_2SO_4,	sulphuric acid.
·00938	,,	$C_2H_4O_2$,	acetic acid.
·02940	,,	$C_4KH_5O_6$,	hydropotassium tartrate.
·01172	,,	$C_4H_6O_6$,	tartaric acid.
·00703	,,	$C_3H_6O_3$,	lactic acid.
·01047	,,	$C_4H_6O_5$,	malic acid.

ASHES OF PLANTS.

The chief substances to be estimated in the ashes of plants are silica, phosphorus pentoxide, sulphur trioxide, iron and manganese oxides, lime, magnesia, and potash. Suitable methods for the determination of all these ingredients have been given under the head of "Soil Analysis." These methods may be easily adapted to suit the present materials; but a few words as to the incineration of vegetable products may be here given.

The material to be burnt should be carefully cleansed from all adhering dirt, dried, and reduced to small fragments, but not to powder. If not too bulky, it may be heated in a platinum or porcelain crucible laid obliquely, and with its cover so adjusted as to send a current of air over the heated mass; stirring is seldom advisable, and the heat must not be so high as to fuse or volatilize the alkalies present: the less bottom heat the better, provided only that the surface of the mass attains a sufficient temperature. When the bulk of material to be used is rather large, it may be burnt on a tray of sheet platinum, having its edges turned up and enclosed in a muffle. This muffle is supported on a fire brick, and heated in a suitable furnace: a pipe at the further end of the muffle passes through the furnace back, and leads away the gaseous products of combustion. The heat, whether from solid fuel or gas, is made to play upon the sides and top of the muffle; the incineration takes place easily and at a low temperature. The ash, however prepared, is collected together, ground and mixed, once more heated to low redness, and preserved in a stoppered weighing-tube for the several estimations. In one portion a determination of carbon dioxide (see page 200) may be made: in a quantity of 3 or 4 grams the silica (and carbon if any) may be estimated, while the filtrate from the silica (which has been rendered insoluble by the usual treatment with HCl, and subsequent taking up with HNO_3) may be treated as follows:—It is divided, by weighing or measuring, into three portions, in one of which the sulphur trioxide is determined by means of precipitation with a barium salt; in another portion the phosphorus pentoxide is estimated by the ammonium molybdate process; while from the third portion the bases are separated by the processes recommended in the case of soils. It should be remembered that some of the sulphur in a vegetable product is always lost during incineration.

In calculating percentages from the results of an ash-analysis, any carbon and carbon dioxide found are first deducted.

The best process for preparing ashes of plants, so as to avoid to a great extent loss of alkalies or chlorine, involves the use of a tube-furnace and a current of carbon dioxide followed by one of oxygen. The substance is weighed in a platinum boat contained in a sliding glass weigh-tube. A small combustion-furnace with six air-burners will suffice. The combustion-tube should be a wide one of hard porcelain. Near the end where the gas enters is a plug of asbestos, then the boat, and then a caoutchouc stopper and exit-tube, leading under the water in a small bottle or tube serving as an indicator of the rapidity of the current: this end of the combustion-tube inclines somewhat downwards. The operation is commenced by filling the tube with carbon dioxide, previously washed with water and passed through sodium bicarbonate. Then, in a steady current of this gas, the platinum boat is heated gradually and gently till empyreumatic products cease to distil off. When inflammable gases are no longer emitted from the end of the tube, the current of carbon dioxide is replaced by a slow one of oxygen. When oxygen only passes out at the extremity of the tube, then the combustion is finished. The burners are turned out, and perfectly dry air is passed through the tube as it cools. A triple tube with three stopcocks enables the carbon dioxide, the oxygen, and the dry air to be successively passed over the boat. When the apparatus has cooled sufficiently the boat is withdrawn with a wire hook, introduced into the sliding weigh-tube, and the weight of ash ascertained. A determination of carbon will not be needed; but the CO_2 in the ash may be estimated in the usual way before proceeding with the further analysis. It is sometimes convenient to char the vegetable matter in the boat at a very low temperature before introducing it into the tube and passing the CO_2 over it.

MILK.

Genuine cows' milk (to which the following remarks and instructions refer, unless otherwise stated) varies somewhat in composition. The decrease in temperature during the night, and the lessened activity of the animal, often cause the morning milk to be a little more aqueous than that of the evening. The length of time that has elapsed since calving, the character of the food given, the temperature and moisture of the air, as well as individual peculiarities in the animals, are among the chief circumstances upon which depend variations in the amount of solid matter in milk, as well as variations in the nature of that solid matter. The whole day's milk of cows to whose ordinary daily ration a moderate addition of oilcake is made, commonly gives about 13·5 per cent. of solid residue as against 12·3 per cent. when that or a similar addition of rich food has not been made. It may be useful to mention here that 100 c. c. of good milk will weigh about 103·2 grams.

The quality of milk may be best determined by means of chemical analysis, the indications of the lactometer and creamometer being too often fallacious. With quite fresh milk fairly accurate results, so far at least as regards the percentage of fat, may, however, be obtained by the use of an instrument known as the *lactoscope*. One of the forms of this instrument consists of an arrangement of two sliding tubes closed by glass plates. The opacity of the milk to the light of a standard candle forms the test of quality; the better the milk the less is the thickness of the stratum required to exclude the light. In Feser's lactoscope 4 c. c. of milk are introduced and then such an amount of water as shall suffice so to lessen the opacity of the milk that the black marks on a scale can just be read.

Milk contains matters in suspension and matters in solution. Of the former, butter or fat, in the form of globules, is the most important; the latter include casein, lactose or sugar of milk, and mineral matters rich in phosphates. Some of the casein of milk appears to be in suspension, while the phosphates are intimately associated with this constituent, being partly precipitated with it when the milk is curdled. Most important indications of the quality of milk are deduced from the determination of water and of milk-fat. When we speak of casein as the nitrogenous constituent of milk, we refer to a mixture of albuminoids and not to a single substance: on this point a note will be found at the end of the directions for the analysis of milk, which we now proceed to give.

WATER.—As it is impossible to secure the perfect desiccation of a considerable quantity of milk, it is best to adopt the plan (first proposed by Doyère in 1851) of using a very small quantity *for the purpose of ascertaining the amount of water and of total solids present.* 5 c. c. of the well-mixed sample of milk are accurately measured from a pipette into a flat platinum or porcelain bason 2 inches in diameter. Great care must be taken to ensure the delivery of the full measure of milk in this as well as in all other quantitative analyses where milk is measured and not weighed. The bason is placed on a boiling water-bath or "steamer," where it remains for sixty to ninety minutes. Then it is removed to the water-oven, where it is dried for at least an hour. It is now to be placed in the desiccator and weighed when cold: another hour in the water-oven, followed by another weighing, will enable the experimenter to make sure that the milk residue is really dry. The weight of this residue may be calculated into a percentage on the *volume* of the milk, or on the *weight*, if the weight of 5 c. c. be determined. It will average 13 °/₀, and will rarely fall below 12 °/₀ in a genuine milk, while, if the cows be properly and liberally fed, it may even exceed 13·5 °/₀. These numbers represent respectively 87, 88, and 86·5 per cent. of water.

SOLIDS-NOT-FAT.—The determination of the solids other than fat in the dry residue of a milk furnishes an important means of learning whether the milk has been watered. This determination may be most accurately made by Adams' Paper-Coil Method, to be described presently. By this method the milk-fat in 5 c. c. is ascertained. This amount is deducted from that of the total solids—the remainder is known as "solids-not-fat." If the milk be of good quality this remainder should amount to 9·3 up to 9·6 %. It may usually be concluded that the milk has been watered should the figure fall as low as 9. But, as under certain rare or exceptional conditions, genuine milk would appear occasionally to contain no more than 8·5 per cent. of solids-not-fat, it is not usual to condemn a milk unless this degree of poverty is reached. Then the amount of added water is calculated on the supposition that genuine milk should contain at least 8·75 % of solids-not-fat. Suppose, for example, that the analysis of a sample has given but 6·2 % of solids-not-fat, we multiply that figure by 100 and divide it by 8·75, and so obtain 70·8 as the quotient, representing the percentage present of real milk:

$$\frac{6{\cdot}2 \times 100}{8{\cdot}75} = 70{\cdot}8.$$

The sample is therefore calculated to contain 29·2 per cent. of added water.

FAT.—Of all the methods of determining the fat in milk that of Adams, in which a coiled strip of bibulous paper is used, appears to yield the most precise results. It is conducted as follows:—

Adams' Paper-Coil Method.

Deliver exactly 5 c. c. of the milk, by means of a suitable pipette, on to a strip of white blotting- or filter-paper, 22 inches long and 2½ inches wide. This strip should have been previously rolled up in the form of a helix, which, if not too tightly coiled, will have a diameter of rather less than one inch. To make this roll, lay the strip on a sheet of glass, and upon it, lengthwise, a piece of thread, one end of which projects 6 inches beyond the further end of the paper-strip. Roll up the strip and tie it up with the free end of the thread. This coil is to be placed upon a sheet of glass; after a little practice it is easy to secure the absorption of every drop of milk by the paper, the glass plate showing no sign of any loss. The coil, after having been dried in the water-oven for an hour, is introduced into a Soxhlet tube and extracted by ether—twelve siphonings at least being necessary. Boil off the ether and place the flask (a small and light one should be used) in the water-oven in a horizontal position. When the flask and contents are dry, cool the flask in a desiccator for ten minutes and weigh. Deduct the tare of the flask, the remainder represents the milk-fat in 5 c. c. of the milk taken. As the weight of 5 c. c. has been previously determined, it will be easy to calculate the percentage of fat present in 100 parts by weight of the milk. But before proceeding with this calculation it is necessary to deduct from the fat found the small quantity of matter soluble in ether which is naturally present in the paper-coil. This is done by introducing, with their pieces of thread, 2 coils of the regulation size and cut from the same sample of blotting-paper, and dried at 100°, into a Soxhlet tube and extracting them with ether, in the manner above described: half of the small quantity of fatty or waxy substance thus obtained is to be deducted from the total amount found in the experiment with the milk. Coils of sufficiently absorbent paper from which all fat has been previously extracted can now be purchased ready for use. Or a suitable paper may be purified by soaking it in several changes of strong alcohol containing 10 per cent. of glacial acetic acid. Some analysts prefer to remove the fat present in each coil before using it.

Werner-Schmid's Method.

To carry out this method, which is peculiarly useful in the case of sour-milks, special calibrated tubes are made by Messrs. Cetti. One of these tubes is first weighed, then about 10 grams of the milk, after having been well shaken, are introduced by means of a funnel: the tube is again weighed that the exact quantity of milk taken may be ascertained. Now add 10 c. c. of concentrated hydrochloric acid and heat the tube in a water-bath until its contents assume a dark brown colour. Cool the tube thoroughly and add such an amount of washed ether (about 30 c. c.) that the upper level of the ether corresponds to the top of the graduations on the tube. The contents of the tube are then mixed by gentle shaking and left for about half an hour to allow the layers to separate. The volume of the ether-layer having been read off, 10 c. c. of this are pipetted into a weighed bason or flask. After evaporation of the ether the fat left is dried for 20 minutes at 100° C., and weighed. The weight of fat thus obtained must be calculated on the total volume of the ether-layer in order to ascertain the amount of fat in the quantity of milk taken.

An improvement on the above process was introduced by Messrs. Leffmann and Beam. In this the whole of the ether-layer is evaporated down and all measurements are consequently avoided. A test-tube of about 30 c. c. is required. It is fitted, like a wash-bottle, with a perforated cork, a blow-tube, and a delivery tube. The last-named tube is of such a length as to descend down the test-tube to about two thirds of its entire depth; its end is turned slightly upwards. A known quantity —say 5 c. c. or about 5 grams—of the milk is heated with 5 c. c. of concentrated hydrochloric acid, as just described. 20 c. c. of washed ether are added to the cooled mixture, the tube closed with a solid cork, and the whole shaken. When the separation of the two layers is complete, the double-tube arrangement is fitted in place of the solid cork, and the up-turned extremity of the delivery tube so adjusted as to be just above the lower layer in the test-tube. The whole of the ether-layer is then blown into a weighed flask. Now 10 c. c. more of ether are added to the tube, shaken, and blown out as before into the flask: these operations are repeated with 10 additional c. c. of ether. The original ethereal solution of fat and the washings are evaporated, and the residual fat weighed after it has been dried at 100° C. for half an hour.

If the total solids and the specific gravity of a milk of fairly normal composition have been ascertained, it is easy to calculate from these data the approximate percentage of fat present. The calculation is based upon the fact that, in accordance with their percentage, the fat *present* depresses to a definite degree, and the solids-not-fat raise to a definite degree, the gravity of the milk. Let, then, T represent the ascertained percentage of total solids, G the figures of the gravity beyond 1000, and F the fat, then the simplest and most easily worked expression for the formula becomes—

$$\frac{5}{6}\left(T - \frac{G}{4}\right) = F.$$

Thus a milk which gave 12·36 % of total solids and had the specific gravity 1032·2 yielded experimentally 3·62 % of fat, while by calculation it was estimated to contain 3·59. For

$$\frac{5}{6}\left(12{\cdot}36 - \frac{32{\cdot}2}{4}\right) = 3{\cdot}59.$$

Another formula for calculating the percentage of fat gives results which average ·26 % too low: it is this:—

$$\cdot833 \times T - \left(2{\cdot}22 \times \frac{100\,S - 100}{S}\right) = F.$$

Here T represents the percentage of total solids, S the specific gravity of the milk (water = 1), and F the percentage of fat.

The specific gravity of milk must be taken with considerable accuracy. For this purpose a lactometer is inferior to a specific-gravity bottle or a Sprengel-tube. But another plan may be adopted, namely, the use of Westphal's Hydrostatic Balance, which affords a ready and accurate method for ascertaining the specific gravity of a sample of milk. In this instrument a counterpoised thermometer, suspended by a piece of thin platinum wire, is attached, as a plummet, to one end of a graduated lever. On immersing the thermometer in a liquid it loses a certain weight. The equilibrium is restored by hanging on the lever a series of riders which are so adjusted in weight as to make the reading of their values very simple. The plummet displaces exactly 5 c. c. of liquid, and hence the weight required to restore equilibrium equals that of 5 c. c. of the fluid of which the density is required. A counterpoised glass rod of known displacement, say 10 c. c., may be used in a similar manner with an ordinary equal-armed balance. On immersing the rod in a liquid it will of course lose a portion of its weight equal to that of its own volume of the liquid employed. Add weights to the pan, below which the rod is hung, so as to restore the equilibrium; and divide the weight in grams thus required by the volume of the plummet in cubic centimeters—the figure thus obtained will represent the specific gravity of the liquid used.

Having obtained, by one of the preceding processes, the percentage of milk-fat present in the sample of milk under examination, it may be used, should it fall below 3 *, to calculate the amount of milk-fat or of cream which has been abstracted from the milk. Assuming that the percentage of milk-fat found is 1·75, then the calculation will be—

$$\frac{1{\cdot}75 \times 100}{3{\cdot}25} = 53{\cdot}5.$$

The sample is thus estimated to have lost by skimming 46·5 per cent. of its cream.

MILK-PROTEIDS OR ALBUMINOIDS.—The casein and other albuminoids of milk may be best determined in the dry residue of 5 c. c. of the milk by the Kjeldahl method, or by burning with soda-lime in the usual way. A long combustion-tube should be used. The percentage of nitrogen found may be multiplied by the usual factor, 6·25. Some chemists, however, employ the figure 6·3, and others 6·45, on the supposition that the milk-albuminoids contain less than 16 per cent. of nitrogen, namely, 15·87 or 15·5 °/₀. It is probable that the factor 6·3 yields results which are very near the truth.

An easier and more rapid but less accurate method of ascertaining the amount of casein and other albuminoids in milk may now be described. Take the milk residue which has served for the determination of total solids; transfer it carefully and completely to a small filter which has been dried and weighed at 100° C., washing out the last traces of the residue in the dish by means of a mixture of ether and alcohol. Wrap the filter in a piece of filter-paper in cartridge-form, and introduce it into a Soxhlet extractor. After extraction of the fat by means of ether, open out the filter and place it in a funnel. Wash the

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* The limit 2·5 is, however, that adopted by the Somerset House authorities.

substance on the filter, first with boiling alcohol of 75 per cent. to which 4 per cent. of phenol and a trace of metaphosphoric acid have been added: the washing is to be completed with a much weaker spirit, also boiling and containing phenol. By this treatment the sugar or lactose is dissolved along with the soluble salts, while the albuminoids with their associated phosphates are left behind. The filter and contents, dried at 100° till constant, must now be weighed: the weight, after deduction of the tare of the filter, represents the amount of crude casein, &c., present in the quantity of residue taken: from this number the percentage in the milk itself may be readily calculated. By carefully burning the filter and contents, the ash may be found; its amount is to be deducted from that of the crude casein; the remainder will represent the albuminoid matter itself.

MILK-SUGAR.—A known weight of the milk, say 10 grams, is to be precipitated with 5 or 6 drops of an acid mercuric nitrate solution, prepared by dissolving mercury in twice its weight of nitric acid of specific gravity 1·42 and adding to the liquid its own bulk of water. After the addition of this mercuric nitrate solution to the milk, the mixture is to be thoroughly shaken and then diluted so as to measure 200 c. c. In this manner the albuminoids and fat are completely separated, and a clear liquid containing all the milk-sugar is obtained. The precipitate is collected on a filter and washed with water until all the milk-sugar has been removed. The filtrate and washings (after having been rendered alkaline by a few drops of sodium-hydrate solution, and filtered, if necessary) are used for the determination of the sugar, an aliquot part, representing 1 or 2 grams of the milk, being titrated with Fehling's solution as directed on pp. 243 to 246. It should be remembered that 10 c. c. of the standard copper-solution used in sugar-determinations correspond to ·06757 gram of sugar of milk in its ordinary state ($C_{12}H_{22}O_{11}, H_2O$), but to ·06419 gram of anhydrous milk-sugar, in which form this body exists in all milk-residues which have been dried at 100° C. The copper-solution used should be titrated with a standard solution of pure lactose.

Ash.—Milk yields between ·7 and ·8 part of ash in 100. The proportion in any sample may be determined by incinerating the total residue from 10 grams of milk, or solids-not-fat. The incineration should be conducted at as low a temperature as possible, preferably in a muffle. The alkaline chlorides in the ash will be in great measure, if not entirely, driven off by half-an-hour's exposure to a bright red heat. As there is some difficulty in producing a white ash at a dull red heat from an ordinary milk-residue, it is safer to char the residue at first, then to extract the charred mass with water, and finally to burn off the charcoal from the insoluble residue. In this way we divide the ash into two portions, insoluble and soluble, for the latter is obtained by evaporating and igniting the watery extract of the charred residue. The two united constitute the total ash. Its percentage should lie somewhere between ·72 and ·82, a figure lower than this minimum tending to show dilution, and a figure higher than this maximum indicating the probability that common salt, sodium carbonate, borax, boracic acid, phosphoric acid, or some other so-called preservative substance has been added to the milk.

It is desirable to test the milk-ash for alkalinity, and to determine the amount of chlorine present. Wash the whole of the ash, obtained as previously directed, from the dish into a beaker by means of a little distilled water: test a drop of the solution with litmus paper; it should give a barely alkaline reaction; an acid reaction indicates the addition of some foreign substance. To the solution add one or two drops of neutral potassium chromate solution and titrate with decinormal silver nitrate (p. 173). Calculate from the silver nitrate used the amount of chlorine, which should not exceed one tenth of the weight of the milk-ash. If any excess over ·082 per cent. be found it may fairly be inferred that common salt has been added to the milk.

Whey, butter-milk, and skimmed milk may be analysed as milk, but for the milk-fat determinations larger quantities must be taken.

Milk which is not fresh will have undergone alterations variable in character and degree, which render a comparison with the same milk in its original state impossible. No system of allowances for such alterations can be applied with success. But milk may be preserved in a state less unsuitable for analysis by adding to it when fresh a known volume of ammonia solution.

The Werner-Schmid method described on page 260 is capable of yielding far more satisfactory results with stale milks than the Adams' method.

Note on the Albuminoids of Milk.—Almost the whole of the nitrogenous matters in milk exists in the form of albuminoids. But casein so-called is not the only albuminoid present, although it constitutes rather more than three fourths of the total. Albumen is present, while there is a third substance of the same group which remains in solution when the casein and albumen have been removed. The albumen may be separated by concentrating the clear whey from a known weight of milk which has been curdled by a few drops of acetic acid. To the evaporated liquid a little metaphosphoric acid solution is added, the mixture heated to the boiling-point and the small curd of coagulated albumen collected on a tared filter, dried at 100° and weighed. In the filtrate, further concentrated to a small bulk, a few drops of an alcoholic solution of phenol or of tannin will produce a small precipitate, which is to be collected on a small tared filter, washed with spirit, dried at 100°, and weighed.

CREAM.

Cream varies much in percentage composition; when made from milk which is becoming sour, more casein is present than when the milk and the cream both remain sweet. It, however, consists essentially of minute globules of milk-fat intimately mingled with small quantities of the other constituents of milk. It may be analysed as milk, determinations of water, of solid residue, of fat, and of ash being generally alone necessary, the albuminoids and sugar being neglected. The quantities of cream taken for the several determinations should be regulated by the proportions of each ingredient usually present. Thus for solid residue and fat less cream will suffice than in the case of milk, but for ash more will be needed. In drying cream it is better to pour small quantities at a time into the evaporating-dish. But a more exact method involves keeping the weighed quantity of cream upon the steamer for 24 hours. Weigh into an evaporating-dish 25 grams of pure dried sand, pour a weighed quantity of cream, about 5 grams, on to the sand, mix thoroughly by the aid of a stiff platinum wire, which must be left in the dish. After drying for some hours, the dish is removed from the steamer, and the mass of cream and sand carefully broken up by the wire. The dish is now placed in the water-oven for some hours. When taken out, any fragments of sand and cream-residue are detached from the wire, and the dish with its contents weighed. The solid matter contained in the cream is deduced from the total weight by subtracting the weight of the sand and of the dish.

BUTTER.

Butter contains, besides milk-fat, a considerable quantity of water and a little salt: traces of milk-sugar, of casein, and of phosphates will likewise be found in it. The percentage of water in genuine fresh butter varies between 5 and 15, the percentage of salt between ·1 and ·3. In salt butter the range is more extensive, the salt sometimes rising to 8 per cent., and the water to 28 per cent.: it has been stated that even 50 per cent. of water may be incorporated with butter: a percentage higher than 20 may be regarded as savouring of fraud.

WATER.—2 or 3 grams of the butter are weighed into a small dish, preferably of platinum, and containing some clean dry sand. The dish and contents are dried in an air-oven at 105° C. and weighed. The loss is water.

SALT.—A separate quantity of butter, varying in amount according to whether the sample is fresh or salt, is employed for the estimation of common salt. The weighed quantity is transferred to a flask of about 250 c.c. capacity, and then about 100 c.c.

of boiling distilled water are added. The flask is to be corked, and the contents briskly agitated with a rotary motion, care being taken to prevent the melted butter-fat from touching the cork. After 2 or 3 minutes' shaking, more boiling distilled water is added, so as to fill the flask up to the base of the neck. The flask is allowed to cool, and, when cold, a gentle shake will detach from it the solid cake of fat; the solution containing the salt can now be decanted through a filter into a beaker. The cake of fat and the flask should be rinsed with a small quantity of cold distilled water, which is added to the original filtrate. The filtrate or an aliquot portion of it can now be titrated with a decinormal solution of silver nitrate, as described on page 173, 1 c.c. of which solution corresponds to ·00584 gram of sodium chloride or common salt.

It is advisable to test this filtrate for alkalinity before titrating it, as small quantities of alkaline carbonates are occasionally found in impure samples of butter.

Ash—Is determined by the ignition of a separate portion of about 5 grams of the sample; the ignition should be as slow as possible. The ash of genuine butters will frequently be found by titration to be rather lower than the percentage of salt; this is due to the volatilization of sodium chloride during the combustion of the fat; if the ash readily fuses in the crucible it is probable that borax, or boracic acid, or phosphoric acid has been added to preserve the butter. A genuine butter leaves no ash other than common salt, with a trace of alkaline or earthy phosphates: any ash insoluble in water indicates the presence of such an adulterant as soapstone or steatite, a hydrated magnesium silicate.

Casein.—Probably the simplest plan for determining the casein in butter, when it is not desired to make a direct determination of nitrogen by combustion with soda-lime, is the following:—

5 grams of butter are weighed into a tared filter contained in a funnel supported by a triangle on a beaker. The arrangement is placed in a hot drying chamber, when most of the fat will soon filter into the beaker. Then the filter is removed from the

funnel, folded so as to prevent loss of curd, and placed in a Soxhlet extractor, where it is exhausted with ether or petroleum spirit. The filter and contents are dried in the water-oven until constant and then weighed. Deduct the tare of the filter from the gross weight, the remainder will be the casein and mineral matter. The filter and contents are to be ignited at as low a temperature as possible; the loss in weight multiplied by 20 gives the percentage of casein.

FAT may be calculated from the amount required to make up 100 parts when the ascertained percentages of water, casein, salt, and other mineral matters, if any, are added together. It is, however, much more difficult, although at the same time much more important, to ascertain whether this fat is genuine butter-fat or the fat known as margarine. As the fatty part of butter is not only its chief constituent, but that in which reside the chief differences between the genuine and the spurious kind, it is to this constituent that our attention is chiefly given. Of all the processes for ascertaining whether the fat of a sample of butter is milk-fat or some other kind, the most certain is known as the *saponification* process. In this, as in other experiments having the same object, the first requisite is a supply of pure, dry, clarified butter-fat; to secure this a small quantity of the sample of butter is melted in a beaker on a steamer, and then filtered through dried Swedish paper, the filtration being performed in a water-oven. Sometimes a perfectly clear sample of fused butter-fat may be obtained without filtration; but in all cases the fat should not be heated for any length of time, or to a temperature more than a few degrees above its melting-point. When a sufficient supply of the clarified butter-fat has been prepared it may be weighed in a small beaker containing a pipette. The quantity required for each experiment may then be removed by the pipette, the beaker, pipette, and remaining fat being afterwards weighed again; the second weight deducted from the first gives the amount of fat taken for one experiment.

We give four methods of applying the saponification process to the detection and estimation of the foreign fat in samples of butter, so-called. The first process, devised by Koettstorfer, is a purely volumetric one: the second process (Hehner's simplified) may be quickly performed and gives the percentage of "insoluble fatty acids" very accurately. In the third process, originally devised by Reichert and subsequently modified by Meissl and Wollny, the volatile acids are alone determined. The fourth process is that invented by Hehner.

Koettstorfer's Saponification Method.

2·5 grams of clarified butter-fat are weighed into a small wide-mouthed flask and 25 c.c. of seminormal alcoholic solution of potassium hydrate added. The mixture is boiled on a water-bath under a vertical condenser for half an hour, 1 c.c. of phenolphthalein solution added and the solution titrated in the flask, while hot, with seminormal hydrochloric acid, care being taken to avoid access of air, as carbonic acid interferes with the accuracy of the result.

The quantity of seminormal hydrochloric acid required to exactly neutralize 25 c.c. of the alcoholic solution of potassium hydrate is ascertained by a blank experiment made under precisely similar conditions.

The number of c.c. of seminormal hydrochloric acid used by the butter-fat under examination, deducted from the number of c.c. used in the blank experiment, will give the quantity of seminormal potassium hydrate solution required for the saponification of the 2·5 grams taken; this figure divided by 2 will give the number of c.c. of normal alkali, therefore:—

$$\text{as No. of c. c. normal alkali} : 1000 = 2{\cdot}5 : x.$$

x = the saturation- or saponification-equivalent, or the number of grams of fat capable of being saponified by 1 litre of normal alkali. The range in butter-fat varies from 241 to 253, in margarine from 285 to 290. The result may also be expressed in grams of potassium hydrate required to saponify 1000 grams of fat, thus:—

$$\text{as } 2{\cdot}5 : 1000 = \text{No. of c. c. normal KHO} \times {\cdot}056 : x.$$

Butter gives from 221·5 to 232·4; margarine from 193·5 to 196·5.

Rapid Saponification Method.

5 grams of the clarified fat are weighed into a glass bason 4½ in. in diameter and melted on the water-bath. About 1 gram of stick sodium hydrate is added and then about 1 c. c. of water. After the lapse of a minute or two 4 c. c. of 60 O.P. alcohol are poured in, and then the contents of the bason are well stirred with a glass rod until the fat has assumed a gelatinous appearance. The resulting soap is evaporated to complete dryness with occasional stirring, to free it from alcohol. The saponification and subsequent evaporation will occupy about half an hour.

The soap is dissolved in the bason with boiling distilled water: the solution should be perfectly clear. Dilute sulphuric acid is added, in quantity sufficient to completely decompose the soap. The insoluble fatty acids will rise to the top in a white semi-solid condition: after a short time they become liquid and are to be decanted on to a tared Swedish filter previously well wetted with boiling distilled water. *Great care must be taken to wash the bason and rod free from fat*: this is readily done if abundance of boiling distilled water be used. The washing of the fatty acids on the filter with boiling water is continued until 6 ounces of the filtrate, to which a few drops of phenol-phthalein solution have been added, are coloured by the addition of not more than 0·2 c. c. of a decinormal solution of sodium hydrate. Usually more than a litre of water is required for the complete washing of the insoluble fatty acids obtained from 5 grams of the clarified fat. They are now allowed to cool in the filter, and then the filter with its contents is removed to a small tared glass bason and dried on the water-bath until the melted fat soaks into the filter-paper. To assist in expelling the last traces of water about 4 to 8 c. c. of absolute alcohol are poured over the paper, and the heating is continued on the water-bath until the alcohol has evaporated. The bason and contents are dried in the water-oven until constant in weight, and then they are finally weighed. From this weight is deducted the tare of the bason and filter; the result, multiplied by 20, gives the percentage of Insoluble Fatty Acids yielded by the clarified butter-fat.

The Reichert-Meissl-Wollny Method.

2·5 grams of the clear fused butter-fat are accurately weighed into a 250 c. c. flask of conical form and having a neck about 2 or 3 centims. long and about 3 centims. wide; 1 c. c. of a 50 per cent. sodium hydrate solution (which must be preserved and drawn from so that not a trace of carbonic acid can be absorbed) together with 5 c. c. of 96 per cent. alcohol are added to the butter-fat and the mixture is heated, in connection with a reflux condenser, for 15 minutes on a water-bath. The alcohol is then distilled off, the flask being heated for at least half an hour. With every precaution 100 c. c. of boiling water are added, and the flask is heated until the soap which has been formed is completely dissolved. A few small fragments of tobacco-pipe and 20 c. c. of sulphuric acid (25 c. c. H_2SO_4 in 1 litre of water) are added; the flask is at once connected with a condenser by means of a glass tube 7 millims. wide, and having, at a distance of 1 centim. above the cork, a bulb of 3 or 3½ centims. in diameter. The tube is bent immediately above the bulb upward at an oblique angle, and extends in this direction for 5 centims.; it is then bent downward, also at an oblique angle, and then is connected with a condenser by means of an india-rubber tube. The flask is heated, by means of a very small flame, until the insoluble fatty acids are completely fused: 55 c. c. are then distilled off into a graduated flask, the distillation lasting 30 minutes; the distillate is mixed by agitation and 50 c. c. of it are filtered off and transferred to a beaker. 1 c. c. of phenolphthalein test solution (·5 gram to 1 litre of proof spirit) is added and the titration with decinormal baryta solution proceeded with. To the volume of baryta solution used one tenth is added and the figure obtained in a corresponding blank experiment subtracted—the latter should not exceed ·33 c. c.

It is necessary in order to secure accurate results in this process that carbonic acid should be excluded, particularly from the strong sodium hydrate solution, and that the distillation of the volatile acids should proceed at the same rate and occupy the same time in all experiments.

Hehner's Saponification Method.

This process is conducted thus:—5 grams of the clarified fat are weighed into a glass bason, melted on the water-bath, and 50 c. c. of a seminormal solution of sodium hydrate in alcohol added. The contents of the bason are stirred with a glass rod, until the fat has assumed a gelatinous appearance and has become a soap. This soap is then treated with enough distilled water to fill the bason two thirds. The mixture is now allowed to evaporate on the water-bath. The soap thus freed from alcohol, but containing an excess of alkali, is dissolved in hot distilled water, and transferred to a flask of about 500 c. c. capacity. Every particle of soap must be rinsed from the bason and rod; but the total volume of soap solution and washings should not exceed 300 c. c. The soap solution is heated most conveniently by holding it under a vertical condenser, using an Argand burner as the source of heat, and protecting the hand by a thick glove. When the solution is almost boiling, 27·5 c. c. of normal sulphuric acid are added, and the heating continued, with constant rotatory agitation of the contents of the flask, until the decomposition of the soap is complete: the insoluble fatty acids will now have risen to the surface, and will form a layer above the acidulated liquid. When this oily layer is continuous and complete, the flask is filled up to the beginning of the neck with boiling distilled water, rotated so as to bring the oily matter together, and set aside to cool. When cold, the insoluble fatty acids will be found as a wax-like cake, which can be detached from the walls of the flask by a slight shake. The soluble fatty acids (characteristic of true butter or milk-fat) and the glycerin are found in the watery liquid. This is decanted through an English filter-paper into a Winchester quart. To wash the cake of solid acids a small quantity of cold distilled water is first poured into the flask, which is to be rapidly, but not violently, shaken for a few seconds; then this water is to be decanted through the same filter into the large bottle. To the flask containing the greater part of the solid acids some boiling distilled water is now added, and the contents thoroughly agitated, the flask being heated to 80° or 90° C. over a flame. Then the flask is once more filled up with boiling distilled water, allowed to cool, the cake of solid acid detached as before, the water poured off and added to the filtrates, and, finally, the cake rinsed once more with cold water. The insoluble fatty acids will now be partly in the flask and partly on the filter: the flask, which contains the greater proportion, is placed in the drying chamber or water-oven. It should be withdrawn about every hour, and a small quantity of air sucked through the neck by means of a bent tube, so as to remove the watery vapour. After 3 or 4 hours it may be weighed; and the tare of the flask being deducted, the weight of the larger part of the insoluble acids will be obtained. The filter, with its fatty acids, must be allowed to dry in the air, or over oil of vitriol *in vacuo*. Then it is placed on a triangle over a small beaker and put into the water-oven. This beaker serves to catch any drops of melted fatty acids which may pass through the filter. When the filter is quite dry, it is removed from the oven, very thoroughly washed with ether, and the ethereal solution, together with any melted fatty acids that may have previously dropped into the beaker, evaporated at a gentle heat, and the residue and beaker weighed. When from this gross weight the tare of the beaker has been deducted, the weight of the fatty acids caught on the filter will be obtained. This weight, added to that (previously ascertained) of the bulk of these acids in the flask, and the sum multiplied by 20, gives the percentage of insoluble fatty acids yielded by the clarified butter-fat. If this percentage be above 88·8, or at most 89, it is clear that margarine or some similar body has been present in the sample of butter examined. If the proportion reach 93 to 95 the fat must have consisted wholly, or almost wholly, of margarine or of other adulterants.

It has been found that 100 parts of the glycerides of which pure milk-fat consists yield, after saponification, from

87·8 to 88·8 parts insoluble fatty acids, and
6 to 8 parts soluble acids.

The insoluble acids are stearic, palmitic, and oleic; the soluble are butyric, caproic, caprylic, and capric,—the last three in smaller quantities. The soluble acids can be got in mere traces from oleomargarine, groundnut-oil, and the other fatty adulterants of butter, which, on the other hand, yield no less than 94 to 95 per cent. of the insoluble acids. There are, however, two reasons why this process, though it yields exact results when due care is taken, must not be held to decide authoritatively as to admixtures or percentages of margarine of less than 10 $^{o}/_{o}$. One of these reasons lies in the natural variations (due to season, food, breed, &c.) in the composition of true milk; the other depends upon the variations in the composition of the adulterants. Nor should it be forgotten that the manufacturers of "butterine," "bosch," and other artificial butters usually add to the clarified animal fat, prepared in New York, Vienna, Paris, and other centres of production, a not insignificant quantity of genuine butter and of milk. By churning together 60 parts of oleomargarine, 28 of milk, 10 of genuine butter, and 2 of earthnut-oil (from *Arachis hypogæa*), a "bosch" is obtained, the clarified fat of which contains between 11 and 12 per cent. of genuine milk-fat. For this cause the clarified fat of artificial butter frequently yields 1 per cent. less solid fatty acids than simple oleomargarine.

If the solid fatty acids obtained in processes 2 or 4 above have been thoroughly washed so as to be free, not only from the easily soluble butyric acid, but from the difficultly soluble caproic, caprylic, and capric acids, we shall find them to amount to 87·8 to 88·8 parts from 100 parts of pure butter-fat. Anything about 89 per cent. is very suspicious, and indicates probable adulteration: 89·5 is certainly bad. We may take 88·5 as the average percentage of insoluble fatty acids obtainable from the fat of genuine butter, and 95 as that of margarine, the difference between these numbers equalling 6·5. This figure, divided into the difference between 88·5 and the percentage of insoluble fatty acids found in an actual experiment, gives, when multiplied by 100, the percentage of margarine:—

$$\frac{A-B}{6\cdot5}\times 100 = C.$$

A = $^{o}/_{o}$ of Insoluble Fatty acids in sample under examination.
B = $^{o}/_{o}$ of Insoluble Fatty acids in pure butter-fat.
C = $^{o}/_{o}$ of Margarine in the clarified fat.

We may now return to the filtrate (in Hehner's method) containing the soluble acids, which, however, need not be directly determined if the previous results have shown the sample to be genuine. If not, the filtrate is made up to a definite volume, and an aliquot part, say $\frac{1}{5}$, titrated to find the total acidity. A quantity of the alcoholic solution of sodium hydrate, exactly corresponding to that which was used for the saponification analysis, must be mixed with the same quantity of the same acid as that which was used for decomposition of the soap, boiled and titrated. The figure thus found represents the excess of acidity due to the acid added. Deducting this from the result obtained by the titration of the filtrate, we get an amount of acidity corresponding to the proportion of soluble fatty acids.

This may be calculated to butyric acid with an equivalent of 88, and should not fall below 6·5 %.

Samples of pure butter kept in well-corked bottles undergo very little change; but if the butter has been exposed to the air for 6 or 8 months considerable change sometimes takes place.

A second process is as frequently used for testing butter-fat as that just described, but it is not so trustworthy. It consists in taking the specific gravity of the clarified fat at a temperature of 37°·8 C. (100° Fahr.). It is necessary to use a pear-shaped sp. gr. bottle provided with a very accurately fitting thermometer-stopper. When the exact capacity of the bottle in c. c. of distilled water at 37°·8 C. has been ascertained, it is dried and filled with the clarified butter-fat to be tested, which should have been previously melted and raised to a temperature of 35° C. The thermometer-stopper must be loosely placed in the bottle, which is to be plunged up to its neck into a water-bath at a temperature of about 39° C., and to be kept in gentle movement until the temperature reaches 37°·8 C. Then the thermometer-stopper is properly inserted, the excess of fat at once removed by filter-paper, the bottle dried, and weighed while warm. The observed or "actual density" (as the figure obtained in this determination is called) is found by dividing the weight of the fat by the weight of the water which the same bottle has been ascertained to hold at 37°·8. The term *actual density*, instead of specific gravity, is adopted, because the comparison is made with water at 37°·8 instead of with water at 15°·5. Clarified butter-fat has an actual density of from 910·5 to 911·5, assuming water to be 1000, whereas oleomargarine and most other fats likely to be used as adulterants have actual densities varying between 904 and 907. It may be added that the specific gravity of pure butter-fat at a temperature of 15°·5, averages 930·7 when compared with water at the same temperature. The specific gravity of butter-fat, at any temperature above its melting-point, may be taken by means of Westphal's hydrostatic balance (see p. 262).

Borax and boracic acid are frequently found in samples of fresh butter. They are best tested for in the ash contained in a porcelain bason. To this a little concentrated sulphuric acid is added, and then about 10 c. c. of 60 per cent. alcohol. The bason is warmed on the water-bath, and the flame of a Bunsen-burner of steatite is brought down upon the surface of the mixture: if boron compounds be present, the characteristic green flame-coloration will be produced. Or the boric ether evolved may be condensed in the form of a white sublimate upon a clock-glass placed upon the bason as a cover.

Cheese

contains the same ingredients as milk,—sugar, however, being present in very small proportions. Cheese contains also a variable quantity of common salt, a notable percentage of phosphates, and a little colouring-matter. When undergoing the process of decay, many additional compounds are formed, chiefly from the breaking up of the casein. The only determinations which are necessary in ordinary cheese-analysis are those of water, fat, casein or albuminoids, and ash or mineral matter. Full directions for these estimations will be found on previous pages devoted to the analysis of milk, cream, and butter; but a few special notes and hints specially applicable to cheese may be serviceable.

Water.—About 5 grams of the cheese, cut, before weighing, into thin shavings, or else grated, are dried in a small tared platinum dish in the water-oven till practically constant in weight. It has been found that a small quantity of cheese can be more completely dried than a large one, and that it is better to dry several portions of 5 grams separately for the determination of different constituents rather than attempt to prepare at once a considerable amount of dry residue. In order to obtain the residue in a satisfactory condition for the subsequent operations, it is a good plan to pour about 5 c. c. of absolute alcohol upon each quantity of 5 grams of cheese weighed out, and to leave the mixture for ½ an hour before drying it in the water-oven.

Fat.—5 grams of the cheese, prepared and treated exactly as described in the last paragraph, are used for this determination; enclose the weighed quantity in a filter-paper properly folded, and place it in the extractor of Soxhlet's apparatus. Dry ether should be used, the operation of extracting the fat being conducted in the usual manner; the ether is finally distilled off from the flask, the residue dried in the water-oven and weighed. If petroleum-spirit be used, it should have been redistilled under 60° C.

CASEIN.—The albuminoids in cheese are estimated in most analyses merely by difference, but they may be determined as in a milk-analysis or else by means of a nitrogen-combustion with soda-lime, not more than ·5 gram of the dried substance being taken. In decayed cheese, however, the nitrogen exists in other forms than the albuminoid; it may therefore be desirable to adopt the phenol-method (see p. 241) for determining the true or albuminoid nitrogen.

SUGAR.—The amount of milk-sugar in ordinary cheeses is not important, but it may be useful to determine its percentage in cream-cheeses. For this purpose the residue remaining in the Soxhlet extractor, after the removal of the fat, may be employed. It should be transferred to a bason, warmed and agitated with water and the whole poured on a plaited filter and washed. In the united filtrate and washings, the lactose is determined by Fehling's solution, as described on p. 243. It has been recommended in this case to weigh the copper suboxide produced.

LACTIC AND BUTYRIC ACID.—The acidity of a sample of cheese may be determined by triturating 5 grams with 10 c. c. of alcohol and a few drops of alcoholic solution of phenol-phthalein and then titrating with the sodium hydrate solution employed in nitrogen determinations until a faint pink colour is produced: 1 c. c. of that solution corresponds to ·00703 gram of lactic acid. The acid present is assumed to be lactic although butyric acid is also present in old cheeses.

AMMONIA.—Besides the albuminoids and certain organic compounds derived from them (leucine &c.), various salts of ammonia occur in old, and especially in decaying cheese. The ammonia in them may be approximately estimated by distilling with magnesia and distilled water a small quantity of the original undried cheese after grating it. The ammonia in the distillate is determined by the Nessler reagent according to the process given under the head of the Analysis of Waters (p. 214).

ASH.—The residue from 5 grams of cheese, dried, as previously described under "Water," is gently calcined until the mass is thoroughly charred. It is then exhausted with hot water, the liquid being afterwards filtered, evaporated to dryness, gently ignited and weighed. The residue consists of the soluble part of the ash. The insoluble part may be obtained by igniting the charred mass and the filter until they have become quite white. The total ash is obtained by adding together the amounts of the soluble and of the insoluble ash.

PHOSPHATES.—The most important of the *natural* constituents of the ash of cheese are the phosphates. These are best determined by the molybdic-acid method in the entire ash of 5 grams of cheese, which, for this purpose, may be directly burnt to a white ash.

COMMON SALT.—The soluble ash, obtained as previously described, is dissolved in water, and the solution, after having been stirred up with a little calcium sulphate to remove soluble phosphates, is filtered and titrated with decinormal solution of silver nitrate, using potassium chromate as the indicator (see p. 173).

The addition of oleomargarine (now legally termed *margarine* in this country) is frequently made to the curd from which certain American cheeses are manufactured. This adulteration can be detected, and its amount estimated, by a modification of Koettstorfer's method. The first step is to separate, in a pure state, a few grams of the fat from the sample of cheese under examination. To effect this, about 45 grams are melted in a bason on the water-bath, and 8 grams of pure warm sand stirred in. The free acid present is then exactly neutralized with the calculated amount of decinormal sodium-hydrate solution—this amount being ascertainable from the datum derived from the determination of free acid previously made. 8 grams more of sand are now added, and the whole mixture dried in the water-oven with frequent stirring. When dry the contents of the bason are transferred to a Soxhlet extractor, and the fat extracted with dry ether in the usual way. With the pure dry fat thus obtained a saponification experiment is made. 2 grams of this melted fat are dropped carefully into a tared wide-mouthed flask of rather more than 200 c. c. capacity—the fat must all fall on to the bottom of the flask. A blank experiment, without any fat, is made in all respects in the same manner as hereinafter directed. Into each of the flasks (one with, and the other without fat) 25 c. c. of a normal solution of potassium hydrate in alcohol of ·835 spec. grav. (56·1 grams per litre) are very accurately measured, taking care to drop the alkali straight on to the bottom of the flasks. The mouths of the flasks are closed with watch-glasses, and the contents brought to the boiling-point and kept in gentle ebullition for 15 minutes. 10 c. c. of alcohol with a few drops of alcoholic phenol-phthalein solution are added to each flask, and the contents titrated with seminormal hydrochloric acid (18·2 grams of real HCl per litre) until the colour just changes from pink to yellow. The amount of real KHO consumed in saponifying the fat is obtained and expressed in milligrams for each gram of fat taken—the correction derived from the blank experiment having been made. Genuine cheese-fat, that is milk-fat, should consume not less than 22·2 milligrams of KHO per gram of fat. If, however, the KHO consumed lies within this limit, then the soluble and insoluble acids in another portion of the extracted fat should be determined by Hehner's process. This should not yield more than 89 per cent. of insoluble acids; but if that limit be distinctly passed, the calculation as to the amount of adulteration should be made upon a basis of 88·5 per cent. (see p. 274).

The colouring of cheese is almost always accomplished by means of annatto (from *Bixa Orellana*); to this no objection can be taken. Chrome-yellow (lead chromate) has been occasionally used for colouring the outside of American cheeses; but it is extremely rare to find it in the body of the cheese, at least in this country.

BREAD.

The principal adulterants found in bread are alum, rice, and potato-starch. Rice is frequently used in small quantities in order, according to the bakers, to improve the character of the crust; it is seldom used in excessive quantity.

Potato-flour and potato-starch are used to increase the amount of moisture which is retained in the baked bread. It is impossible to detect an admixture of any small percentage of rice or potato by chemical means after the flour has been made into bread. These adulterations must be searched for by the microscope; and even with this instrument it is often impossible to detect them, because the character of the starch-granules is greatly altered by heat.

The only adulterant of any serious importance is alum; and the proportion of this which has been used has to be estimated by the determination of one of its constituents, alumina. The quantitative estimation of alumina in bread is a tedious process, especially when only small proportions have been used; and it is therefore desirable to employ the following qualitative process whenever possible.

Qualitative process by logwood.—This process aims simply at proving the absence of alum. In order to carry it out, a tincture of logwood is made by steeping logwood chips or cuttings in 60 O.P. alcohol or methylated spirit, in the proportion of 5 parts of logwood to 100 parts of spirit. This tincture can be kept without change if carefully stoppered. To use the test, one part of the tincture is mixed with three parts of a saturated solution of ammonium carbonate, and the mixed solution diluted with 3 times its bulk of water. The diluted solution is poured over the bread to be examined; this should be free from crust, or if the sample be very small the crust should be carefully scraped. If the bread contains alum even in such a small proportion as 4 grains to the 4-pound loaf, the sample will, after standing for half an hour, assume a dark violet-blue tinge. If salts of magnesia or certain other earthy salts which are occasionally added to bread be present the sample will assume a more purple tint; while if the bread be free from alum and these foreign salts the colour will remain of a full reddish plum-colour, gradually fading to a very dirty pink without any trace of purple or blue.

In applying this process to flour it is more convenient to make a small proportion of the flour into a thick cream with cold water and then add the logwood tincture and solution of ammonium carbonate so as to reduce the whole to the consistency of thin cream.

When it becomes necessary to determine the proportion of alum present, the following process must be adopted:—100 grams of the bread are carefully burnt to ash in a platinum dish. This ash is fused with 3 or 4 times its weight of white flux (mixed carbonate of soda and potash) which has been previously tested for alumina; the fused mass, when cold, is moistened with hydrochloric acid and evaporated to dryness, the residue is redissolved in acid and the silica filtered off. The filtrate is treated with ammonia until a slight permanent precipitate is produced, which is then redissolved by a few drops of hydrochloric acid. Ammonium acetate having been added, the filtrate is set aside overnight to precipitate, and is then filtered; the precipitate contains all the alumina freed from a large proportion of the foreign matters which would have rendered the estimation untrustworthy: this precipitate after having been washed is redissolved on the filter in hydrochloric acid. The solution is boiled for a few minutes with a solution of sodium bisulphite, caustic soda is added in excess, and the solution boiled again. By this process the iron is separated in the form of magnetic oxide, which is separated by filtration, while the alumina contained in the alum (if any has been added) is retained in solution; the filtrate is acidified again with hydrochloric acid, ammonium acetate added in slight excess, and the solution allowed again to stand overnight. If any alumina is present, a precipitate will form, which will consist of pure aluminium phosphate, formed by the combination of the phosphoric acid present in the flour with the traces of alumina contained in the wheat and the alumina contained in any alum added. This precipitate is filtered off, washed, dried, ignited, and weighed. By multiplying the weight of the precipitate thus obtained by 542 we obtain the number of grains of potash-alum contained in two pounds of the flour examined, or by multiplying by 1084 we obtain the number of grains of potash-alum contained in a 4-pound loaf, which is the mode in which the results of the analysis are usually reported in this country.

The first multiplier (542) is more suitable to flour, and the second (1084) to bread.

Note.—As a small quantity of alumina is sure to be present in the reagents employed, while further traces will be derived from the glass and porcelain vessels used in the analysis, it is better to make a blank analysis as nearly as possible with the same materials, quantities, and vessels as those employed in the actual analysis. The alumina found in the former determination is deducted from that of the latter: the difference is that due to alum. Note, however, that traces of alumina may be derived from earthy matters adherent to the original corn, or from mineral dust from the attrition of the mill-stones; but since the general introduction of steel-rollers into flour-mills the last source of aluminous impurity has generally ceased to exist. As, however, the percentage of Al_2O_3 in such impurities is very low, any considerable trace of this body thus originating will involve the presence of several times its own weight of other mineral matters, which will therefore notably increase the percentage of ash, other than salt, in the bread. It is customary to deduct, from the alum found as above described, 6 grains per 4-lb. loaf, reporting the remainder as *added* alum. This deduction probably suffices to cover any usual natural or accidental aluminous impurity.

Newly baked bread, when cold, seldom contains less than 40 per cent. of water, often more. The moisture, dextrin, sugar, starch, cellulose, alcohol, and true albuminoids in bread may be readily determined by processes already given in the Guide (see pp. 46–49 and 226–254).

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APPARATUS.

Besides the water-oven, blowpipe-table, sand-bath, accurate balance and gram weights, large glass measures, combustion-furnace, sieves, and a small mill for preparing samples, together with a number of pieces of apparatus and tools of different kinds, mentioned in the pages of this Guide (for the common use of the laboratory), each student will require at the back of his bench a set of ordinary reagents, of which the following is a list:—

Acetic acid.
Hydrochloric acid.
Hydrosulphuric acid.
Nitric acid.
Sulphuric acid.
Sodium acetate.
Sodium carbonate.
Sodium hydrate.
Sodium phosphate.
Ammonium chloride.
Ammonium carbonate.
Ammonium hydrate.
Ammonium oxalate.
Ammonium sulphide.
Potassium ferrocyanide.
Calcium chloride.
Calcium hydrate.
Calcium sulphate.
Barium chloride.
Ferric chloride.

The special reagents, tests, and materials should be arranged so as to be readily accessible when required for use. They will be found described on pp. 65 to 76 of the Guide, or under the head of the several operations in which they are employed.

Each student will require, for his individual and sole use, the apparatus, reagents, &c. comprised in the following lists, which correspond to the three parts into which the Laboratory Guide is divided:—

PART I.

Chemical Manipulation.

Wedgwood mortar and pestle.
Earthenware furnace-support.
Berlin porcelain basons (3).
Berlin porcelain crucibles (3).
Test-tube rack.
Test-tube cleaners (2).
Test-tubes (12).
Funnels (4).
German glass flasks (4).
Watch-glasses (2).
Beakers, nest of 5, small.
Wash-bottle.
Glass stirring-rods (2).
Glass spirit-lamp.