THE BOOK WAS DRENCHED

THE LABORATORY GUIDE

CHURCH'S
LABORATORY GUIDE

A MANUAL OF PRACTICAL CHEMISTRY FOR COLLEGES AND SCHOOLS, SPECIALLY ARRANGED FOR AGRICULTURAL STUDENTS

REVISED AND LARGELY REWRITTEN BY
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NINTH EDITION

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PREFACE TO THE EIGHTH EDITION

THE first edition of Church's *Laboratory Guide* was published in 1864; it consisted mainly of directions for the quantitative analysis of Agricultural products drawn up by Mr Warington. In subsequent editions the scope of the work was enlarged by the Author, so as to include a complete course of laboratory practice for Agricultural Students.

The present edition has retained the form and general arrangement of its predecessors. Thus it is divided into three parts:—

Part I. comprises a series of elementary lessons on Manipulation and Simple Analysis, drawn from familiar or important materials with which every one should be acquainted.

Part II. deals with Qualitative Analysis, omitting, however, the rare elements and nearly all those which are not of importance from an agricultural point of view. By this many of the analytical processes are able to be simplified.

Part III. is concerned with the Quantitative Analysis of those substances, produced on the farm or used on the farm, which are likely to engage the attention of the agricultural analyst—*i.e.*, soils, manures, farm crops, cattle foods, dairy produce, waters, bread, etc.

The *Laboratory Guide* was intended primarily for use in the Royal Agricultural College; but it has rendered a much wider service in extending the study of practical chemistry in relation to agriculture. This is shown by the fact that the work has been adopted not only in agricultural colleges in Great Britain, but also in Australia, India, Italy, and Japan. It reached its seventh edition in 1894.

The present edition has been carefully revised and largely rewritten.

In Part I. some new lessons, dealing with manures and with dairy products, have been introduced, and some less directly connected with agriculture omitted.

In Part II. some simplifications have been made and a general scheme for the examination for bases introduced.

In Part III., Quantitative Analysis, some of the older and less trustworthy methods have been taken out and improved methods introduced. Modifications of Kjeldahl's method for the estimation of combined nitrogen in agricultural materials or products have quite superseded the soda-lime and other methods. The metric system of weights and measures is used to the exclusion of the more cumbersome English systems.

It is hoped that the *Laboratory Guide* will continue its career of usefulness in Agricultural Schools and Colleges and to Students of Agricultural Chemistry, and also prove of use to Public Analysts, County Analysts, and others whose work requires the analysis of agricultural materials and products.

After a long experience in teaching Agricultural Students, both in Japan and this country, with the aid of the *Laboratory Guide*, I am indebted to Professor A. H. Church (now Sir Arthur H. Church) for asking me to undertake the revision of the work for a new edition, and for handing to me his rights in the book. I am specially grateful to Mr Cecil C. Duncan, Public Analyst for Worcestershire, formerly my chief assistant at the Royal Agricultural College, for help in the work of revision; and to Dr Bernard Dyer, Mr W. F. Lowe, and other friends for suggestions.

Many new figures of apparatus have been introduced; for the loan of the blocks of some of these, we are indebted to Messrs Baird & Tatlock, London.

EDWARD KINCH.

ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER, *October* 1906.

PREFACE TO THE NINTH EDITION

I AM fortunate, in preparing a new edition of the *Laboratory Guide*, in having the advice and assistance of the friends named above; also, Mr M. Kershaw, my chief assistant here, has drawn a few new figures for the book.

The methods of analysis under the Fertilisers and Feeding Stuffs Regulations (1908) of the Board of Agriculture and Fisheries [under the provisions of the Fertilisers and Feeding Stuffs Act, 1906] are introduced; also Polenské's method for the determination of coco-nut fat in butter, and a few other improved methods of analysis.

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ROYAL AGRICULTURAL COLLEGE,
CIRENCESTER, *October* 1911.

CONTENTS

PART I.—CHEMICAL MANIPULATION

PART II.—QUALITATIVE ANALYSIS

CHAPTER I

CHAPTER II

PART III.—QUANTITATIVE ANALYSIS

CHAPTER I

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 realised 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 realise 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 2 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 three 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, etc., 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 blackboard, 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 you 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*. Also, do not call calcium carbonate, lime; nor aluminium silicate, alumina.

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.

Each working bench must be provided with a Bunsen gas burner (Fig. 1) or similar suitable heating apparatus. Failing a gas supply, nearly all experiments requiring heat can be performed with the aid of a good spirit-lamp (Fig. 2) or oil lamp.

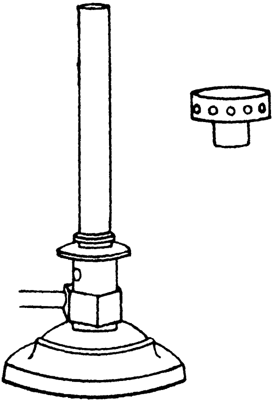

FIG 1.

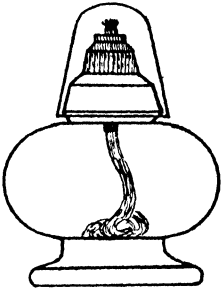

FIG. 2.

LESSON I

SOLUTION AND FILTRATION

Apparatus required--Retort-stand ; funnel ; filter-papers ; two porcelain basins ; two beakers ; wash-bottle ; scales and weights ; litmus paper ; glass rod

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 of a mixture (A) of sand and salt. Place the weighed substance on a filter-paper 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 basin: this washing 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 basin. Pour off the water, leaving the sand in the basin. Turn the basin about so that the wet sand forms a thin layer all over it; then heat it cautiously over a Bunsen burner, with continual stirring 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, gives you the *percentage* of sand in the original mixture.

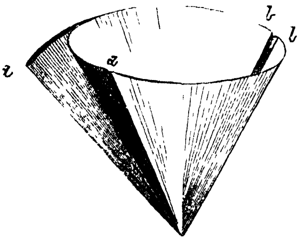

Fig. 3.

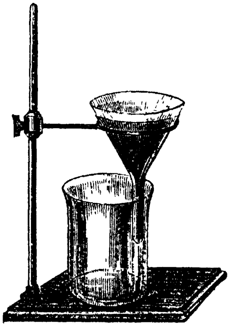

Fig. 4.

2. Weigh out 10 grams 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 until the last washing is free from acid, which is found out by the use of blue litmus paper. Care must be taken not to lose any of the sand. The sand should now be syringed, as before described, into a porcelain basin, 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
Chalk, insoluble in water.		Hydrochloric acid.		Water.		Calcium chloride, dissolved in the water.		Carbon dioxide, goes off as gas.

LESSON II

CRYSTALLIZATION

Apparatus required.—Furnace-support ; wire gauze ; retort-stand ; wash-bottle ; two porcelain basins ; two porcelain crucibles ; triangle ; test-tubes ; scales and weights; filter-papers.

Special materials.—Solutions of copper sulphate, sodium sulphate, calcium chloride, and sodium chloride ; piece of wire.

1. Evaporate ½ of a test-tube full of a solution of copper sulphate over the lamp in a porcelain basin 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 of crystals of copper sulphate ($CuSO_4, 5H_2O$). 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 changed to white. If too strongly heated the salt will become darker in colour. When the crucible is cold, weigh it again. The difference in weight will be the *water of crystallization* lost by the salt. Calculate the percentage of water of crystallization.

4. A solution of sodium chloride, when evaporated as in experiment 1 above, will deposit on cooling crystals (NaCl), which contain no combined water. Collect and dry some of these crystals between filter-paper. Weigh out 2 grams and heat gently, in a crucible, over a gas flame. Cool and weigh.

Crystals are regular geometrically-shaped solids, naturally formed. Their faces and angles are symmetrically arranged in regard to certain axes.

Look at and closely observe crystals of common salt, fluor-spar, alum, nitre, and Epsom salts.

LESSON III

SUBLIMATION

Apparatus required. — Retort-stand ; triangle ; porcelain crucible ; scales and weights ; 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 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 Bunsen burner till no more fumes are given off. This should be done in a fume cupboard. 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 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 brass, glass, apatite, aluminium, and iron; thread; and a 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 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

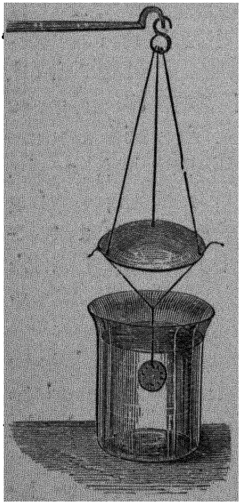

FIG. 5.

the weight in air by the above difference, the quotient will be the required specific gravity.

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

Weight in air of a piece of glass .	10·95	grams.
Weight in water of the same . .	6·52	„
Difference	4·43	„

This difference, 4·43 grams, represents, then, the weight of the volume of water displaced by the immersion of the glass—that is, the weight of an equal volume of water. Divide the weight of the glass in air by this difference; and the dividend will express how many times the weight of the volume of glass contains the weight of an equal volume of water.

$$\frac{10{\cdot}95}{4{\cdot}43} = 2{\cdot}47, \text{ spec. grav. of glass.}$$

Or we may express the same facts in another form. We may say that the weights of equal volumes of water and glass are in the ratio of 4·43 to 10·95 ; and then, assuming the specific gravity of water to be 1, we have the following proportion :—

$$\underbrace{4{\cdot}43}_{\text{Weight of water displaced by glass.}} \; : \; \underbrace{1}_{\text{Spec. grav. of water.}} \; = \; \underbrace{10{\cdot}45}_{\text{Weight of glass.}} \; : \; \underbrace{x}_{\text{Spec. grav. of glass.}}$$

$$x = \frac{1 \times 10{\cdot}95}{4{\cdot}43} = 2{\cdot}47$$

2. The same experiment may be tried with a piece of brass, 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 basin; furnace-support and wire gauze; glass rod.

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

1. Take 10 grams 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 basin, 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 beaker, 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 basin before drying it. Calculate the percentages of sand and of clay.

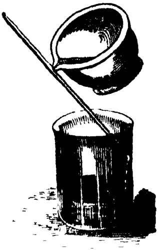
FIG. 6.

2. Take 10 grams 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, but not violently ground up, 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. Calculate the percentage of sand.

LESSON VI

PREPARATION OF HYDROGEN

Apparatus required.—Flask or bottle; small funnel; mortar; wash-bottle; test-tubes; indiarubber tubing; rat-tail file; beaker.

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 wood.

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 means of a piece of vulcanized indiarubber 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.

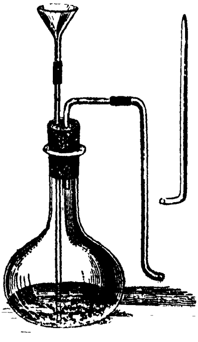
FIG. 7.

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 basin 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.

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—

$$\underset{\text{2 vols.}}{H_2} + \underset{\text{1 vol.}}{O} = \underset{\text{Water.}}{H_2O.}$$

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 ; retort-stand with clamps ; test-tubes and stand ; rat-tail file ; 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 ;[1] 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 rat-tail 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,

---

[1] The oxygen mixture is made of potassium chlorate in powder mixed into one-fourth its weight of manganese dioxide.

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. Now weigh out 3 grams of the oxygen mixture, chiefly potassium chlorate, introduce them into the test-tube, insert the cork and bent delivery-tube, and fix the apparatus with a clamp on 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, oxygen gas will be given off. The end of the delivery-tube should dip

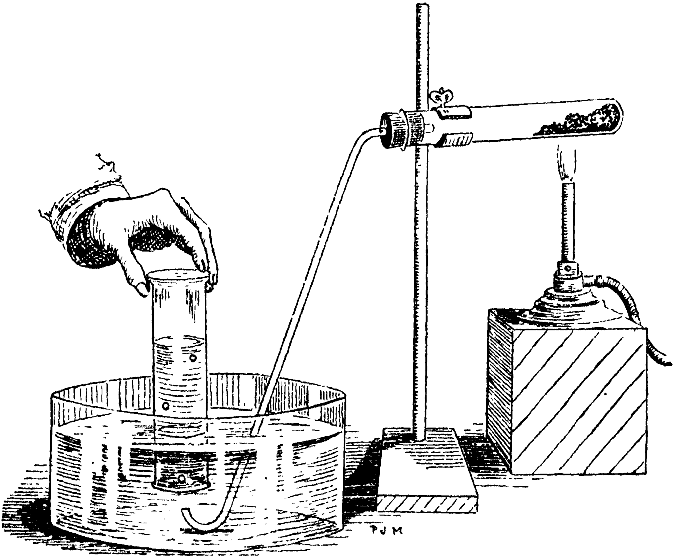

Fig. 8.

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.

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, then drop in a blue flower and warm gently.

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 and shaking.

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

$$2KClO_3 = 2KCl + 3O_2.$$

LESSON VIII

PREPARATION OF SULPHUR DIOXIDE

Apparatus required.—Retort-stand; test-tubes; 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 1 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 ½ a test-tube of distilled 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. Sulphites, when treated with dilute sulphuric acid, give off SO_2. Mercury or copper heated with H_2SO_4 gives off pure SO_2.

LESSON IX

PREPARATION OF AMMONIA

Apparatus required.—Retort-stand; 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 of ammonium chloride and 3 grams 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 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:—

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

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. To 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.

$$\underset{\text{Calcium carbonate, insoluble.}}{CaCO_3} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium bicarbonate, soluble.}}{CaH_22CO_3}$$

Divide the clear solution into two 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:—

$$\underset{\text{Calcium bicarbonate.}}{CaH_22CO_3} + \underset{\text{Calcium hydrate in the lime-water.}}{CaH_2O_2} = \underset{\text{Precipitate.}}{2CaCO_3} + 2H_2O$$

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. $CaH_22CO_3 = CaCO_3 + H_2O + CO_2$.

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; 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 of potassium nitrate, place them in a retort, and add carefully 60 cub. cent. 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. 9, p. 30). 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, nitrites, 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; 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 of sodium acetate, put them carefully into a retort. Pour in with a funnel 60 cub.

cent. 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 3 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 1 or 2 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; porcelain basin; silver nitrate solution; test-tubes; flask; 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, *e.g.*, rain-water, river-water, spring-water, and well-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. of well- or river-water just to dryness in a porcelain basin. 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 offensive smell.

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 five drops of Nessler's test; a yellow or brown colour indicates *ammonia.*

6. To 100 cub. cent. of each water, warmed till the temperature of about 27° C. has been reached, contained in flasks, add 5 cub. cent. of pure dilute sulphuric acid and 1 drop of potassium permanganate solution: if the colour disappears, add more permanganate until the purple colour is permanent after the lapse of ten 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 or sulphuretted hydrogen exert the same effect upon this reagent.

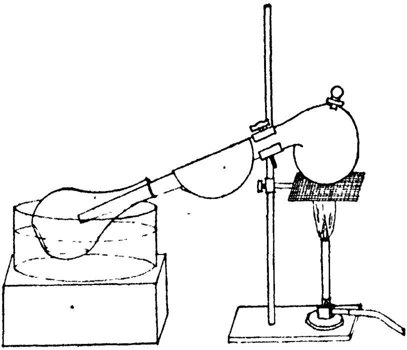

FIG. 9.

7. Place 130 cub. cent. 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.

LESSON XIV

DETECTION OF ARSENIC

Apparatus required.—Test-tubes; wash-bottle; filter-paper; blowpipe.

Ordinary reagent.—Ammonium hydrate.

Special materials and tests.—Solution of arsenic trioxide in HCl; copper foil; 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 a piece of bright copper foil; after a few minutes a dark grey

compound of arsenic and copper will form on the foil. Remove the foil from the tube, rinse with water, and dry it gently between filter-papers. The foil is 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 (white arsenic), 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 in 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 elementary 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 the air has been driven out of the apparatus (see § 2 of the Lesson on Hydrogen, p. 18), light the jet and depress into the flame for a few seconds one or two fragments of white 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 arseniuretted hydrogen (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 narrow glass tube through which arseniuretted hydrogen (arsine) is passing, and experimenting with the black arsenic mirror which will be formed in the tube.

The arsenic is deposited on the tube immediately beyond the heated spot as a black stain; very small quantities of arsenic can be detected in this way. Great care must be taken to use pure reagents.

LESSON XV

EXAMINATION OF BRONZE COIN

Apparatus required. — Flask; furnace-support; 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 $\frac{1}{6}$ 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 [illegible] possible of the tin

dioxide in the flask. Test the filtrate, which will contain copper nitrate ($Cu2NO_3$), as follows:—

a. Pour 1 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 basin, 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; porcelain basin; 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, slip it gently into a flask, and cover it half an inch deep with dilute nitric acid.

Keep the flask warm, 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 a few drops of the last 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 :—

$$(1)\ 2HCl + Zn = ZnCl_2 + H_2;$$
$$(2)\ 2AgCl + H_2 = 2HCl + Ag_2.$$

LESSON XVII

EXAMINATION OF A ZINC ALLOY

Apparatus required.—Flask ; retort-stand or furnace-support ; wire gauze ; 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. 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 redissolve 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 2 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 1 drop of potassium ferrocyanide. To
b add 1 drop of potassium ferricyanide. To
c add 1 drop of potassium sulphocyanide. To
d add some sodium acetate.

LESSON XVIII

REDUCTION AND OXIDATION

Apparatus required.—Flask; furnace-support and wire gauze; 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, etc., 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 burner. 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 2 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 XIX

MANGANATES AND PERMANGANATES

Apparatus required. — Retort-stand; 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 hydroxide; 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 of manganese dioxide, and 1·4 of a gram of a mixture of potassium chlorate and sodium hydroxide; mix the two substances, and place them in a small porcelain crucible. 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 XX

BLOWPIPE EXPERIMENTS—PART I

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

Special materials.—Quill tubing ; sawdust ; hay ; gelatin ; gypsum ; mercuric oxide ; red lead ; white arsenic ; paper gutters ; solutions of chlorides of barium, calcium, strontium, copper, potassium, and sodium.

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 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

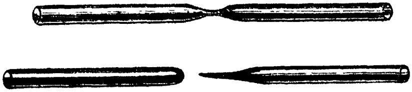

FIG. 10.

should, however, be open at both ends, though drawn to a point at one end.

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.

9. 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, calcium, 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.

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 XXI

BLOWPIPE EXPERIMENTS—PART 2

Apparatus required.—Blowpipe; cobalt nitrate solution; platinum wire; test-tubes and stand; wash-bottle; 2 porcelain dishes.

Ordinary reagent.—Dilute hydrochloric acid.

Special materials.—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; so'utions containing copper, iron, manganese, chromium, and cobalt.

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; heat before the blowpipe, and 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 recognised 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. 11) 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. 11.

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, heat it till it fuses, then jerk it over a porcelain dish so that the bulk of the bead falls into the dish. In another porcelain dish place some dilute hydrochloric acid; reheat the residue of borax bead on the platinum wire and plunge it whilst red hot into the hydrochloric acid; the bead will then be loosened, and may be removed by pressure between the fingers and washing with water.

LESSON XXII

PREPARATION OF SUPERPHOSPHATE

Apparatus required.—Test-tubes; funnels and filters; wash-bottle; scales and weights.

Ordinary reagent.—Dilute nitric acid.

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

1. Boil ·2 gram of bone-ash or ground mineral phosphate 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 solution; 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 of 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 a small quantity of ammonium molybdate solution; 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 of ground mineral phosphate (which chiefly consists, 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 ammonium molybdate solution and heat nearly to boiling; a yellow precipitate shows that sulphuric acid converts the insoluble phosphate of the mineral phosphate and the 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:—

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

LESSON XXIII

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 material and tests.—Freshly burnt lime; 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 parts of lime, by weight, combine with 18 of water and produces 74 parts of 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.

Some samples of quicklime slake more quickly than others.

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

mainly of compounds of the element calcium—the metallic basis of lime. These four substances are :—

1. Lime, quicklime or burnt lime = CaO.

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 XXIV

LIME AND OXIDE OF IRON IN SOILS

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

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

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

1. Boil ·5 gram 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 still 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.

3. Pour on to the insoluble matter on the filter-paper some dilute hydrochloric acid and collect the filtrate in a test-tube; add to it a few drops of potassium ferrocyanide. A precipitate of Prussian blue shows the presence of ferric oxide in the soil.

LESSON XXV

TESTING FOR NITROGEN IN MANURES

Apparatus required.—Test-tubes; wash-bottle; test-papers.

Ordinary reagents.—Sodium hydroxide solution.

Special materials.—Samples of nitrate of soda, sulphate of ammonia, and powdered rape cake. Soda-lime; strong sulphuric acid; indigo sulphate solution.

Combined nitrogen may exist in manures in the form of nitrates (nitric nitrogen), ammonia (ammoniacal nitrogen), or in organic matter (organic nitrogen).

1. To test for ammoniacal nitrogen.

Take 3 test-tubes; to one add a little nitrate of soda; to the second add a little sulphate of ammonia; and to the third some rape cake. To each add some sodium hydroxide solution, about $\frac{1}{3}$ of the test-tubeful, and boil. Note that ammonia is given off from one only.

2. To test for organic nitrogen.

Take 3 small test-tubes containing respectively nitrate of soda, sulphate of ammonia, and rape cake, and add some soda-lime and heat. Note that ammonia is given off from two of the manures; but they are distinguished by the previous test for ammonia.

3. To test for nitrates or nitric nitrogen.

Take separate tubes containing small quantities of nitrate of soda, sulphate of ammonia, and rape cake, add a little water, shake well, and filter the latter. To 2 cub. cent. of the solutions, in each case, add carefully an equal volume of strong sulphuric acid and mix by shaking; then add a few drops of indigo sulphate solution. With the nitrate of soda the indigo will be bleached.

LESSON XXVI

TESTING SOME MANURES

Apparatus required.—Test-tubes; wash-bottle; pestle and mortar; platinum foil or porcelain crucible; test-papers.

Ordinary reagents.—Dilute hydrochloric acid; dilute nitric acid; barium chloride solution.

Special materials.—Samples of nitrate of soda, sulphate of ammonia, superphosphate, and basic slag. Silver nitrate solution.

1. Make a dilute solution of nitrate of soda by dissolving 1 gram in a test-tubeful of water; divide it into 2 parts.

2. Make a solution of sulphate of ammonia by dissolving 1 gram in a test-tubeful of water; divide it into 2 parts.

3. Test the two manures for *chlorides* by adding to a solution a few drops of dilute nitric acid and then a few drops of a solution of silver nitrate. A white precipitate indicates chlorides—these should be present in very small quantities.

4. Test for *sulphates* by adding to the solutions of the manures dilute hydrochloric acid and barium chloride. A white precipitate indicates sulphates. The nitrate of soda should contain very little sulphate.

5. Heat ·2 gram of the sulphate of ammonia on a piece of platinum foil or a porcelain crucible until no more fumes are given off. Note if there is a weighable residue left. Ammonium sulphate is completely volatile; most of its adulterants are not volatile

6. Action of basic slag on sulphate of ammonia.

To a small quantity of sulphate of ammonia in a mortar add four or five times its weight of basic slag and mix them thoroughly with a pestle. Ammonia is given off. Test by holding a piece of moist turmeric paper in the fumes.

Mix some superphosphate and sulphate of ammonia in a similar way. No ammonia is given off.

7. Action of superphosphate on nitrate of soda.

Mix some nitrate of soda with twice its weight of superphosphate in a mortar. Notice the smell. Put a little of the mixture in a test-tube and warm. Notice the reddish-brown fumes given off, due to the action of acid in the superphosphate on the nitrate of soda liberating nitric acid.

LESSON XXVII

EXPERIMENTS WITH SOILS

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

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

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

1. Boil 2 grams 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 of peat in a flask with enough sodium hydroxide 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, etc.), which are nearly insoluble in water, but form soluble salts with alkalies. They are derived from the decay of organic matter.

3. To about 100 c.c. of water add 5 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; wire gauze; porcelain basin; test-tubes and rack; funnels and filters; wash-bottle; turmeric paper.

Ordinary reagents.—Sodium hydroxide; ammonium oxalate; barium chloride.

Special materials and tests—Wide-mouth 4-oz. bottles; dilute solutions of sodium phosphate, ammonium phosphate, potassium nitrate, and ammonium sulphate; "magnesia mixture"; tartaric acid; ferrous sulphate; oil of vitriol; air-dry sifted soil.

1. Into a wide-mouth bottle introduce some sifted soil, cover it with water (about 100 c.c.), add 5 drops of sodium phosphate solution, and shake the mixture for five 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 hydroxide 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 hydroxide; 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; test-tubes; 2 flasks; cut filters; funnels; pestle and mortar; wash-bottle.

Ordinary reagents.—Sodium hydroxide 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 3 test-tubes, *a*, *b*, and *c*.

To *a*, when cold, add 1 drop of tincture of iodine; observe the production of a blue colour and its disappearance on warming the mixture.

To *b* add 10 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 10 drops of the "sugar test" and enough sodium hydroxide to produce a clear blue colour; boil.

2. Place ½ of a small dry filter-paper 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 10 drops of sugar test and enough sodium hydroxide 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 20 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 10 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, boil for a few minutes, and then add sodium hydroxide 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 (dextrose). 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 experiment 6. The preparation of the "sugar test" is described further on amongst the "special reagents," on p. 86.

LESSON XXX

EXPERIMENTS WITH MILK, BUTTER, AND CHEESE

Apparatus, etc., required.—Test-tubes; funnels; beakers; wash-bottle; filters; porcelain basin; retort-stand; wire gauze; furnace-support; silver nitrate solution.

Ordinary reagents.—Dilute sulphuric acid; sodium hydroxide.

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

1. To ½ a test-tubeful of milk add 5 or 6 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 hydroxide solution and 20 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 basin, 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 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 2 or 3 grains of grated cheese with a little soda-lime in a small tube, and heating it strongly: ammoniacal vapours will be given off.

LESSON XXXI

DETECTION OF BORON COMPOUNDS AND OF FORMALIN IN MILK AND ITS PRODUCTS

Apparatus required.—Retort-stand; wire gauze; pipeclay triangle; 3 porcelain dishes; beaker; funnel and filter-paper; test-tubes.

Reagents.—Dilute hydrochloric acid; strong sulphuric acid; alcohol; turmeric paper; solution of sodium carbonate; lime-water.

Special materials.—Samples of milk and butter, with and without preservatives; strong sulphuric acid containing a little ferric chloride. [200 c.c. sulphuric acid with 10 c.c. 5 per cent. ferric chloride solution.]

1. Take 20 cub. cent. of milk, add 10 cub. cent. of lime-water, place in a porcelain dish, and evaporate to dryness. Burn the residue (in a fume cupboard) at as low a temperature as possible. Cool the residue, moisten with strong sulphuric acid, add alcohol, and stir well. Heat gently, and apply a flame to the alcohol vapour—this will burn with a green colour at the edges of the flame if boric (boracic) acid or borax has been added to the milk.

2. The ash of 20 cub. cent. of the suspected milk may be moistened with dilute hydrochloric acid and a piece of turmeric paper placed in the dish.

Remove the paper and gently dry it; if the milk contained boric acid the paper will turn a reddish-brown colour, and if then treated with sodium carbonate solution, will become bluish-black in colour.

3. Boric acid can be detected in butter by melting the butter at a gentle heat, shaking it in a large test-tube with warm water containing a little sodium carbonate, filtering, evaporating the water extract, burning the residue at a gentle heat, and treating the ash as above mentioned in 1 or 2.

4. Formalin (formic aldehyde) can be detected as follows. Take $\frac{1}{3}$ of a test-tubeful of milk, add an equal volume of water, then add, drop by drop, down the side of the test-tube strong sulphuric acid containing a very small quantity of ferric chloride. If formalin is present a violet ring will be formed at the junction of the liquids. In the absence of formalin a slight green or brown tint only will be noticed. If the amount of formalin is very small the colour may take half an hour to develop.

LESSON XXXII

DEXTRIN AND GUM

Apparatus required.—Furnace-support and gauze; porcelain basin; 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 basin, and cautiously heat it, with constant stirring or shaking, until it has all acquired a pale fawn-colour. Allow the basin to cool completely, and then pour $\frac{1}{2}$ a test-tubeful of distilled water upon the roasted starch.

Filter the cold-water solution of dextrin thus prepared, and divide the filtrate into 2 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 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 2 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 XXXIII

EXPERIMENTS WITH BREAD

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

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

Special materials and tests.—Bread-crumb; grated bread-crust; bread adulterated with alum; iodine solution; sugar test; linen filter; 4 per cent. carbolic acid solution.

1. In order to ascertain roughly the amount of water present in bread, weigh out 10 grams of bread-crumb, put them into a porcelain basin, 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 2 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. Alum ($Al_2K_24SO_4$, $24H_2O$) has been fraudulently used by bakers, to enable them to employ damaged flour in bread-making. Alum may generally be detected in bread by agitating the crumb for some time with a cold 4 per cent. 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.

Further and more precise directions for the detection of adulterations in bread will be found in the third part of this volume.

LESSON XXXIV

ASHES OF PLANTS

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

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

Special materials and tests.—Ammonium molybdate; dried beech-leaves or hay; platinum tetrachloride; strong solution of tartaric acid; alcohol.

1. Roll up and crush some dried beech-leaves, grass, or other suitable vegetable matter; place in a porcelain crucible supported on a triangle on a ring of the retort-stand. Heat and set fire to the vegetable matter, and continue the heating until nothing remains but a white or grey ash. The charred leaves may be occasionally stirred with a wire or rod to facilitate the burning. With the ash or mineral matter thus obtained, the following experiments may be tried:—

2. Place a few particles of the ash in a test-tube, add 1 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 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 10 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 drops of hydrochloric acid and 6 drops of platinum tetrachloride: a yellow crystalline precipitate forming slowly proves the presence of potassium compounds in the ash.

Or, to the filtrate add 6 drops of strong solution of tartaric acid and 20 drops of alcohol; a white crystalline precipitate forming on standing shows the presence of potassium compounds.

5. The residue on the filter will probably contain some charcoal and calcium carbonate. Pour upon it 10 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.

6. Oxide of iron may be tested for in the still undissolved residue by treating it with dilute hydrochloric acid and adding potassium ferrocyanide to the filtrate.

LESSON XXXV

VEGETABLE COLOURS

Apparatus required.—Test-tubes; mortar; flask; funnel and filters; basin; retort-stand; wash-bottle.

Ordinary reagents.—Sodium hydroxide; 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 in water, 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 hydroxide, 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 hydroxide 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 is now 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 hydroxide solution, its colour may be removed.

4. Pour a little sulphindigotic acid into a basin 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 hydroxide, and then dilute sulphuric acid.

6. Repeat experiment 5 with litmus instead of turmeric.

LESSON XXXVI

EXPERIMENTS WITH BONE AND FLESH

Apparatus required.—Flask; funnel and filter; 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 proteids. It may be purified

from fat, etc., 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 substance 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 XXXVII

EXPERIMENTS WITH BLOOD

Apparatus required.—Three beakers; test-tubes; 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 2 parts, a yellow liquid or serum, and a red clot which contains both corpuscles and fibrin.

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 albumin will take place; nitric acid 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 XXXVIII

COTTON, WOOL, AND SILK

Apparatus required.—Furnace-support; wire gauze; filters and funnels; porcelain basin; wash-bottle; test-tubes.

Ordinary reagents.—Sodium hydroxide 6 per cent.; 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 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 reprecipitated. 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 specific gravity 1·53.

2. Wool and silk both dissolve when boiled with sodium or potassium hydroxide solution of specific

gravity 1·05. Cellulose is undissolved 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 hydroxide 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.

3. 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 10 per cent. solution of sodium hydroxide, which dissolves the wool.

The cotton now alone remains, and may be recognised 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 recognised when clean and dry.

LESSON XXXIX

WINE AND BEER

Apparatus, etc., required.—Retort and stand ; flask ; test-tubes ; mortar ; porcelain basin ; blowpipe ; platinum wire ; spirits of wine ; glass rod.

Ordinary reagents.—Hydrochloric acid ; sodium hydroxide.

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

1. Pour 50 cub. cent. of claret or other light red wine into a retort and distil over about 10 cub. cent.: pour this distillate into 2 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 XVIII.).

2. Pour half the residue in the retort (from experiment 1) into a flask, add a little sodium hydroxide 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 acid 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 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; the tests for uric acid, hippuric acid, urea, with the artificial formation of the latter compound; and the examination of pigments and of feeding cakes, and the saponification of fats, 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 or group of elements. 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 recognised 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 recognisable 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 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 elements—approximately eighty—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 is generally regarded as a non-metallic element, though in some of its characters and properties it more nearly resembles the 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 can be liquefied; the liquid boils at −252° C. and solidifies at −257° C.; its specific gravity is ·0763. In its combinations this element is what is called a *monad*, having only one bond of attachment to other elements; or it may be said to be *univalent*: its compounds with other monad elements show this, the formula of its compound with chlorine being, for instance, HCl. Three of the 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 specific gravity is 10·53, and melting-point about 960°. Mercury is a mobile, greyish-white, lustrous liquid, of specific gravity 13·55; it becomes solid at −39°. The boiling-point of mercury is 357°. Lead is soft and bluish-grey; its specific gravity is 11·38; it melts at 326°.

GROUP II. *Metals of which the sulphides are insoluble in hydrochloric acid*:—Copper, Tin, Arsenic, Antimony, Platinum, and Gold. Copper is red; its specific gravity is 8·95, and its melting-point 1080°. Tin is soft, white, and crystalline; its specific gravity 7·3, and its melting-point 232°. Arsenic is a greyish-white semi-metal, having the specific gravity 5·73, and volatilizing at 180°. Antimony is bluish-white, brittle and lustrous, having the specific gravity 6·6 to 6·8, and melting-point 450°. Platinum is greyish-white, and has the specific gravity 21·5. It melts at about 1775° C., and is not attacked by hydrochloric or nitric acid alone, but by a mixture of the two acids. Gold is highly lustrous, of an orange-yellow colour; has the specific gravity 19·3, and the melting-point 1062°.

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; melting-point about 1575°. Manganese is greyish-white; its specific gravity is 7·4; it melts at about 1245°. Aluminium is bluish-white, having the remarkably low specific gravity 2·58; it melts at 655°. This is a pseudo-triad, being in reality quadrivalent. Zinc is bluish-white, hard and crystalline; its specific gravity is 6·9 to 7·1, and its melting-point 419°, and boiling-point 918°.

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. They are diad elements. Calcium, specific gravity 1·55; melting-point about 800°. Strontium, specific gravity 2·5; melting-point about 800°. Barium, specific gravity 3·78; melting-point about 850°.

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 specific gravity is 1·74, and its melting-point 633°. Potassium has the specific gravity ·875, and its melting-point is 62·5°. Sodium is soft, pinkish-white; specific gravity ·97, and melting-point 95·6°; boiling-point 877°. The compound radicle ammonium, NH_4, has not been isolated. Potassium, sodium, and ammonium are 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 valency, into four groups. They are sometimes called acid elements, in contradistinction to the basic elements. Arsenic, antimony, and tin, however, play the parts of metals and of non-metals: they are intermediate in their properties. 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 univalent, and combine in the proportion of 1 atom or 1 gaseous volume to 1 atom or 1 volume of hydrogen, yielding 2 volumes 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, 35·26 times as heavy as hydrogen; 2·5 volumes of it dissolve in 1 volume of cold water; it may be liquefied by pressure; melting-point 33·6°, and boiling-point 102°. It is a powerful bleaching-agent. Bromine is a red-brown liquid, boiling at 59°, freezes at −70°, and of specific gravity 3·19. Its vapour is red; it turns starch-paste orange. Iodine is a bluish-black solid, of specific gravity 4·95, melting at 114°, and boiling at 184°. Its vapour is violet; it turns starch-paste blue. Fluorine has been isolated as a light greenish-yellow gas; its compound with hydrogen, hydrofluoric acid, acts upon glass, etching it rapidly. Fluorine combines with hydrogen very energetically, even at the lowest temperature obtainable. Liquid fluorine boils at −187°; it freezes at −223°.

GROUP II. Diad or bivalent acid elements, which combine in the proportion of 1 gaseous volume to 2 volumes of hydrogen, yielding 2 volumes of a compound gas, in which the acid character is indistinct. These are Oxygen and Sulphur. Oxygen is a colourless gas, 15·87 times as heavy as hydrogen; 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 −182° under atmospheric pressure, and when frozen melts at −223°. Sulphur is a yellow solid, of specific gravity 2·05, melting at 115°, and boiling at 440° It yields an orange-coloured vapour. It exists in several allotropic modifications.

GROUP III. Triad or trivalent non-metals or acid elements, which combine in the proportion of 1 gaseous volume or 1 atom to 3 volumes or 3 atoms of hydrogen, yielding 2 volumes of a basic compound. These are Nitrogen and Phosphorus (arsenic and antimony also). Nitrogen is a colourless gas nearly 14 times as heavy as hydrogen. It has been reduced to the liquid state, when it has the specific gravity ·81; liquid nitrogen boils at −195·5°, and freezes at −214°. Solid nitrogen has a specific gravity of 1·026. It is incombustible, nor does it support combustion. Phosphorus is known chiefly in two forms—a colourless, wax-like solid, of specific gravity 1·83, melting under water at 44°, and boiling at 290° (this variety may be crystallized); and a chocolate-red powder, of specific gravity 2·21, which at 350° 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 quadrivalent non-metals or acid elements, which combine in the proportion of 1 gaseous volume or 1 atom to 4 volumes or 4 atoms of hydrogen, yielding 2 volumes of a neutral compound gas. These are carbon and silicon. Carbon occurs in three forms—diamond, graphite, and amorphous carbon. The diamond crystallizes in octahedra, of specific gravity 3·53; graphite is greyish-black, of specific gravity 2·3; while charcoal, lampblack, etc., 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 oxide is silica, SiO_2.

Annexed is a list of the names, symbols, and atomic weights of 81 substances believed to be simple or elementary, as adopted by the International Committee on Atomic Weights, on the basis of oxygen = 16, when hydrogen becomes 1·008.

Symbols and International Atomic Weights. O = 16.

ALUMINIUM	Al	27·1
ANTIMONY	Sb	120·2
Argon	A	39·88
ARSENIC	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
BROMINE	Br	79·92
Cadmium	Cd	112·4
Cæsium	Cs	132·81
*CALCIUM	Ca	40·09
*CARBON	C	12·0
Cerium	Ce	140·25
*CHLORINE	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
COPPER	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
*FLUORINE	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
GOLD (*Aurum*)	Au	197·2
Helium	He	3·99
*HYDROGEN	H	1·008
Indium	In	114·8
IODINE	I	126·92
Iridium	Ir	193·1
*IRON (*Ferrum*)	Fe	55·85
Krypton	Kr	83·0
Lanthanum	La	139·0
LEAD (*Plumbum*)	Pb	207·1
Lithium	Li	6·94
Lutecium	Lu	174·0
*MAGNESIUM	Mg	24·32
*MANGANESE	Mn	54·93
MERCURY (*Hydrargyrum*)	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
*NITROGEN	N	14·01
Osmium	Os	190·9
*OXYGEN	O	16·0
Palladium	Pd	106·7
*PHOSPHORUS	P	31·04
PLATINUM	Pt	195·2
*POTASSIUM (*Kalium*)	K	39·1
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sm	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
*SILICON	Si	28·3
SILVER (*Argentum*)	Ag	107·88
*SODIUM (*Natrium*)	Na	23·0
Strontium	Sr	87·63
*SULPHUR	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tm	168·5
TIN (*Stannum*)	Sn	119·0
Titanium	Ti	48·1
Tungsten (*Wolfram*)	W	184·0
Uranium	U	238·5
Vanadium	V	51·06
Xenon	Xe	130·2
Ytterbium (*Neoytterbium*)	Yb	172·0
Yttrium	Yt	89·0
ZINC	Zn	65·37
Zirconium	Zr	90·6

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

§ 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. It should be kept in a glass-stoppered bottle.

Iron (Fe). Some kinds of steel and soft iron wire, notably piano-wire, contain a very small percentage of impurities. Keep covered with quicklime in a glass bottle.

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 sometimes contains iodate in small quantities. Evaporate the alcoholic solution to dryness, and make a 10 per cent. (%) 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 Thiocyanate or *Sulphocyanide* ($KCNS$). The commercial salt may be used: 10 per cent.

Potassium Ferrocyanide (K_4FeCy_6, 3aq.) occurs pure in commerce: 8 per cent.

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 per cent.

Potassium Sulphide (K_2S). The commercial salt may be used: 4 per cent. Should be freshly prepared.

Potassium Hydroxide (KHO). Commercial caustic 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 caustic potash be dissolved in alcohol, and the clear liquor evaporated (in the absence of CO_2) in a silver dish, the hydroxide is obtained nearly pure: 5 per cent.

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 used. Make a saturated solution.

Potassium Chromate (K_2CrO_4). The commercial salt sometimes contains a little chloride: 5 per cent. solution.

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

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

SODIUM SALTS.—*Sodium Hydroxide* (NaHO) is used for the same purposes as potassium hydroxide. When required pure, that made from sodium should be employed: 5 per cent.

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 bicarbonate; in the case of the latter salt magnesium should be first looked for: 10 per cent.

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 per cent.

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 5 times its weight of water.

AMMONIUM SALTS.—*Ammonium Chloride* (NH_4Cl). This salt may readily be obtained pure: 20 per cent.

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, specific gravity ·88, if it leave no residue on evaporation, may be used in analysis. 8 per cent. solution: mix one volume of strong ammonia solution, specific gravity ·88, with three volumes of water; adjust this to a specific gravity of ·967 by the addition of more water or more ammonia solution as required. 2 per cent. solution: mix one volume of 8 per cent. ammonia solution with three volumes 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 per cent. 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 ($[NH_4]_2MoO_4$). One hundred and twenty-five grams of molybdic acid and 100 cubic centimetres of water are placed in a litre flask, and the molybdic acid dissolved by the addition, while the flask is shaken, of 300 c.c. of 8 per cent. ammonia solution. Four hundred grams of ammonium nitrate are added and the solution made up to a litre. This is then gradually added to 1 litre of nitric acid, specific gravity 1·19: keep the solution at a temperature of about 35° C. for 24 hours and then filter.

SILVER SALT.—*Silver Nitrate* ($AgNO_3$). The recrystallized salt may be used: or it is 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 per cent.

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

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 per cent.

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 per cent.

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 per cent.

Ammoniacal Magnesium Chloride (magnesia mixture). One hundred and ten grams of crystallized magnesium chloride and 140 grams of ammonium chloride are dissolved in 1300 c.c. of water, and the solution mixed with 700 c.c. of 8 per cent. ammonia solution, and the whole allowed to stand for not less than three days and then filtered.

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. It may be bought in short sticks for use in making sulphuretted hydrogen.

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

COPPER SALT.—*Copper Sulphate* ($CuSO_4$, 5aq.). The commercial salt is usually contaminated with iron sulphate and sometimes with lead sulphate. For analytical purposes, the metallic copper obtained by electrolysis may be dissolved in hot pure sulphuric acid: the salt should then be crystallized from its solution: 10 per cent.

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 hydroxide, having the specific gravity 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 per cent.

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 per cent.

Potassio-mercuric Iodide, or Nessler's test. This excessively delicate test for ammonia is a solution of HgK_2I_4 in potassium or sodium hydroxide. 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 hydroxide 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 hydroxide solution. The yellow mercuric hydrate at first thrown down passes, after thorough washing and drying at 100° C., into the oxide.

URANIUM SALT.—*Uranic Acetate* and *Nitrate* may be purchased in a state of purity. They 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* ($PtCl_4$). The salt sold under the name of platinic chloride is $PtCl_4$, $2HCl$, $6H_2O$; it may be obtained fairly pure; but it is sometimes purposely adulterated with sodium chloride, and may contain Iridium chloride. It is made by dissolving platinum 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. When dried at 100° C., it consists of H_2PtCl_6 ($=PtCl_4$, $2HCl$): 10 per cent. solution in water.

ETHYL COMPOUNDS. — *Ether* or *Ethyl Oxide*, ($[C_2H_5]_2O$). 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. On evaporating 20 c.c. no obvious residue should remain.

Alcohol or *Ethyl Hydrate* (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. Two 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. Arsenic is the most persistent impurity. One part of the strong acid, specific gravity 1·2, diluted with 4 parts of water is used as dilute hydrochoric acid.

Nitric Acid (HNO_3). The commercial acid generally contains a little hydrochloric and sulphuric acid; it may, however, be purchased pure. One volume of strong acid, specific gravity 1·42, is to be mixed with 4 volumes 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 specific gravity 1·048. To make the dilute acid, add 3 volumes of water to the strong commercial, or 9 volumes 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). Ferrous 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 volume of oil of vitriol is very gradually and cautiously poured, with constant stirring, into 5 volumes of water: after twenty-four hours decant the clear liquid from any 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 per cent.

Phenol or *Carbolic Acid* (C_6H_5HO). The crystallized carbolic acid of commerce may be dissolved in distilled water: 4 per cent.

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 volumes of water.

Tartaric Acid ($H_2C_4H_4O_6$). The commercial acid is sufficiently pure; though it sometimes contains a small quantity of lead: 20 per cent.

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 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.

Hydrofluoric acid is made from 1 part of 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 AND INDICATORS

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 (boric 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 narrows 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 acetic 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.

Phenolphthalein Solution.—Turned a violet or rose colour by a trace of alkali. This solution is made by dissolving 5 grams of this substance in 1 litre of proof spirit: it cannot be used in volumetric analysis in the presence of ammonia or ammonium salts; but may be used for all organic acids.

Methyl - orange Solution (Dimethylamido - azo - benzene sulphonate). One gram to 1 litre of water. This solution is turned pink by acids: it can be used in the presence of carbonic acid and of ammonia, but not for organic acids.

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 constituent or radicle: common salt is a compound of this order. Its formula (NaCl) indicates that it contains, as its metallic or basic radicle, 1 atom of the metal sodium, and as its non-metallic or acid radicle, 1 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 two 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 five 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 being generally employed. Copper belongs to group 2: we shall require 7 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 HCl and some hydrosulphuric acid (H_2S); 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 readily dissolves to a deep blue liquid in excess of ammonia.

b. Add sodium hydroxide ($NaHO$); 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 hydroxide a hydroxide 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.

$$(1)\ AgNO_3 + HCl = HNO_3 + \underset{\text{White ppt.}}{AgCl}$$

$$(2)\ 2AgNO_3 + H_2S = 2HNO_3 + \underset{\text{Black ppt.}}{Ag_2S}$$

$$(3)\ 2AgNO_3 + (NH_4)_2S = 2NH_4NO_3 + \underset{\text{Black ppt.}}{Ag_2S}$$

$$(4)\ 2AgNO_3 + (NH_4)_2CO_3 = 2NH_4NO_3 + \underset{\substack{\text{White ppt.}\\ \text{sol. in excess.}}}{Ag_2CO_3}$$

Special Tests.

$$(a)\ AgNO_3 + KI = KNO_3 + \underset{\text{Yellow-white ppt.}}{AgI}$$

$$(b)\ 2AgNO_3 + K_2CrO_4 = 2KNO_3 + \underset{\text{Dull-red ppt.}}{Ag_2CrO_4}$$

$$(c)\ AgNO_3 + NaHO = NaNO_3 + \underset{\text{Buff ppt.}}{AgHO}$$

$$(d)\ 6AgNO_3 + 3Na_2HPO_4 = 6NaNO_3 + H_3PO_4 + \underset{\text{Lemon ppt.}}{2Ag_3PO_4}$$

A very convenient and simple way of writing equations consists in placing the formulæ of the materials which react in horizontal lines in such a manner that when the same symbols are read vertically the products of the reaction are expressed. Thus, in (1) above, where silver nitrate and hydrochloric acid react,

$$\begin{array}{c:c} Ag & NO_3 \\ \hline Cl & H \end{array}$$

we read the formulæ of the products as separated by the dotted line, in the expressions for silver chloride and nitric acid. The only drawback to this contrivance is the occasional difficulty of so grouping the symbols as to indicate clearly the formulæ of the products.

No more of a reagent is to be added than is necessary to produce the complete effect desired; a large excess is seldom necessary, except where a reagent, such as calcium sulphate, is very slightly soluble, or where the precipitate produced has to be dissolved, and requires much water or other solvent to dissolve it. Reagents must, in nearly all cases, be thoroughly *mixed* with the solutions to which they are added by shaking, or by stirring with a glass rod.

All apparatus used must be perfectly clean. Glass and other vessels are more effectually cleansed by several rinsings with small quantities of distilled water than with twice the quantity used at once. All solutions must be perfectly clear; and filters, after having been fitted into the funnels, before using, must be wetted with distilled water; the filter-paper must not project above the edge of the funnel. Although the various operations, known as decantation, filtration, ignition, digestion, precipitation, may be best learned under the personal supervision of a teacher, yet the student who has carefully gone through the lessons in Part I. of this book will have acquired a familiarity with chemical manipulation sufficient for all ordinary analytical processes.

The following list gives in full the special and general tests for the bases of each of the five groups. It must be remembered that some of the metals form two series of salts, in which the proportion of basic to acid radicle differs, and which behave differently with reagents.

GROUP I.—*Group Reagent, Hydrochloric Acid*, precipitates as chlorides, Silver, Lead, and Mercurous salts.

Special tests.—SILVER: its chloride is a white curdy precipitate, soluble in ammonia, insoluble in nitric acid. Solutions of silver give a dull crimson precipitate with potassium chromate; a yellow precipitate, soluble in nitric acid and in ammonia, with sodium phosphate; and a buff precipitate with sodium hydroxide. Silver salts fused with sodium carbonate on charcoal give white lustrous malleable globules of silver.

LEAD: its chloride is crystalline, soluble in hot or much cold water; its solutions give yellow precipitates with potassium chromate and with potassium iodide (the latter crystallizing in golden scales from hot water), and a white precipitate with sulphuric acid. Lead salts heated on charcoal with sodium carbonate in the blowpipe flame yield soft malleable globules of metallic lead, with an incrustation of orange-coloured oxide.

MERCUROSUM: the monad mercury occurring in the proto- or mercurous salts yields an insoluble chloride, which is blackened by ammonia and is volatile in the blowpipe flame. The metal may be obtained as a sublimate of globules, by heating a mixture of its chloride with dry sodium carbonate in a small tube; and when any mercury compound is heated with hydrochloric acid, water and a slip of copper wire or foil, the latter metal acquires a silvery white film of metallic mercury. With potassium iodide a mercurous salt gives a greenish-grey precipitate; with sodium hydroxide 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 99.

MERCURICUM: the chloride of diad 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 hydroxide 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 under the behaviour of mercurous salts.

COPPER: the special tests for copper have been already described (see pp. 95, 96).

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 pp. 31 and 122).

ARSENICUM: the reactions are similar to the above, save that the precipitate by silver nitrate is brick-red; soluble arsenic salts also give 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 ammonium 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 hydroxide 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, Aluminium.

Special tests.—FERROSUM: its sulphide is black; solutions of ferrous salts yield a greenish-grey precipitate with sodium hydroxide, 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 hydroxide, and a dark blue precipitate (Prussian blue) with potassium ferrocyanide; with potassium ferricyanide an olive-green coloured liquid is produced. Potassium sulphocyanide yields a blood-red solution.

MANGANESE: its sulphide is flesh-coloured; with sodium hydroxide its salts give a white precipitate, 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 hydroxide 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 hydroxide, 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 most 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 caustic soda evolve ammonia gas, recognised 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 pp. 112 to 114 and 134, for nitrates, silicates, acetates, iodides, etc. 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.
*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, 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, 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. 112 to 114, and 134), 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 familiarised 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 diad 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 XII. 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, etc., 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 gelatin.
	The water has an acid reaction to test-papers..........	Salts of volatile acids, as HCl, HNO_3, HF, H_2SO_4, H_2SO_3.

EXPERIMENT.	OBSERVATION.	INFERENCE.
I. (*continued*).	*Substance volatilizes*, and a sublimate forms in cool part of tube	NH_4, As, Hg, Sb, Sn chlorides, oxalic acid, iodine.
	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.

EXPERIMENT.	OBSERVATION.	INFERENCE.
I. (*continued*).	*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.
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, Hg, $CuCl_2$.
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.	Fe, Mn.
	(If metallic globules appear, see experiment IV.)	
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.

EXPERIMENT.	OBSERVATION.	INFERENCE.
IV. (*continued*).	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 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.
VI. 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, VII.-XII., 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.

EXPERIMENT.	OBSERVATION.	INFERENCE.
VII. 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.
VII. (*continued*)	ζ. Colourless gases of pungent odour........	ζ. Chlorides and iodides.
	η. $HC_2H_3O_2$; smell of vinegar.....	η. Acetates.
VIII. 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. *Greenish-yellow fumes* of Cl bleaching litmus or indigo sulphate........................	ζ. Chlorides, probably with a nitrate or peroxide.
	η. *Reddish-brown fumes* of NO_2	η. Nitrates.
IX. 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. [Iodides give a similar colour.]
X. 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.

EXPERIMENT.	OBSERVATION.	INFERENCE.
XI. Add a small portion of the substance to a clear bead of fused microcosmic salt; heat.	*An undissolved skeleton* (of SiO_2) floating in the fused bead . . .	Silica or silicates.
XII. To a weak solution of the substance add dilute HCl, and then $BaCl_2$ solution.	*A fine white precipitate* .	Sulphates.

The experiments just described, excepting IX. and XII., 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. 124). 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 recognised by their odour.

3. *The reaction is alkaline.*—Free ammonia is recognised by its smell. The solution is acidified with nitric acid: if effervescence take place, the nature of the gas evolved is ascertained (see p. 112, "Preliminary Examination," Exp. VII.). If neutralization 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 p. 135.

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. 137; 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. 112). 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 the substance be neither carbon, phosphorus, nor sulphur (recognised by their behaviour when ignited), it must be fused with the mixed potassium and sodium carbonates according to the directions given at p. 135.

§ 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. 117.</td><td colspan="4"><i>Filtrate</i> add 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. 119.</td><td colspan="3"><i>Filtrate</i>:,(see p. 123), add NH_4Cl, NH_4HO, $(NH_4)_2S$, agitate, filter:—</td></tr>
<tr><td rowspan="2"><i>Precipitate of Group III.</i>:—
FeS
ZnS
MnS
$Al_2H_6O_6$
(with phosphates, etc.).

Wash, and examine by Scheme III., p. 124.</td><td colspan="2"><i>Filtrate</i>: add $(NH_4)_2CO_3$ filter:—</td></tr>
<tr><td><i>Precipitate of Group IV.</i>:—
$BaCO_3$
$SrCO_3$
$CaCO_3$

Wash, and examine by Scheme IV., p. 127.</td><td><i>Filtrate.</i>
Mg
K
Na
NH_4 } Salts.

Examine by Scheme V., p. 128.</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.

The undissolved *residue* is to be warmed with solution of ammonia; if it entirely dissolves, it is silver chloride; decant or filter the solution in ammonia:—		**Pb.** The *filtrate* or solution is divided into two parts:— 1. To one add dilute sulphuric acid and a little alcohol: a white precipitate indicates lead. 2. To the other add potassium chromate: a yellow precipitate indicates lead.
Hg. The undissolved *residue*, if black or grey, indicates monad mercury (mercurosum). Place it in a test-tube with a little 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 tube; metallic mercury will sublime in globules.	**Ag.** The *filtrate* is to be tested for silver by adding to it a slight excess of nitric acid: a white precipitate indicates silver.	

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. 121. 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 hydroxide,[1] 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 hydroxide, to filter the mixture, and to examine the black residue which remains on the filter according to the scheme for subgroup A below.

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 hydroxide) 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:—

---

[1] Ammonium sulphide dissolves traces of CuS, while HgS is slightly soluble in sodium hydroxide.

<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 hydroxide) 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 for some time :—</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.
(<i>See Note below.</i>)</td>
</tr>
<tr>
<td>Sn. Remove some of the zinc and dissolve it together with any adherent tin in hot HCl. Dilute, and add $HgCl_2$: a white or grey precipitate indicates tin.</td>
<td>Sb. A black stain on the platinum foil 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, arseniuretted hydrogen (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

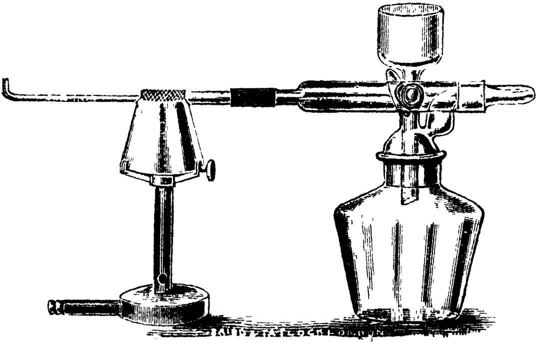

FIG. 12.

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 hydroxide, 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 p. 101.

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, Group III. B., described further on (p. 126).

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.

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 dissolved in dilute hydrochloric and boiled to expel H_2S. If the precipitate was black, add a few drops of strong nitric acid and boil for some minutes to oxidize ferrous into ferric salts.[1] If necessary,

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[1] See if the oxidation is complete, by adding to a few drops of the solution in a test-tube some sodium hydroxide; the precipitate should have a reddish colour.

filter to remove suspended sulphur. *Nearly* neutralize the solution with ammonia; add sodium acetate and a little acetic acid; heat to boiling for some time, and filter:

<table>
<tr><td colspan="2">The *precipitate* may consist of phosphate of iron and aluminium. Dissolve in hydrochloric acid, add excess of sodium hydroxide, boil, and filter :—</td><td colspan="4">The *filtrate* may contain aluminium,[1] manganese, zinc, barium, strontium, calcium, and magnesium [the latter as phosphate]. Add a *slight* excess of Fe_2Cl_6, boil, and filter. The precipitate consists of ferric phosphate and basic ferric acetate; neglect this. To the *filtrate* add NH_4Cl, NH_4HO, and $(NH_4)_2S$; filter :—</td></tr>
<tr><td rowspan="2">**Fe.** The *precipitate* is dissolved in HCl and potassium ferrocyanide added: a blue precipitate indicates iron.</td><td rowspan="2">**Al.** The filtrate is acidified with HCl, and then NH_4HO added in excess: a colourless gelatinous precipitate indicates aluminium.</td><td colspan="2">The *precipitate* may contain manganese and zinc sulphides. Dissolve in HCl, boil to expel H_2S, add NaHO till alkaline, boil, and filter :—</td><td colspan="2">The *filtrate* may contain barium, strontium, calcium, and magnesium. Add HCl till acid, boil to expel H_2S, filter off suspended sulphur, make alkaline with ammonia, add $(NH_4)_2CO_3$, warm, and filter :—</td></tr>
<tr><td>**Mn.** The *precipitate* is fused on platinum foil with a mixture of Na_2CO_3 and KNO_3: a green mass indicates manganese.</td><td>**Zn.** To the *filtrat* add H_2S: a white precipitate indicates zinc.</td><td>**Ba. Sr. Ca.** The *precipitate* may contain carbonates of these metals. Examine according to directions under Group IV.</td><td>**Mg.** The *filtrate* may contain magnesium. Add Na_2HPO_4: a white crystalline precipitate on standing indicates magnesium.</td></tr>
</table>

[1] In the presence of much iron and little P_2O_5, this filtrate may contain aluminium but no P_2O_5. Treat it by Table for Group III. B.

TABLE FOR GROUP III. B

If P_2O_5 *be absent.* To the main portion of the solution add NH_4Cl, NH_4HO, and $(NH_4)_2S$, warm gently, and filter. Examine the filtrate for Groups IV. and V. The precipitate is washed with water or, if black, with weak ammonium sulphide solution: it may contain $Al_2(HO)_6$, FeS, MnS, and ZnS. Dissolve the precipitate in HCl, boil to expel H_2S. If the precipitate was black, add a few drops of strong nitric acid and boil for some minutes to oxidize the ferrous salt to ferric.

To the solution add NH_4Cl and NH_4HO in excess; filter quickly.

The *precipitate* may contain aluminium and iron. Dissolve in HCl, add NaHO in excess, boil, and filter :—		The *filtrate* may contain manganese and zinc. Acidulate with HCl, add NaHO in excess, boil, and filter :—	
Fe. The *precipitate* is dissolved in HCl, and potassium ferrocyanide added: a blue precipitate indicates iron.	**Al.** The *filtrate* is acidulated with HCl, then ammonia added till alkaline, and warmed: a colourless gelatinous precipitate indicates aluminium.	**Mn.** The *precipitate* may contain manganese. Mix with dry sodium carbonate and potassium nitrate, and fuse on platinum foil: a green mass indicates manganese.	**Zn.** The *filtrate* may contain zinc. Add H_2S: a white precipitate indicates zinc.

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. 111	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, p. 110.

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 recognised 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. Carefully observe the colour given to a flame by the original substance heated with hydrochloric acid on a clean platinum wire.

§ v. Analytical Schemes for the Detection of the Non-Metallic or Acid Radicles.

In the Preliminary Examination (see Experiments VII. to XII.) 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. 138, 139.

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 XII., p. 114. 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 or basic radicles, fusion with the mixed sodium and potassium carbonates will be found to answer the purpose in view (see p. 135). In this case, however, organic acids are 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.[1] 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, pp. 43 and 124.

F. (2) Add calcium chloride solution. A white gelatinous precipitate is calcium fluoride. Confirm by etching glass, as in Preliminary Examination, p. 113.

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 effer-

---

[1] 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.

vescence 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.

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 hydroxide, 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 hydroxide, 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.

To a solution of a tartrate or a citrate add a small quantity of mercuric sulphate solution with excess of sulphuric acid: heat to boiling and drop in a solution of potassium permanganate. The colour is discharged and, if citrate be present, decolorisation is at once followed by the formation of a copious white precipitate.

SPECIAL TESTS FOR ACID RADICLES.

Acetates.—See Preliminary Examination, Experiment X., p. 113. 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 for a few minutes, 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 IX., p. 113.

Phosphates.—See pp. 43 and 124.

Silicates.—See Exp. XI., p. 114. The silicic radicle present in its soluble form may be recognised 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 XII., p. 114.

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 phosphorous 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 some 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, and other acid radicles. 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, pp. 138, 139, 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).

TABLE OF

		Acetate.	Arsenate.	Arsenite.	Carbonate	Chloride.	Citrate.	Cyanide.	Hydrate.	Iodide.
Aluminium .	Al'''	S	I	I	...	S	(S)	...	I	...
Ammonium.	Am'	S	S	S	S	S	S	S	S	S
Antimony .	Sb'''	S	I	S	...	S	..	I	I	I
Arsenic .	As'''	...	...	..	...	S	..	...	S	(S)
Barium .	Ba''	S	I	(S)	I	S	(S)	S	(S)	S
Calcium .	Ca''	S	I	I	I	S	(S)	S	(S)	S
Copper .	Cu''	S	I	I	I	S	S	I	I	I
Ferric. .	Fe'''	S	I	I	I	S	S	I	I	I
Ferrous .	Fe''	S	I	I	I	S	S	I	(I)	S
Lead . .	Pb''	S	I	I	I	(S)	(S)	I	(S)	(S)
Magnesium	Mg''	S	I	I	I	S	S	S	I	S
Manganese .	Mn''	S	I	I	I	S	I	I	I	S
Mercuric .	Hg''	S	I	I	I	S	..	S	I	(I)
Mercurous .	Hg'	(S)	I	I	I	I	I	S	I	I
Potassium .	K'	S	S	S	S	S	S	S	S	S
Silver . .	Ag'	(S)	I	I	I	F	I	I	I	F
Sodium .	Na'	S	S	S	S	S	S	S	S	S
Stannic .	Sn^{iv}	S	..	I	I	S	...	...	I	(S)
Stannous .	Sn''	S	I	I	I	S	..	...	I	(S)
Strontium .	Sr''	S	I	(S)	I	S	(I)	S	S	S
Zinc . .	Zn''	S	I	I	I	S	(S)	I	I	S

S = Soluble in water ; (S) Sparingly soluble in water.

F = Insoluble in water and acids.

I = Insoluble in water, but soluble in HCl, or HNO_3, or nitrohydrochloric acid.

(I) = Insoluble in water, sparingly soluble in one or other of the above acids.

Notes to Table of Solubilities.

Arsenic, antimony, tin, lead, aluminium, and zinc oxides or hydrates are soluble in KHO or NaHO.

Arsenic, silver, copper, manganese, zinc, and magnesium oxides or hydrates are soluble in NH_4HO or ammonium salts.

Some salts insoluble in water or acids are soluble in saline

SOLUBILITIES.

Nitrate.	Oxalate.	Oxide.	Phosphate.	Silicate.	Sulphate.	Sulphite.	Sulphide.	Tartrate.	
S	I	I	I	F	S	I	I	S	Aluminium.
S	S	S	S	. .	S	S	S	S	Ammonium.
...	(S)	I	I	...	S	I	I	I	Antimony.
...	...	(S)	S	...	...	...	I	S	Arsenic.
S	I	S	I	I	F	S	I	I	Barium.
S	I	(S)	I	I	(S)	(S)	(S)	(S)	Calcium.
S	I	I	I	I	S	I	I	(S)	Copper.
S	S	(I)	I	I	S	(S)	I	S	Ferric.
(S)	I	I	I	...	S	(S)	I	(S)	Ferrous.
S	I	I	I	.	F	I	I	I	Lead.
S	S	I	I	F	S	S	S	S	Magnesium.
S	I	I	I	I	S	I	I	(S)	Manganese.
S	I	I	I	...	S	I	I	I	Mercuric.
S	I	I	I	...	S	I	I	I	Mercurous.
S	S	S	S	S	S	S	S	S	Potassium.
S	I	I	I	...	(S)	I	I	I	Silver.
S	S	S	S	S	S	S	S	S	Sodium.
S	S	I	I	...	S	S	I	S	Stannic.
S	I	I	I	...	S	(S)	I	(S)	Stannous.
S	I	(S)	I	I	F	S	(S)	(S)	Strontium.
S	I	I	I	I	S	S	I	(S)	Zinc.

solutions, as calcium tartrate in ammonium salts, and lead sulphate in solution of alkaline tartrates or acetates.

Some metals (Ag, Cu, Hg, Pb) and alloys not affected, or scarcely so, by HCl, are dissolved by HNO_3.

Many sulphides insoluble in HCl are decomposed by HNO_3.

HgS, Hg_2Cl_2, Fe_2O_3 (ignited), etc., scarcely attacked by either HCl or HNO_3, are dissolved by nitrohydrochloric acid.

Sand, many silicates (pipeclay), fluor-spar, sulphates of barium, strontium (calcium), tin-stone, glass, AgCl, $PbSO_4$, carbon and sulphur, chrome iron-ore are not attacked by these acids: C and S are recognised by their behaviour when heated; and the others may, for the most part, be decomposed by fusion with potassium and sodium carbonates.

If large quantities of tin be present, traces of other metals may occur in this residue.

After thoroughly washing the residue, fuse it with 3 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. 109, 110, 111, and 112), when changes occurred in the following experiments only :—

I. *A white sublimate in tube, and on further heating, fumes of* NO_2.

I*a*. *Fumes of ammonia given off.*

II. *Bluish-green flame.*

III. *Substance deflagrated.*

IV. *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, with incrustation orange whilst hot, yellow when cold.*

IV. *Globules as in* III.

From these results we infer the presence of Ca, 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. 117) in order, each precipitate obtained being further examined according to the table for the group to which it belonged. In Group II. (pp. 119 to 121) a brownish-black precipitate, proved by further treatment and special tests to be *copper* sulphide; in Group III. (pp. 123 to 127) 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. 110), *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. 135). 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 Experiments VII.-X. (pp. 112 and 113) were performed:—

VII. CO_2 *evolved*, carbonates.

IX. *Brown ring*, nitrates.

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. 130). With this liquid the systematic examination for acids was conducted, a small portion, however, being used for Experiment XII., Preliminary Examination, p. 114, when *sulphuric* acid was found. In Group I. of the acids *chlorine* 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 recognising 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, etc.

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, etc., 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 1 atom of sodium, 1 of nitrogen, and 3 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, etc., 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, etc., 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 c.c., *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 in $\frac{1}{10}$ths c.c.

6. A pipette to hold 10 c.c., either graduated or simply marked to show when it contains the desired quantity.

All new measuring vessels, such as graduated flasks, pipettes, and burettes, should be checked against standard measures kept for that purpose only, before they are admitted to use in the laboratory.

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:—

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

The balance should be kept in a place not subject to acid fumes, and free from vibration. 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 indiarubber permanently fixed to the table; or three boxwood 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 swing an equal number of degrees to each side of the zero of the ivory scale. 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 gilt 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 Gilt 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 half-way 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 right-hand pan for the weights.

4. Never weigh any crucible, etc., 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 and noted down when the index swings an equal number of degrees on either side of the zero of the scale, and again checked on returning to the box.

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 anything to, or taking anything from, either pan.

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

9. 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.

10. 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 mm. broad at its base, 34 mm. at top: its height may be 37 mm.; 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 mm. while the breadth of its flange is 2 mm., 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. Any mixture of nitric acid and hydrochloric acid dissolves platinum. For many purposes a crucible of hard Berlin porcelain may be substituted for one of platinum. Still better is a crucible of fused quartz, which may be used in nearly all cases instead of a platinum crucible, it will withstand very sudden changes of temperature.

2. A platinum spatula, spud-shaped at one end and

pointed at the other, of the form and size shown in Fig. 13, 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. 13.

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.

A very convenient form of portable desiccator may be obtained of the dealers in chemical apparatus. In shape it somewhat resembles an hour-glass, 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 fused calcium chloride, the desiccating agent, are arranged, while the upper compartment is closed with a ground-glass plate.

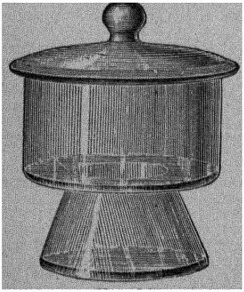

Fig. 14.

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

5. Besides the ordinary wash-bottle with movable 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 ammonia, and for alcohol and ether, should also be at hand.

6. A few funnels having four internal ribs 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.

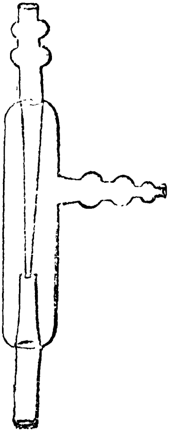

FIG. 15.

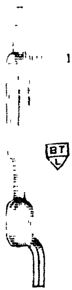

FIG. 16.

5. A small hand-mill for grinding samples.

6. A set of cylindrical zinc sieves of graduated

fineness, and fitting into one another; and a set of wire sieves of varying fineness.

7. An apparatus for filtering under reduced pressure. For this purpose, when a good water-supply is at hand, one of the filter-pumps figured on the previous page is most convenient (Figs. 15 and 16).

For further details concerning laboratory apparatus and fittings, reference may be made to larger works; 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 as Carbonate.

Solution employed, $CaCO_3$ in HCl ($=CaCl_2$), containing about ½ 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 a good 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 rod, one end of which has an inch of indiarubber 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:—

$$CaCl_2 + (NH_2)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl;$$
$$\text{by heat, } CaC_2O_4, = CaCO_3 + CO;$$

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 as Lime. Calcium Oxide.

Leave the calcium carbonate in the crucible and heat it for five minutes over a Bunsen burner, then for five minutes strongly over the Herapath blowpipe; cool in the desiccator, and weigh. It should now be all converted into quicklime, CaO. Repeat the ignition, and reweigh. See if its weight corresponds with the weight of the calcium carbonate first obtained.

$$CaCO_3 : CaO :: 100 : 56.$$

When the amount of lime is small, it is often more convenient to convert it into quicklime and weigh it as such.

Estimation of Magnesia as Pyrophosphate.

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 well mix; 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 (2 per cent.) until a few drops of the filtrate, acidified with nitric acid, give no cloudiness with silver nitrate. Dry, ignite the paper scraped as clean as possible, in a coil of platinum wire, with all the precautions mentioned in the preceding account relating to lime, add the ashes to the precipitate in the crucible, and ignite gently at first, and finally before the blowpipe.

Reactions :—

$$MgSO_4+Na_2HPO_4+NH_4HO = MgNH_4PO_4+Na_2SO_4+H_2O$$

$$\text{on ignition, } 2Mg(NH_4)PO_4 = \underset{\text{Magnesium pyrophosphate.}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Calculation :—

As molecule $\frac{Mg_2P_2O_7}{2}$: molecule $MgSO_47H_2O$ = amount of $Mg_2P_2O_7$ found : amount of $MgSO_47H_2O$ given.

$$\frac{222 \cdot 7}{2} : 246 \cdot 4 = a : x.$$

Estimation of Baryta as Barium Sulphate.

Solution of barium chloride ($BaCl_22H_2O$) employed, containing about $\frac{1}{2}$ per cent.

Make the solution (50 c.c.) up to about 120 c.c. (or 4 oz.) with distilled water, add a little dilute HCl, and heat just to boiling; add dilute sulphuric acid as long as a precipitate forms; keep the mixture near the boiling-point for some time, allow the precipitate to subside, and decant through a good filter-paper; heat the precipitate twice more with water, then transfer to the filter (waiting after the addition of every fresh portion until the fluid has completely passed through the filter), and continue the washing with hot water until the filtrate is no longer rendered turbid by a drop of barium chloride. Dry and ignite, scraping the paper as clean as possible, and burning it in a coil of platinum wire.

Reaction :—

$$BaCl_2+H_2SO_4 = BaSO_4+2HCl.$$

Calculation :—

As molecule $BaSO_4$: molecule $BaCl_22H_2O$ = amount of $BaSO_4$ found : amount of $BaCl_22H_2O$ given.

$$233 \cdot 4 : 244 \cdot 3 = a : x.$$

Estimation of Phosphorus Pentoxide as Magnesium Pyrophosphate.

Solution of sodium phosphate ($Na_2HPO_412H_2O$) employed, containing about 1 per cent.

Add to the solution (about 50 c.c.) ammonium chloride, ammonia till the smell is strongly ammoniacal, and then, very gradually, magnesia mixture (a mixture of $MgCl_2$, NH_4Cl, and NH_4HO; see p. 85). Mix well (but avoid using a glass rod), cover the beaker, and let it stand twelve hours in the cold; collect the precipitate on a filter, wash with ammonia water (2 per cent.) until the filtrate, after acidifying with nitric acid, is not rendered turbid by silver nitrate. Dry and ignite, at first gently, and finally with the blowpipe.

Reactions:—

As in estimation of magnesia.

Calculation:—

As molecule $\frac{Mg_2P_2O_7}{2}$: mol. $Na_2HPO_412H_2O$ = amount of $Mg_2P_2O_7$ found : amount of $Na_2HPO_412H_2O$ given.

$$\frac{222 \cdot 7}{2} : 358 \cdot 2 = a : x.$$

Estimation of Potash as Potassium Platinic Chloride.

Solution of potassium sulphate employed (K_2SO_4), containing $\frac{1}{10}$th per cent.

Evaporate the solution (about 50 c.c.) to half its bulk; add a little HCl and excess of platinic chloride solution, and carry the evaporation nearly to dryness on a water-bath away from any ammonium fumes; add strong alcohol, specific gravity ·864, and wash the substance first by decantation, finally collecting it on a filter dried previously at 100° and weighed till constant. After washing with more strong alcohol, the filter and contents are dried at 100° and weighed. The salt weighed is $PtCl_4$, $2KCl$.

Reaction :—

$$K_2SO_4 + 2HCl + PtCl_4 = PtCl_4 2KCl + H_2SO_4.$$

Calculation :—

As molecule $PtCl_4 2KCl$: molecule K_2SO_4 = amount of $PtCl_4 2KCl$ found : amount of K_2SO_4 given.

$$486{\cdot}2 : 174{\cdot}3 = a : x.$$

A stoppered tube, about ¾ of an inch broad and 3½ inches long, serves for holding the filter-paper whilst drying and weighing.

Preparation of Volumetric Solutions.

A *normal solution* of a reagent is one that contains in a litre that proportion of its molecular weight in grams which corresponds to 1 gram of available hydrogen, or its equivalent in some other element. Thus a normal solution of sulphuric acid contains 49 grams of pure sulphuric acid per litre: for H_2SO_4 molecular weight $= 98 \div 2 = 49$. In the case of hydrochloric acid (HCl) 36·5 grams of pure hydrochloric acid will be contained in 1 litre.

Potassium permanganate ($K_2Mn_2O_8$) will yield 5 atoms of oxygen (the equivalent of 10 atoms of hydrogen) for oxidizing purposes: its molecular weight is 316. A normal solution of potassium permanganate contains 31·6 grams of this salt per litre. A normal solution of silver nitrate contains 169·9 grams per litre. A normal alkali solution neutralizes an equal volume of a normal acid solution. A normal solution of sodium hydroxide contains 40 grams per litre.

Normal solutions may be expressed thus, $\frac{N}{1}$ H_2SO_4 ;

seminormal solutions contain one-half the amount of active agent of the normal solution, and are thus expressed, $\frac{N}{2}$ HCl; a decinormal solution, $\frac{N}{10}$, is one-tenth, and a centinormal solution, $\frac{N}{100}$, one-hundredth, of the strength of a normal solution.

The indicator used in standardizing acid and alkali solutions should be noted, and used in all experiments made with the same solutions.

Preparation of Acid and Alkali Solutions used in the Determination of Nitrogen.

Normal sulphuric acid. — Take 28 c.c. of pure sulphuric acid, having a specific gravity about 1·842. This will contain about 96 per cent. of real sulphuric acid. Sulphuric acid sold as pure sometimes contains ammonium sulphate as an impurity; this must be avoided. Take a litre flask about one-half full of distilled water, to this slowly add the 28 c.c. of sulphuric acid: fill up to the mark on the flask with distilled water, mix thoroughly, and allow to cool. When quite cold, add a little distilled water to make the volume up to the mark on the flask and again thoroughly mix.

The exact strength of the acid is now to be ascertained by making three determinations as follows:— Measure 10 c.c. of the acid, by means of a pipette kept for this purpose only, into a beaker, add 200 c.c. of water, a few drops of dilute hydrochloric acid, and heat the liquid just to the boiling-point. Remove the Bunsen burner, and after a minute add from a test-tube an excess of hot barium chloride solution. Heat the mixture just to boiling for five minutes, remove the flame and let the barium sulphate settle, then add a few drops more barium chloride solution. If no further precipitate is formed, the whole of the sulphuric acid has been precipitated as barium sulphate; if a further precipitate is produced, some more hot barium chloride solution must be added, the liquid again boiled, and re-tested. When the precipitate has completely settled, the hot liquid is to be filtered through a good filter-paper, the precipitate washed with hot water, by decantation, and finally washed out on to the filter-paper. The precipitate must be washed until a few drops of the last filtrate collected in a test-tube give no precipitate with dilute sulphuric acid, showing that all the excess of barium chloride has been washed away. Should the precipitate show signs of passing through the filter-paper, dilute hydrochloric acid should be used for the first washing. The precipitate is dried, removed from the paper which is burnt separately, burnt, and treated as described under the estimation of baryta, p. 157. The weights of the three precipitates should not differ from each other by more than ·003 gram.

The amount of H_2SO_4 per 10 c.c. is then calculated from the mean result of the three determinations, *e.g.*:

Weight of $BaSO_4$ = 1·1655.

Mol. Weight, $BaSO_4$: Mol. Weight, H_2SO_4 :: $BaSO_4$ found : H_2SO_4 present.
233 : 98 :: 1·1655 : ·49

Ten c.c. of the acid contain ·49 gram of H_2SO_4; 1 c.c. contains ·049, or 1 litre contains 49 grams of sulphuric acid.

The standard acid should also be standardized against a pure sodium carbonate solution. 1 c.c. $\frac{N}{1}$ H_2SO_4 will neutralize ·053 gram of Na_2CO_3. This test, when compared with the above, will serve to indicate if the acid contain any sulphate, such as ammonium sulphate.

1 c.c. of normal acid = ·014 N = ·017 NH_3.
1 c.c. of normal acid = ·028 CaO = ·050 $CaCO_3$.
1 c.c. of normal acid = ·040 NaHO = ·053 Na_2CO_3.

Alkali.—The alkali is a weak solution of sodium or potassium hydroxide, of which 100 c.c. should exactly neutralize 10 c.c. of the acid: *i.e.* a decinormal solution.

The hydroxide employed should be free from carbonate; if not so, it must be rendered caustic by boiling with fresh milk of lime in a clean iron vessel. The caustic soda made from sodium is the best material to use.

Preparation.—Having determined to make a certain volume of the alkali (say 2 litres), calculate the amount of hydroxide required; thus, if sodium hydroxide be used, and the acid contain exactly 49 grams H_2SO_4 in a litre = ·49 gram in 10 c.c., then, since H_2SO_4 saturates 2NaHO,

Molecular Weight, H_2SO_4		Molecular Weight, 2NaHO		H_2SO_4 in 10 c.c.		NaHO in 100 c.c.
98	:	80	=	·49	:	·4
c.c.		NaHO		c.c. taken.		NaHO required.
100	:	·4	=	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 10 c.c. of the acid, a little methyl-orange solution being added to the portion of acid measured out in order that, by its change of colour, 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. remaining,

$$90 : 100 = 1848 : 2053{\cdot}3,$$

the number of c.c. to which the alkali must be made up. This is then done and the strength again tested, when 10 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.

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

$$\overset{H_2SO_4}{98} : \overset{2NH_3}{34} = \overset{H_2SO_4 \text{ in } 10 \text{ c.c.}}{{\cdot}49} : \overset{NH_3}{{\cdot}17}$$

Ten c.c. of the acid are neutralized by 100 c.c. of the alkali; therefore each c.c. of the latter corresponds to $\frac{{\cdot}17}{100} = {\cdot}0017$ gram NH_3, or ·0014 gram N. This is $\frac{N}{10}$ NaHO solution.

Suppose that, after a nitrogen determination, 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 experiment equal in saturating power to 35 c.c. of the alkali, since 10 c.c. of the acid were originally taken; $35 \times {\cdot}0017 = {\cdot}0595$, the weight of NH_3 obtained, or $35 \times {\cdot}0014 = {\cdot}049$, the weight of N; from either of which the percentage is obtained.

As an indicator in acid and alkali determinations "methyl-orange" is the best for general use; it can be used in the presence of carbonates, ammonia. potash, soda, lime, baryta, and of all mineral acids. Phenolphthalein, a very sensitive reagent, should not be used in the presence of ammonia.

Another very good example of a quantitative volumetric estimation for practice is furnished by *iron*. Full directions are given on pp. 189, 190.

Estimation of Nitrogen (other than Nitric Nitrogen).

The nitrogen in all the common nitrogenized substances likely to be met with in agricultural materials can be determined by the following method, which has practically superseded all others:—

Kjeldahl's Method (Modification of).

In this method the organic nitrogen present is converted into ammonia by digesting the substance with pure strong sulphuric acid, the ammonia formed being afterwards liberated by means of caustic alkali, distilled off, collected in standard acid, and titrated with standard alkali. When heating with the sulphuric acid the addition of a small quantity of potassium sulphate, or of sodium pyrophosphate, in order to raise the temperature of the boiling acid, is desirable. With refractory substances, which are difficult to oxidize by the sulphuric acid, the addition of a small quantity of copper sulphate, or a few small drops of mercury, is an advantage and expedites the process.

One gram, or other suitable weight, of the substance to be analysed is placed in a round-bottomed Jena glass flask of about 750 c.c. capacity, 10 grams of potassium sulphate and 25 c.c. of the strongest sulphuric acid free from all nitrogen compounds are added. The flask, placed in an inclined position, is gently heated in a fume cupboard, over a Bunsen or an Argand burner

(Fig. 17), until frothing has ceased (generally twenty to thirty minutes); the temperature is then raised until the boiling-point of the acid is reached. When the contents, though they may still be black, are free from solid carbonaceous particles, the flask is placed in a vertical position, and one gram of copper sulphate introduced: the flask is then inclined as before and the heating continued. At the higher temperature which the mixture now reaches on the continued application of heat, carbonaceous matter present is oxidized and the liquid becomes less and less dark in hue. Instead of the copper sulphate a globule of mercury may be introduced to the flask to hasten the oxidization: in that case some sodium or potassium sulphide must be added with the sodium hydroxide before distilling off the ammonia. When the mixture has lost all or nearly all its colour, the flask is allowed to cool. During the operations above described it will

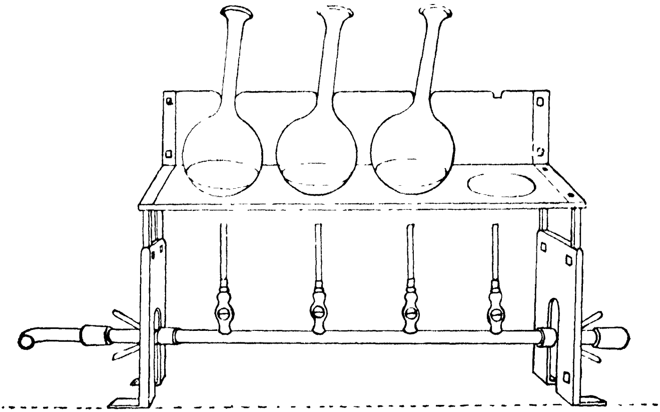

FIG. 17.

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 in 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 distilling the liquid previously diluted and rendered alkaline, the ammonia being carried forward through a Liebig condenser, or other suitable condensing apparatus (see Fig. 18).

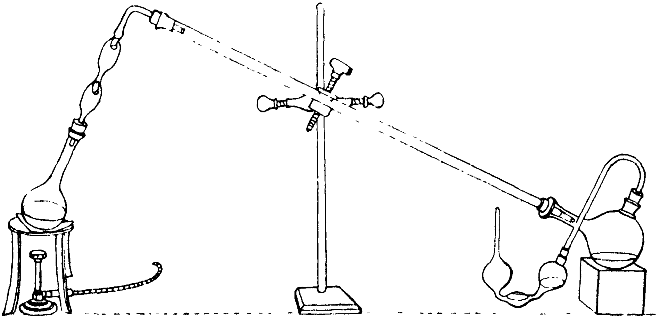

FIG. 18.

Dilute the cooled acid liquid in which the substance to be analysed has been decomposed with about 100 c.c. of pure distilled water. Add carefully 100 c.c. of strong sodium hydroxide solution (360 grams NaHO per litre) and a few fragments of granulated zinc; if mercury has been used also add a few c.c. of a strong solution of sodium sulphide, and immediately attach the flask to the condenser and receiver through a reflux adapter (Fig. 19). The alkaline solution introduced must be more than sufficient to neutralize the acid, and is mixed by careful shaking or by admission of steam after the flask has been attached to the condenser.

The receiver may be an Erlenmeyer flask of about 250 c.c. capacity, to the bottom of which a wide tube from the beak of the condenser passes; or it may be a bulb apparatus as shown in the sketch. The condenser must contain 10 c.c. of the normal standard sulphuric acid delivered from the pipette. In that case the Kjeldahl flask is fitted with an indiarubber stopper having two perforations. Through one of these a tube passing nearly to the bottom of the flask is inserted; this is for the supply of steam. The second perforation receives the neck of the reflux adapter (Fig. 19), which is itself connected with a condenser which is connected with the receiver for the ammoniacal distillate.

The distillation continues for about half an hour, or until a drop of the distillate shows no ammonia when tested with turmeric paper.

Transfer the contents of the receiver to a white porcelain dish, rinsing the receiver with distilled water two or three times, add a few drops of methyl-orange solution, and then titrate the unneutralized acid with standard alkali solution, as described on p. 162.

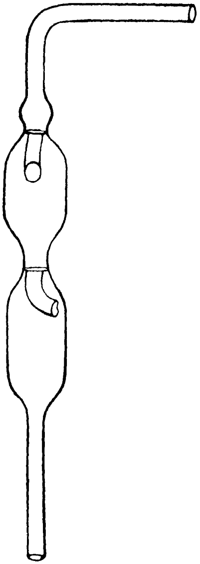

FIG. 19.

A blank experiment should always be made with the reagents employed.

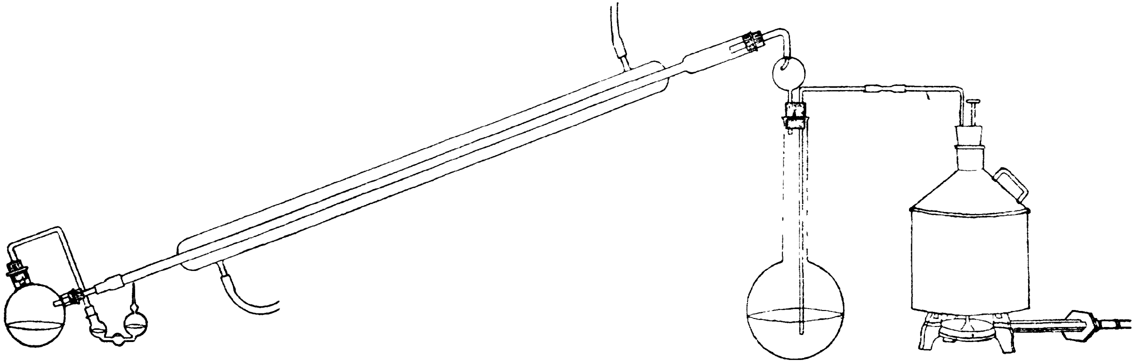

FIG. 20.

For the Determination of Total Nitrogen (including Nitric Nitrogen) by a modified Kjeldahl Method.

Take 1 gram or less of the finely powdered and well-mixed sample, place it in a Kjeldahl's flask with 30 c.c. of strong sulphuric acid in which is dissolved 1 gram of salicylic acid. Mix well by shaking immediately. The shaking must be continued at intervals during ten minutes, the flask being kept cool, then add 5 grams of crystallized sodium thiosulphate and 10 grams of potassium sulphate. Heat till decomposition is complete; copper sulphate or mercury may be used as before described (p. 164) to expedite the process. Proceed as in the ordinary Kjeldahl's process, taking care that the solution is made alkaline by excess of caustic soda before distilling.

Dumas' Method.

The nitrogen in all organic substances may be estimated by DUMAS' method, but this requires further gas analysis apparatus.

DETERMINATION OF PHOSPHORUS PENTOXIDE

A very accurate gravimetric method for the determination of P_2O_5, which with proper precautions may be used for all manures, soils, ashes of plants, ashes of foodstuffs, etc., is that known as the *Molybdate Method.*

Since it is of general application we give the method here, whilst giving other methods later on in connection with instructions for analysis of various materials to which the methods are most adaptable. The general directions for the *Molybdate Method* as given in the

Regulations (1908) of the Board of Agriculture under the provisions of the Fertilisers and Feeding Stuffs Act of 1906, are as follows:—

Total Phosphoric Acid.

A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition and the silica removed by appropriate means, shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method prescribed below.

Molybdate Method.

To the solution, which should preferably contain from 0·1 to 0·2 gram of phosphoric oxide (P_2O_5), 100 to 150 c.c. of molybdic acid solution prepared as described below, or an excess of such solution, *i.e.*, more than is sufficient to precipitate all the phosphoric oxide present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath maintained at 70° C., for fifteen minutes, or until the solution has reached 70° C. It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 per cent. nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution, and allowed to stand for some time in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

The phospho-molybdate precipitate shall be dissolved in cold 2 per cent. ammonia solution prepared as described below, and about 100 c.c. of the ammonia solution shall be used for the solution and washings. Fifteen to twenty c.c. of magnesia mixture prepared as described below, or an excess of such mixture, *i.e.*, more than sufficient to precipitate all the phosphoric oxide present, shall then be added drop by drop, with constant stirring. After standing at least two hours with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent. ammonia solution, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings shall be tested by the addition of more magnesia mixture.

Preparation of Molybdic Acid Solution.

The molybdic acid solution shall be prepared as follows:—

One hundred and twenty-five grams of molybdic acid and 100 c.c. of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 c.c. of 8 per cent. ammonia solution, prepared as described below. Four hundred grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water, and the whole added to 1 litre of nitric acid (sp. gr. 1·19). The solution shall be maintained at about 35° C. for twenty-four hours and then filtered.

Preparation of Magnesia Mixture.

The magnesia mixture shall be prepared as follows:—

One hundred and ten grams of crystallized magnesium chloride and 140 grams of ammonium chloride shall be dissolved in 1300 c.c. of water. This solution shall be mixed with 700 c.c. of 8 per cent. ammonia solution, and the whole shall be allowed to stand for not less than three days and shall be then filtered.

Preparation of the Ammonia Solutions.

The 8 per cent. ammonia solution shall be prepared as follows:—

One volume of ammonia solution of sp. gr. 0·880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution, or water as required, until the specific gravity of the solution is 0·967.

The 2 per cent. ammonia solution shall be prepared as follows:—

One volume of 8 per cent. ammonia solution shall be mixed with three volumes of water.

The magnesium pyrophosphate precipitate, after ignition, has the formula $Mg_2P_2O_7$.

$$Mg_2P_2O_7 \times 1{\cdot}3939 = Ca_3P_2O_8.$$
$$Mg_2P_2O_7 \times {\cdot}6379 = P_2O_5.$$

CHAPTER II

§ i Sampling of Manures.

A SAMPLE of manure or feeding stuff should fairly represent the bulk from which it was taken: this average sample is not always a simple thing to arrive at, and in the case of a bulky and mixed material like farmyard manure, obviously requires very great care and much time to obtain.

The sample, when obtained, must be stored in such a way that it does not alter, *e.g.*, by giving off water or other ingredient, or by absorbing water, or by acting on the material of the vessel in which it is packed.

In sampling manures which are sent out in bags, the sample should be drawn from several bags and mixed. With any ordinary manure, such as superphosphate, kainite, etc., six to twelve bags should be taken from the bulk for the purpose of obtaining the sample. This may be best done with the aid of a "sampler";—an iron tool, shaped like a cheese-sampler, about 2½ feet long, made of V-shaped iron, the diameter of the groove being about an inch, and with the end and edges sharpened.

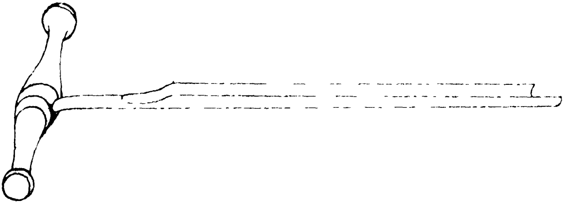

FIG. 21.

This tool can be driven down into each of the selected bags from top to bottom, and by tilting the bag, and giving the sampler a twist round, and then withdrawing it, a section of the contents of the bag is obtained. Similar sections are taken from each of the selected bags. The different lots are thoroughly well mixed, on a board or sack, any lumps being broken down. The sample must then be reduced in amount by repeated division and subdivision. The heap is turned over with a shovel several times, in different directions, and then divided into two halves; one-half is rejected, the remainder is quickly again turned over and mixed, and again divided. Half is again taken and treated as before, until about three or four pounds only remain. From this, two wide-mouthed glass bottles, well corked, holding each half to one pound, are filled. Good cylindrical tins, with well-fitting lids, may be used for neutral salts like nitrate of soda or sulphate of ammonia.

The sampling must be done as quickly as possible, having regard to the care necessary, in order that the material may not lose water during the process.

If a sampling tool is not available, the selected bags should be emptied and a couple of shovelfuls taken from each, these thoroughly mixed by turning over together, and divided as before. When the fertiliser is in a dry, or moderately dry condition, the whole sample should be passed through a sieve with perforations 1 mm. in diameter: any lumps being powdered, and the whole afterwards thoroughly mixed in a mortar.

Any adventitious substances—which cannot be conveniently powdered—such as metal in basic slag, must be removed and allowed for.

In cases where the sampling takes a long time and water is lost during the process—*e.g.*, shoddy, which requires to be cut up with scissors—the water must be determined in a large sample of the original material, and again in the smaller sample taken for analysis after division, and allowance made for any loss of water.

§ ii. Analysis of Manures.

Before beginning the several operations and analysis 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, ETC.

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.

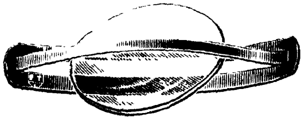
FIG. 22.

MOISTURE.—A convenient quantity, say 2 or 3 grams, is weighed into a watch-glass, provided with a cover-glass and clips (Fig. 22), 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 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 black 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 carbonate acid from the calcium carbonate. In any case, 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 with hot water, dried, burnt, and weighed.

The phosphorus pentoxide and lime are now determined by one of the following processes:—

Oxalic-acid Method.

LIME.—A few drops of very dilute ammonia are first added to the solution, with constant stirring, till a *very 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 with hot water, dried, ignited for some time at a very low red heat, and weighed as $CaCO_3$; or very strongly heated and weighed as CaO. Any lime found in the 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 in the cold the precipitate is collected, washed with 2 per cent. ammonia water, dried, ignited gently for some time, and afterwards at a very high temperature before the 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.

$$Mg_2P_2O_7 \times 1{\cdot}3935 = Ca_32PO_4.$$
$$Mg_2P_2O_7 \times {\cdot}6378 = P_2O_5.$$

Acetic-acid Method.

LIME.—To the filtrate from the sand, add about 3 grams of citric acid; boil, and add 3 grams of finely powdered ammonium oxalate; make slightly ammoniacal, and add an excess of acetic acid; boil for a few minutes, and filter through a good filter-paper; wash with hot water, dry, ignite the calcium oxalate at a gentle heat (p. 155), and weigh as calcium carbonate.

This precipitate always contains a small quantity of phosphate. After weighing, it should be dissolved in hydrochloric acid, boiled, slight excess of ammonia added, the small precipitate filtered off, redissolved and reprecipitated, collected on a filter-paper, washed, dried, burnt, and weighed. If it weighs only a few milligrams, one-half its weight may be assumed to be phosphorus pentoxide and added to the total phosphoric acid found. If the weight of the precipitate is more than a few milligrams, and in very accurate determinations, the phosphorus pentoxide in it should be determined by the molybdic acid method.

PHOSPHATES.—The filtrate from the lime precipitate is concentrated to about 100 c.c., about 25 c.c. of *strong* ammonia solution added and a considerable excess of magnesia mixture, slowly and with constant stirring. After standing two hours with occasional stirring; the supernatant liquid is decanted through a filter: any small precipitate on the filter is dissolved back into the original beaker with dilute hydrochloric acid, in such quantity as to dissolve the whole of the precipitate in the beaker. A few drops of a solution of citric acid are added, then strong ammonia, *drop by drop*, with constant stirring. After standing two hours, the ammonium-magnesium phosphate is filtered off, washed with ammonia water, dried, burnt, and weighed as $Mg_2P_2O_7$.

The *phosphates* alone may be directly determined in a nitric acid solution of the ash, obtained by burning about ·5 gram of the bones in a crucible.

NITROGEN.—Make a determination of nitrogen by Kjeldahl's method (p. 164), in 1 gram of the finely powdered material. This nitrogen is contained in the organic matter. It may be calculated into its equivalent in ammonia.

ALKALINE SALTS, ETC.—The sum of the percentages of moisture, organic matter, sand, phosphates, and calcium carbonic should be nearly 100. Any slight deficiency may be due to small quantities of alkaline salts.

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 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 specific gravity 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, ETC.

Partially burnt bones are to be analysed in the same way as fresh bones. 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, collecting the residual sand and carbon on a tared filter, washing with hot water, 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 should be taken for analysis.

A nitrogen determination is unnecessary.

APATITE,

and its numerous varieties, known as phosphorite, osteolite, etc., 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 crucible moistened with oil of vitriol, and the vessel covered with a watch-glass thinly coated with wax, through which a few fine lines have been traced with a point of wood or bone: the platinum crucible is then very slightly warmed and the watch-glass cooled by filling with water. 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 affected as follows:—The precipitate is separated from the paper with a platinum spatula, 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 as $AgCl$. Calculate into its equivalent in $CaCl_2$.

COPROLITES AND MINERAL PHOSPHATES

Coprolites consist chiefly of calcium phosphates 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, but in dissolving the sample a larger quantity of strong hydrochloric acid should be used, and the excess evaporated off: this gets rid of most of the fluorine.

To acquire an accurate knowledge of the value of such phosphates, the phosphorus pentoxide present must be determined. This, with the determination of lime, silica, and volatile matter, will be sufficient for many purposes; but if they are to be used in making superphosphate, the amounts of alumina and oxides of iron must be known.

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 a complete analysis be desired, a determination of carbon dioxide will be necessary; for this purpose see Analysis of Soil (p. *passim*).

MOISTURE AND ORGANIC MATTER are determined together, as in bone-ash.

SILICIOUS MATTER.—1 to 2 grams of the powdered phosphate is digested in a beaker with 30 to 40 c.c. of 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 hydrochloric 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. For this purpose the filtrate and washings are collected in a graduated 200 c.c. flask, allowed to cool, diluted with water to 200 c.c., well mixed, and 100 c.c. drawn off with a pipette.

PHOSPHATES AND LIME.—The phosphorus pentoxide and lime are now determined by the oxalic-acid method (p. 176); or the acetic-acid method (p. 177). When, however, the greatest accuracy is desirable, the "Molybdate Method" should be followed for the determination of the P_2O_5.

For many manures, where extreme accuracy is not required, the following method of determining phosphorus pentoxide is rapid and in most cases of considerable accuracy:—

The Direct Citrate Method for Determining Phosphorus Pentoxide.

This method gives a direct precipitation of ammonium-magnesium phosphate in the presence of salts of iron, aluminium, and calcium. An alkaline solution of ammonium citrate will hold in solution these salts and at the same time allow of the precipitation of ammonium-magnesium phosphate. Whilst the process is not rigidly exact, its inherent errors are in different directions and tend to compensate each other. It affords a quick and ready method for the control of fertilisers, and in the majority of cases the results correspond with those of the molybdate method.

It is essential that silica be removed, also the lime present should be as sulphate, and there must be a considerable excess of magnesia mixture. For most substances heat 5 grams, in a 500 c.c. flask, with 20 c.c. nitric acid, sp. gr. 1·42, and 50 c.c. strong sulphuric acid for half an hour. If much organic matter is present more nitric acid may be needed. Cool, add water, again cool, and make up to 500 c.c. with water. Use 100 c.c. of the solution (= 1 gram of substance). To this add 100 c.c. of citrate solution made as described below, cool if necessary, and then slowly add about 25 c.c. of magnesia mixture, keeping the mixture cool, and seeing that it is very distinctly ammoniacal. Stir for fifteen minutes, and let stand for two hours. Filter off the ammonium-magnesium phosphate, wash with dilute ammonia, dry, heat, and weigh as pyrophosphate.

The citrate solution is made by dissolving 150 grams of citric acid in water, adding ½ litre of 24 per cent. ammonia, and making up to 1½ litres with distilled water.

Another quick method which gives excellent results with care and skill is a volumetric molybdate method.

Volumetric Estimation of Phosphorus Pentoxide.
(Modification of Pemberton's method).

Reagents required.—Ammonium molybdate solution in water, 3 per cent.

Strong nitric acid, sp. gr. 1·42.

Ammonia solution, sp. gr. ·9.

Standard potash solution.—Made of such a strength that 1 c.c. = ·001 P_2O_5, 100 c.c. neutralize 32·65 c.c. acid of normal strength. But the strength of the solution must be found by comparison with a solution of a phosphate of known strength.

Standard nitric acid.—Made by diluting 326·5 c.c. of normal nitric acid to 1 litre. It is of the same strength as the standard KHO.

Indicator.—Alcoholic solution of phenol-phthalein, 1 gram to 100 c.c. 60 per cent. alcohol. Use ½ c.c. for each titration.

Sodium nitrate solution.—1 per cent.

One gram of phosphate rock, or 2 to 3 grams of phosphatic manure, is dissolved in nitric acid and diluted to 250 c.c. Twenty-five c.c. is placed in a beaker and neutralized with ammonia solution, 25 c.c. strong nitric acid added, and the solution diluted to about 180 c.c. Then add 20 c.c. ammonia solution, sp. gr. ·9. The nitric acid and ammonia solution being volumetrically equivalent, this leaves an excess of 5 c.c. of nitric acid after the formation of ammonium nitrate. The solution is warmed to 60° C., and a 3 per cent. solution of ammonium molybdate, warmed to the same temperature, is added slowly with constant stirring. Use 1 c.c. of molybdate solution for each percentage of P_2O_5 present, and about 15 c.c. in excess. Allow to stand for some time to settle in a warm place, not exceeding 55° C. Filter and wash the yellow precipitate with a 1 per cent. solution of sodium nitrate until the washings are neutral to litmus paper. Transfer the filter-paper and contents to the beaker used for the precipitation, and add 50 c.c. standard alkali [1 c.c. $=$ ·001 P_2O_5]. Add $\frac{1}{2}$ c.c. of the phenolphthalein indicator, and titrate back the excess of alkali with standard acid of equivalent strength. The difference between the amounts of standard alkali and acid used, that in the number of c.c. of alkali used for neutralizing the yellow molybdate precipitate, is equal to the number of mg. of P_2O_5 present: *i.e.*, if the amount of material taken were ·1 gram, the number of c.c. neutralized expresses the percentage of P_2O_5.

In H_3PO_4 two atoms of hydrogen, H_2, must be replaced to make the salt neutral to phenolphthalein.

$$\underset{\text{yellow precipitate}}{(NH_4)_6(PO_4)_2(MoO_3)_{24}} + \underset{\text{potassium hydroxide}}{46KHO} = \underset{\text{neutral ammonium phosphate}}{(NH_4)_4(HPO_4)_2} + \\ \underset{\text{ammonium molybdate}}{(NH_4)_2MoO_4} + \underset{\text{potassium molybdate}}{23K_2MoO_4} + 22H_2O$$

Determination of Alumina, Ferric Oxide, etc.

ALUMINA.—The acid solution of coprolite, freed from silica, is precipitated by pure sodium hydroxide solution, 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 hydroxide. 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 hydroxide 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 hydroxide 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 filter-paper 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 hydroxide 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; fairly 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 $Fe_2 2PO_4$.

Another method of determining the alumina, ferric oxide, etc., in a phosphate is as follows, being a modification of the Glaser method:—Dissolve 4 grams of the phosphate in hydrochloric acid, evaporate to complete dryness, and digest with 10 c.c. of strong sulphuric acid with about its own volume of water. Wash into a 200 c.c. flask with alcohol, cool, and make up to the mark. Shake well, allow to stand till clear, filter, evaporate 100 c.c. of the clear filtrate (equal 2 grams of the phosphate) in a large platinum or porcelain crucible till fumes of sulphuric acid are given off strongly, and charring is complete. Wash into a beaker with water, add bromine water and boil, to peroxidize the iron; add a slight excess of ammonia, digest on a water-bath for half an hour, add a very slight excess of acetic acid, then filter, and wash the precipitate with water, dry and weigh. The precipitate consists of ferric oxide, alumina, and phosphoric acid: *i.e.*, phosphates of iron and aluminium.

The filtrate should be boiled with a little ammonia to see if any further precipitate comes down. If so, it should be treated with a slight excess of acetic acid, collected, washed, and added to the main precipitate.

The precipitate, after weighing, is dissolved in a little hydrochloric acid, enough citric acid added to prevent precipitation by ammonia, which is added in excess, and then, slowly, magnesia mixture in excess. The magnesium-ammonium phosphate, after standing at least two hours, is filtered off, washed with ammonia water, dried, burnt, and weighed, and from it the P_2O_5 present determined. The filtrate, from the phosphate, contains the iron and aluminium. The iron is precipitated as sulphide by adding ammonium sulphide, the beaker being covered with a clock-glass and placed on the water-bath for an hour. The black precipitate, of sulphide of iron, is then filtered off and washed with water containing a little ammonium sulphide. The precipitate may be dried and burnt at a strong heat, when it is converted into Fe_2O_3. Or the iron in it may be determined volumetrically. The phosphoric acid and the oxide of iron being now known, the alumina is estimated from the original precipitate by difference.

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.

$$\begin{aligned} &10FeSO_4 + 8H_2SO_4 + K_2Mn_2O_8 \\ &= 5(Fe_23SO_4) + K_2SO_4 + 2NnSO_4 + 8H_2O. \end{aligned}$$

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 1 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 twice at right angles; a few fragments of pure zinc are introduced, and the flask placed in an upright position on a water-bath away from any flame. The open end of the tube is made to dip into a small beaker of distilled water. 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 thiocyanate in a porcelain dish, will give no colour if the reduction of the iron is complete. The flask is then allowed to cool; the water from the beaker will ascend the tube and enter the flask. When perfectly cold, the clear solution is 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* shaken 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 decinormal solution is a convenient strength for the purpose. Dissolve 3·163 grams of dry crystals of pure potassium permanganate in a litre of distilled water; keep in stoppered bottle. It will be seen by the equation, p. 189, since an equivalent of $K_2Mn_2O_8$ has 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 3·163.

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 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.

BASIC SLAG OR BASIC CINDER; PHOSPHATIC GUANOS

Basic slag, or basic cinder, or Thomas powder, is a product of the conversion of cast iron into steel by the basic (Thomas-Gilchrist) process.

The phosphates present are insoluble in water, but when the phosphate is *very finely divided* are largely soluble in water charged with carbon dioxide, in very dilute acids and in various saline solutions. The phosphates seem to be partly there in the form of silico-phosphates and of tetra-calcium phosphate, $Ca_4P_2O_9$: it varies rather widely in quality, and may contain from 11 per cent. to 20 per cent. of P_2O_5.

It also contains silica, oxides of iron and manganese, lime, magnesia, alkalies, and small amounts of sulphates, sulphides, and generally vanadium oxide.

PHOSPHATES.—The total phosphates in basic slag are best determined by taking 1 gram of the finely powdered sample, placing it in a round-bottomed Kjeldahl flask, adding 20 c.c. of strong sulphuric acid, and heating over a gas flame until no more black specks remain. The liquid in the flask is cooled, diluted with distilled water, made up to 500 c.c. in a half-litre flask, and well shaken.

Filter, or allow to settle, and determine the phosphates in 100 c.c. (=·2 gram of the original sample) by the molybdate method (p. 169). The silica is rendered insoluble in this method, and so does not interfere with the phosphoric determination.

CITRATE-SOLUBLE PHOSPHATES IN BASIC SLAG (BOARD OF AGRICULTURE REGULATIONS)

Phosphates Soluble in the Prescribed Citric Acid Solutions.

Five grams of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. Ten grams of pure crystallized citric acid shall be dissolved in water, the volume shall be made up to 500 c.c., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 c.c. of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 c.c. instead of 500 c.c. The bottle shall be at once fitted into a mechanical shaking apparatus, and shall be continuously agitated during thirty minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

Fifty c.c. of the filtrate shall be taken, and the phosphoric acid shall be determined by the molybdate method (p. 169). By far the greater part of the phosphates in basic slag should be soluble in this solvent.

The manurial value of basic slag (Thomas powder), as also of phospho-guanos, is largely dependent on the fineness of the particles. Basic slag or 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. One hundred grams should be shaken in a closed sieve with meshes of these dimensions, and the finer portion weighed.

Sombrero, or Rock Guano, Navassa and Redonda 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 above; but the most satisfactory way of determining the phosphorus pentoxide is by the molybdate method, see p. 169, 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.

SUPERPHOSPHATES

contain considerable quantities of three compounds not found in bone-ash or coprolites, namely, phosphoric acid (H_3PO_4), monocalcic phosphate (CaH_42PO_4), and calcium sulphate. The other constituents of a superphosphate are insoluble calcium phosphate (Ca_32PO_4), dicalcic phosphate ($Ca_2H_22PO_4$), 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 2 grams in the water-oven for about two 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 eighteen to twenty-four hours under the receiver of the air-pump.

ORGANIC MATTER AND COMBINED WATER, OR LOSS ON IGNITION.—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 is placed in a beaker, digested with hydrochloric acid, and slowly evaporated just to dryness, etc., 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. 176, "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 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. The Board of Agriculture directions are as follows:—

PHOSPHATES SOLUBLE IN WATER.—In the case of superphosphates, dissolved bones, and similar substances, 20 grams of the sample shall be continuously agitated for thirty minutes in a litre flask with 800 c.c. of water. The flask shall then be filled to the mark, and again shaken, and the contents shall be filtered. Fifty c.c. of the filtrate shall be boiled with 20 c.c. of concentrated nitric acid, and the phosphoric acid shall be determined by the molybdate method.

In the case of fertilisers in which the proportion of phosphates soluble in water is small, a larger quantity of the filtrate prepared as above shall be taken.

When a mechanical shaker is not available:—

Five grams of the well-mixed sample are taken; ½ a litre of cold 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 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 $\frac{1}{2}$ litre of water is now added, and the bottle shaken at short intervals during three hours. The 100 c.c. equal to 1 gram of the sample, required for the determination of monocalcic phosphate is now filtered off through a good filter-paper. The 100 c.c. are treated according to the directions given for the oxalic-acid method, or the acetic-acid method, omitting, however, the weighing of the calcium oxalate precipitate; or by the molybdate method. 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 = per cent. of x: per cent. of CaH_42PO_4. One part of this monocalcic phosphate corresponds to 1·33 part of "bone-phosphate rendered soluble." 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—"tribasic phosphate made soluble." But as monocalcic phosphate constitutes a part only, and sometimes 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 "tribasic phosphate made soluble" to which it corresponds: 1 part of P_2O_5 corresponds to 2·183 parts of Ca_32PO_4.

The phosphoric acid may be determined by either the oxalic-acid method, or the acetic-acid method, or the molybdate method, and, from the amount of $Mg_2P_2O_7$ obtained, the percentage of so-called "soluble phosphate" ($Ca_3P_2O_8$ rendered soluble), or of phosphoric acid, P_2O_5, calculated.

TRICALCIC PHOSPHATE.—The insoluble phosphates of a superphosphate are regarded as consisting almost entirely of unchanged bone-earth, *i.e.*, tricalcic phosphate, Ca_32PO_4. In order to determine them, the filtrate and washings, obtained from 1 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. 176, 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. 195); then calculate the remainder into tricalcic phosphate thus:—

As eq. of P_2O_5 : eq. of Ca_32PO_4 = residual per cent. of $P_2O_5 : Ca_32PO_4$. But a simpler plan may be adopted; in this the residual percentage is not converted into its equivalent of Ca_32PO_4, but directly entered in the tabulated results.

The total phosphoric acid may be determined by the molybdate method in a nitric acid solution of about ·5 gram of the superphosphate.

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. An ammoniacal 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 neutralize with ammonia to exact neutrality, using coralline as an indicator. Make up the volume to 2 litres, and test its specific gravity, which should be 1·09 at 20° C. To each litre of this neutral solution add 50 c.c. of ammonia, specific gravity ·92. 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 thirty 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 "molybdate method," or by the "oxalic-acid method." Calculate the amount found into $Ca_3 2PO_4$, add this to the "tribasic-phosphate made soluble," and subtract the sum from the total phosphate; the remainder represents the amount of "reduced" or "citrate-soluble" phosphate expressed as $Ca_3 2PO_4$.

The CITRATE-SOLUBLE phosphate in manures is rather an indefinite determination, as different processes are in use for its estimation, and these give different results, which are dependent not only on the nature and strength of the citrate solution used, but also on the temperature and time of the maceration, on the amount of agitation, and on the nature of the original natural phosphate.

The solutions chiefly used are (1) a neutral solution of ammonium citrate, specific gravity 1·09; (2) an alkaline solution of ammonium citrate, as given above; (3) an acid solution of ammonium citrate containing 3 per cent. of citric acid as ammonium citrate and 2 per cent. as free citric acid; (4) a 2 per cent. solution of citric acid; and (5) a 1 per cent. solution of citric acid.

For superphosphates, the ammoniacal ammonium citrate solution is generally to be recommended with digestion either for half an hour at 65° C., or at the ordinary temperature for fifteen to eighteen hours with occasional agitation. It is better to determine the phosphoric acid remaining undissolved rather than that which goes into solution, as, if the amount is small, it is likely to be underestimated if precipitated directly from the ammonium citrate solution

For basic slag, the 2 per cent. solution of citric acid is generally used. (See p. 192).

For the available phosphoric acid in soils, the 1 per cent. solution of citric acid is the best. (See p. *passim*).

In stating the results of an analysis, the method adopted should always be indicated.

NITROGEN.—If the superphosphate be a bone superphosphate or made partly from bones, a nitrogen determination is made by Kjeldahl's method, using 1 or 2 grams of the manure. Superphosphates made entirely from bone-ash, apatite, coprolites, etc., 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 superphosphates is driven off, save, indeed, the constitutional water of the monocalcic phosphate, and of the phosphoric acid.

MONOCALCIC PHOSPHATE, ETC.—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. Hot water should not 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.

$Mg_2P_2O_7$ × 0·6379 = P_2O_5
" × 1·3939 = $Ca_3P_2O_8$
" × 1·0515 = $CaH_4P_2O_8$
$Ca_3P_2O_8$ × 0·4578 = P_2O_5
" × 0·7544 = $CaH_4P_2O_8$
P_2O_5 × 2·1844 = $Ca_3P_2O_8$
" × 1·6484 = $CaH_4P_2O_8$
$CaH_4P_2O_8$ × 1·3251 = $Ca_3P_2O_8$

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		15·46
COMBINED WATER AND ORGANIC MATTER . .		8·62
TOTAL PHOSPHORUS PENTOXIDE,[1] including—		
"Soluble" P_2O_5	12·06	
"Reduced" P_2O_5	1·06	
"Insoluble" P_2O_5	1·14	
	——	14·26
CALCIUM SULPHATE, $CaSO_4$		43·50
ALKALINE SALTS, etc., undetermined . . .		2·62
SILICIOUS MATTER		5·72

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[1] Often called "Phosphoric acid" or "Phosphoric anhydride."

The more common way of tabulating the analytical results is given below:—

Moisture, or loss at 100° C.	15·46
Organic Matter and Combined Water	8·62
Monocalcic Phosphate, $CaH_4P_2O_8$, equal to 26·33 *tribasic phosphate made soluble*	19·80
Tricalcic Phosphate, $Ca_3P_2O_8$, of which 2·31 was "reduced" phosphates	4·81
Calcium Sulphate, $CaSO_4$	43·50
Alkaline Salts, etc., undetermined	2·09
Silicious Matter	5·72
	100·00

BASIC SUPERPHOSPHATE

This manure is prepared by mixing finely ground lime with mineral superphosphate in suitable proportions, to remove the acid character of the superphosphate and render it slightly alkaline. It is specially adapted to soils poor in lime, and rather occupies an intermediate position between superphosphate and basic slag. It is in a dry powdery state, much less dense, and more easily distributed evenly than basic slag. Although it contains no phosphate soluble in water, its precipitated phosphate is readily soluble in very dilute acids, *e.g.*, $\frac{1}{10}$ per cent. solution of citric acid. It contains about 11·5 per cent. of P_2O_5.

Total Phosphorus Pentoxide.—This should be determined in about 1 gram of the manure if the oxalic-acid method or acetic-acid method be used, or in ·5 gram if the molybdate method be used.

Phosphorus Pentoxide Soluble in ·1 per cent. citric acid.—One gram of the finely powdered manure is placed in a bottle with 1 litre of water in which 1 gram of citric acid has been dissolved. This is allowed to stand with occasional shaking for twenty-four hours, then filtered, and the residue and filter washed with a little distilled water, the filtrate evaporated to about 200 c.c., and in this the phosphorus pentoxide estimated in the usual way. Nearly the whole of the phosphate should be soluble in this dilute acid.

BEET MANURE. TURNIP MANURE. CORN AND GRASS MANURE. PHOSPHO-GUANO. SULPHATED GUANO. DISSOLVED GUANO, ETC.

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 determined by the modified Kjeldahl's process for total nitrogen, p. 169. The potassium is determined as follows:—Ignite gently 10 grams of the sample: heat with 10 c.c. of strong hydrochloric acid for a short time. Dilute to about 300 c.c. with hot water, boil, filter into a 500 c.c. flask, and whilst hot add a slight excess of powdered barium hydrate. Cool, make up to 500 c.c. with water, and filter.

Two hundred and fifty c.c. of the filtrate are made alkaline with ammonia, and a slight excess of ammonium carbonate added. Bring the solution to the boil and add a little ammonium oxalate, cool; make up to 500 c.c., and filter. Take 100 c.c. of this solution, evaporate to dryness in a platinum dish, gently ignite to drive off ammonium salts, extract the residue with hot water, filter if necessary, and determine the potash as described on p. 158.

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 paragraphs 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 p. 160. 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.

$BaSO_4 \times \cdot343 = SO_3$
$SO_3 \times 1\cdot7 = CaSO_4$
$SO_3 \times 2\cdot15 = CaSO_4, 2H_2O.$

PERUVIAN GUANO

This valuable manure consists chiefly of the more or less altered excreta and carcases of sea-birds. It contains a large quantity of 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 poorer in nitrogen compounds and more variable in composition than the old Chinca 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. 180. 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.

Most of the Peruvian guano now imported contains a high percentage of "natural" sand.

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 determination 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, 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 may be determined as in bone-dust.

ALKALIES.—These are for commercial purposes determined by difference; any phosphorus pentoxide they contain should, however, be estimated, as it is of equal importance with that of soluble monocalcic phosphate.

PHOSPHORUS PENTOXIDE IN ALKALIES. — Five grams are extracted with cold water and treated exactly as for soluble phosphate in superphosphate, p. 195.

TOTAL NITROGEN.—This is determined in 1 gram, by Kjeldahl's method for total nitrogen, p. 164 or p. 169.

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 Kjeldahl flask introduce 1 gram of the guano, a little water, and 2 grams of calcined magnesia. Attach it to the condensing apparatus and receiver containing 10 c.c. of standard sulphuric acid. After boiling for some time, all the ammonia present in the guano will have been disengaged and then absorbed by the acid in the receiver, which is then titrated with standard alkali solution in the usual way (p. 162).

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 the modification of Kjeldahl's process (p. 169).

We then proceed to the determination of the nitrogen existing as nitrate. For this purpose a modification of the Ulsch method may be used. One gram of the manure is placed in a 500 c.c. Erlenmeyer flask with 50 c.c. water, 10 grams of "reduced iron," and 20 c.c. of sulphuric acid, specific gravity, 1·35. Through the stopper of the flask is passed a thistle tube, the lower end of which is plugged with glass wool. The thistle is then partly filled with glass beads. After adding the acid, allow the reaction to go on without heating until effervescence has ceased. Then heat to boiling for five minutes, remove the flask from the flame, and rinse any liquid from the beads back into the flask with water. Boil again for three minutes, and again rinse the beads. The nitrogen of the nitrate is now in the form of ammonium sulphate. Cool, wash into a distilling flask, add a little granulated zinc, make alkaline with caustic soda, and distil into 10 c.c. of standard acid. The ammonia obtained will be that present in the manure both as ammonia and derived from the nitrate: calculate into nitrogen, and from the total nitrogen deduct that present as ammonia, the remainder represents nitric nitrogen. The nitric nitrogen may also be determined by Schloesing's method, p. 213; or by the indigo method, p. *passim*, with proper precautions.

Gravimetric Uranium Method for Phosphates.

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 1 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 for Phosphates.

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 molybdate method. Before using this nitric acid solution, however, the free nitric acid must be removed by adding a little sodium hydroxide 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 the 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 water-bath 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 tile. 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, etc., 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 except 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. The uranium solution must be standardized by means of repeated trials, and 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, etc., 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, OR LIME

The proportion of real sodium or potassium nitrate in a sample is often 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 should be very carefully prepared.

MOISTURE is determined by heating about 3 grams to 120° 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 neutral 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 16·997 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 $\frac{1}{10000}$ the molecular weight of Cl = ·003545 gram, or of NaCl = ·00585 gram, etc. Titrate with pure sodium chloride to find the exact strength.

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. The testing should be carried out in a white porcelain dish.

LIME is determined in the usual way, in the filtered solution from 7 grams in the case of sodium or potassium nitrates.

Since the commercial nitrate of lime contains free lime it should be dissolved with the aid of dilute hydrochloric acid for this determination, taking about ·25 gram of the substance.

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.

Determination of Nitrogen in Nitrates.

Several methods are available.

ULSCH'S METHOD, p. 207, using ·5 gram of substance, gives good results.

SCHLOESING'S METHOD.—In this the nitrate is decomposed by means of strong sulphuric acid and ferrous sulphate, with the formation of nitric oxide, which is measured.

$$2NaNO_3+5H_2SO_4+6FeSO_4 \\ = 3Fe_2 3SO_4+2NaHSO_4+4H_2O+2NO.$$

The apparatus used, when a sample of nitrate of soda is being examined, may consist of a round-bottomed

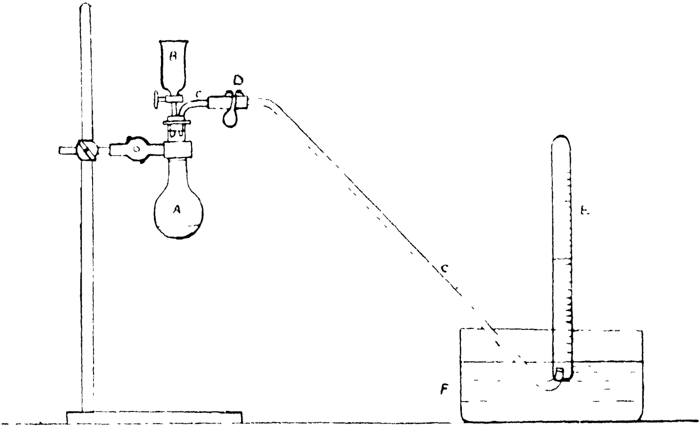

FIG. 23.

flask, A, of about 175 c.c. capacity, fitted with an india-rubber stopper with two holes. Through one hole passes a thistle-headed funnel, B, through the other the delivery-tube for the gas, C: this is in two parts, joined by a short piece of indiarubber tubing fitted with a pinchcock, D. The trough, F, contains water.

Prepare a 1 per cent. solution of pure nitrate of soda, and a 4 per cent. solution of ferrous sulphate slightly acidified with sulphuric acid. Make a 1 per cent. solution of the sample under examination. Measure out 20 c.c. of the pure nitrate solution with a pipette and introduce it to the flask, washing it in with 20 c.c. of water. Boil the liquid in the flask until it is reduced to about 20 c.c. in volume in order to expel the air. Close the indiarubber joint at D, and add 25 c.c. of the ferrous sulphate solution. Place the calibrated measuring-tube, E, over the end of the delivery-tube, add, through the funnel, 50 c.c. of strong sulphuric acid slowly and cautiously, at the same time opening the delivery-tube at D. Reaction at once begins with the evolution of nitric oxide; heat the flask at first gently, and when no more gas is given off, boil briskly for a minute. Remove the eudiometer, allow the gas to cool, and read off the volume: this is the nitric oxide obtained, under these conditions, from ·2 gram of pure sodium nitrate.

Wash out the apparatus, and repeat the operation with 20 c.c. of the sample to be tested. The two operations are to be conducted under the same conditions as nearly as possible, when no corrections for temperature and pressure will be required. With the pure nitrate x cubic centimetres of gas were obtained, with the impure sample y cubic centimetres: then $100\,y \div x =$ percentage of pure nitrate in the sample under examination.

Determination of Nitric Nitrogen by means of a Nitrometer.

A suitable apparatus is a Lunge's Nitrometer, of the form shown in Fig. 24.

A is a calibrated tube graduated to $\frac{1}{10}$ c.c., having a three-way tap, c, which connects it with a funnel or cup, *d*, and with a thick-walled capillary tube, *e*, which should be bent downwards. The calibrated tube A is connected below with a stout-walled indiarubber tube, to which is attached a straight tube, B, of the same diameter as A, but not calibrated. The cup *d* is used to introduce liquids into A and the tube *e* to let off or to introduce gases into A. The estimation of nitric nitrogen is made as follows:—The apparatus is filled about ⅔ full of mercury; turn the tap *c* so as to open A to the air; raise the tube B until mercury entirely fills A, and then close the tap. Return B to the same level as A. Dissolve 1 gram of nitrate of soda in water to 10 c.c.; take 1 c.c. of this solution and place in the cup, and draw it into A by opening the stopcock *c*; take care that no air gets access. Now put into the cup 2 c.c. of pure strong sulphuric acid, and draw this slowly into the nitrometer; repeat this till about 8 or 9 c.c. of sulphuric acid have been added. Any gas given off at once is CO_2. If chlorides are present HCl will be given off rather quickly. These gases are removed from the nitrometer by raising the reservoir of mercury B and opening the tap. The tube A is then unclamped, slightly inclined, and shaken vigorously with a rotatory motion so as to bring the surface of the mercury, broken into a number of globules, in contact with the nitric acid liberated by the action of the sulphuric acid on the nitrate. Shake, with slight intervals, for about ten minutes, when all the nitrogen

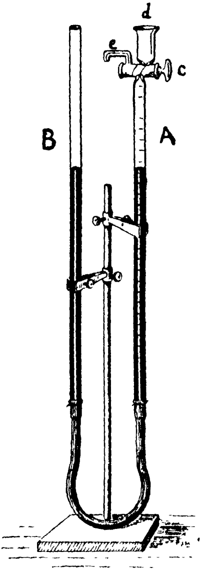

Fig. 24.

in the nitric acid will have been converted into nitric oxide gas, NO. Allow the apparatus to cool for about half an hour; adjust the liquids in the two tubes to the same level, allowing that the mercury has about seven times the specific gravity of the sulphuric acid. Read off the volume of the gas, and the barometer, and note the temperature of the room at the time. Reduce the volume of gas to the standard temperature and pressure, 0° C. and 760 mm. Bar. by the following formula:—

$$V' = \frac{V \times P}{760\,(1 + \cdot003665t)}$$

V' = Volume of Gas at 0° C. and 760 mm. Bar.
V = Observed volume of Gas in c.c.
P = Observed pressure in mm. of mercurial barometer.
t = Temperature in degrees Centigrade.

For example, ·1 gram of sodium nitrate gave 27 c.c. of NO gas at 14° C. and 750 mm. Bar.

$$V' = \frac{27 \times 750}{760\,(1 + \cdot003665 \times 14)} = \frac{20250}{760 \times 1{\cdot}05131} = \frac{20250}{798{\cdot}9956} = 25{\cdot}34.$$

i.e., 25·34 c.c. NO at 0° C. and 760 mm.

1 c.c. NO at 0° and 760 mm. = ·003805 gram of $NaNO_3$.

25·34 × ·003805 = ·0964 gram $NaNO_3$ in ·1 gram of the sample taken = 96·4 per cent. of pure sodium nitrate.

1 c.c. NO at 0° C. and 760 mm. Bar. = ·001343 gram NO
1 c.c. NO at 0° C. and 760 mm. Bar. = ·003805 gram $NaNO_3$
1 c.c. NO at 0° C. and 760 mm Bar. = ·004521 gram KNO_3
1 c.c. NO at 0° C. and 760 mm. Bar. = ·000627 gram N.

Nitric nitrogen may also be determined by the indigo method, p. *passim.*

Determination of Sodium Perchlorate in Sodium Nitrate.

Heat 5 grams of the dried sample with 7·5 grams of pure slaked lime in a covered platinum crucible over a Bunsen burner for a quarter of an hour. The mass is then extracted with water and the residue washed, making up to about 150 c.c. of filtrate; this is exactly neutralized with dilute nitric acid, and the chloride present determined by titration with silver nitrate. From the percentage of chlorine found, deduct that originally present as chloride, and calculate the remaining chlorine into perchlorate.

$Cl = 35{\cdot}5, NaCl = 58{\cdot}5, NaClO_4 = 122{\cdot}5, KClO_4 = 138{\cdot}6.$

CALCIUM CYANAMIDE (NITROLIM).

The nitrogen in this may be determined in ·5 gram by Kjeldahl's method.

The lime may be determined in about ·5 gram, after solution in dilute hydrochloric acid, in the usual way.

POTASH SALTS, KAINITE, SYLVINITE, ETC.

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 suited for the analysis of the commercial sulphate and the "muriate."

The sample must be powdered and carefully mixed before analysis.

The following determinations should be made:—

MOISTURE in 2 or 3 grams in the usual way.

LOSS ON IGNITION in 3 to 4 grams heated very gently and carefully over a Bunsen burner for five 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.

The official (Board of Agriculture) process for potash determinations is as follows:—

DETERMINATION OF POTASH

(*a*) *Muriate of Potash free from Sulphates.*—A weighed portion of the sample (about 5 grams in the case of concentrated muriate of potash, or 10 grams in the case of low-grade muriate) shall be dissolved in water, the solution shall be filtered if necessary and made up to 500 c.c. To 50 c.c. of the solution placed in a porcelain basin, a few drops of hydrochloric acid shall be added, and also 10 c.c. or 20 c.c. (according to whether the portion weighed was 5 grams or 10 grams) of a solution of platinum chloride containing 10 grams of platinum per 100 c.c. After evaporation to a syrupy consistency on a water-bath, the contents of the basin shall be allowed to cool and shall then be treated with alcohol of specific gravity 0·864, being washed by decantation until the alcohol is colourless. The washings shall be passed through a weighed or counterpoised filter-paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100° C., and weighed.

The precipitate is to be regarded at K_2PtCl_6.

(*b*) *Salts of Potash containing Sulphates.*—A weighed portion of the sample (about 5 grams in the case of concentrated sulphate of potash or 10 grams in the case of kainite or other low-grade salts) shall be boiled with 20 c.c. of hydrochloric acid and 300 c.c. of water in a half-litre flask. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid (without filtration) shall be cooled and made up to 500 c.c. A portion shall then be filtered, and 50 c.c. of the filtrate shall be treated as above described, 10 c.c. or 20 c.c. of platinum chloride solution, as the case may be, being used.

(*c*) *Potash in Guanos, and Mixed Fertilisers.*—Ten grams of the sample shall be gently ignited in order to char organic matter, if present, and shall then be heated for ten minutes with 10 c.c. of concentrated hydrochloric acid, and finally boiled with 300 c.c. of water. The liquid shall be filtered into a half-litre flask, raised to the boiling-point, and a slight excess of powdered barium hydrate shall be added. The contents of the flask shall be cooled, made up to 500 c.c., and filtered. Of the filtrate, 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate, and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 c.c., and filtered. Of the filtrate, 100 c.c. are to be evaporated in a platinum dish, and the residue heated, first in the air-bath and then very gently over a low flame, till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be treated with hot water, filtered if necessary, and the potash shall be determined in the filtrate as above.

$$K_2PtCl_6 \times \cdot 3067 = 2KCl$$
$$K_2PtCl_6 \times \cdot 1938 = K_2O$$
$$K_2PtCl_6 \times \cdot 3584 = K_2SO_4.$$

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 to 150 c.c., made ammoniacal, cooled, 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. 157. 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. 211.

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.

$CaO \times 1{\cdot}7857 = CaCO_3$ $MgO \times 3 = MgSO_4$
$CaO \times 2{\cdot}4286 = CaSO_4$ $MgO \times 2{\cdot}375 = MgCl_2$

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.

COMMON SALT

The amount of sodium chloride is determined volumetrically, p. 211. 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. 212-216.

AMMONIUM SULPHATE. AMMONIACAL SALTS

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, alkaline salts, 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 2 grams in the water-oven in the usual way.

NON-VOLATILE MATTERS are estimated by the residue left on ignition of 2 or 3 grams. Ferric oxide, if present, remains as a dark red powder : sodium salts as a nearly white fusible residue.

AMMONIA.—This is determined by distilling 0·5 gram with excess of pure caustic soda and collecting the ammonia in standard acid, and titrating the excess with standard alkali. Take care that the amount of substance taken does not contain more ammonia than the equivalent of the acid in which it is collected. The ammonia found may be calculated into sulphate $(NH_4)_2SO_4$.

SOOT

Ordinary soot consists mainly of finely divided carbon; it contains, besides, a small quantity of ammonium sulphate, ammonium chloride, and complex nitrogenous compounds, with various inorganic substances, such as constituents of the fuel-ash or fragments of broken masonry, and small quantities of arsenic; 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 Kjeldahl's determination is made with 1 or 2 grams. 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.

§ iii. 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 a clearer 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 25 mm.
4. Small stones, remaining on a sieve of 10 mm.
5. Gravel, remaining on a sieve of 3 mm.
6. Gravelly sand, remaining on a sieve of 1 mm.
7. Coarse sand: ·2 – 1· mm.
8. Fine sand: ·04 – ·2 mm.
9. Silt: ·01 – ·04 mm.
10. Fine silt: ·004 – ·01 mm.
11. Finest silt: ·002 – ·004.
12. Clay: under ·002 mm.
13. Organic matter.

It should be noted that the eight 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 quantitative 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 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. 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.

At Rothamsted a steel box, without top or bottom, 6 inches square in section and 9 inches deep, is used; the sides are wedge-shaped, $\frac{3}{4}$ inch thick at top, tapering to a cutting edge at bottom. The surface of the soil is raked and gently beaten level, the box placed in position and driven down with a heavy wooden rammer till the top of the box is level with the soil. The soil enclosed by the box is then carefully dug and scraped out, and placed in a bag or box; two or three samples are taken from the same field and mixed. If samples of the subsoil are required, the box is left in position after its contents are removed, the surrounding soil is dug away to the 9-inch level and the box then rammed down another 9 inches, and its contents removed. The process can be repeated to any required depth.

On soils which do not contain many stones, samples may be taken with an auger. A convenient tool is a cylindrical steel auger (Fig. 25), 2 inches internal diameter, about $\frac{1}{16}$ inch thick, and 12 inches deep, with a slot $\frac{3}{4}$ inch wide running from top to bottom. The edges of the slot and the lower edge of the cylinder are sharpened; a handle with a wooden cross-bar is fitted to the top of the cylinder. To take a sample, the auger is gently forced into the soil with a twisting motion to the required depth, when the tool is withdrawn and the core scraped out. Ten or a dozen cores should be taken from the same field. By using a tool with a longer handle, samples of subsoil can be obtained. The auger cannot be satisfactorily used when the soil is dry.

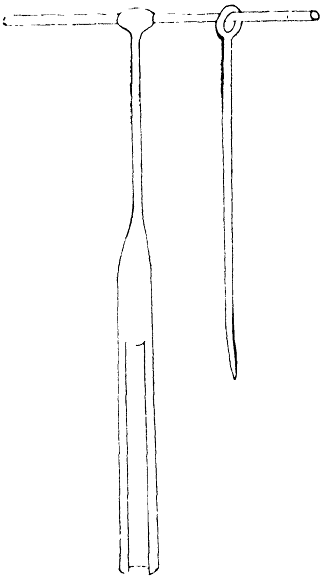
FIG. 25.

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, and of total nitrogen, p. 164. 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 a 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 25 mm. are picked out, weighed, then dried in the water-oven, and again weighed. Similarly those not passing a sieve 10 mm. mesh. 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 are sifted through a wire sieve, the meshes of which

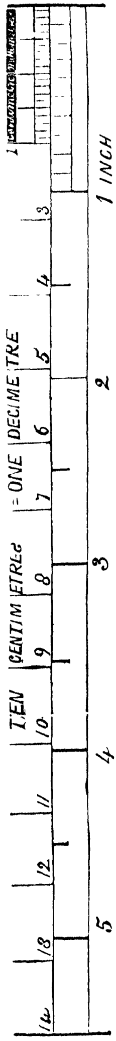

FIG. 26.

have a diameter of 3 mm.,[1] 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 basin 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.

That soil which passes the 3 mm. sieve is fine earth.

The subsequent mechanical analysis of soils divides the fine earth into a series of fractions consisting of particles of which the size is approximately known. The coarser particles can be separated by sieves, but the finer ones by their relative powers of remaining suspended in water.

The methods in use depend on two principles. In one, the hydraulic method, followed by Hilgard, Schöene, and Nöbel, the soil is washed by successive currents of water of varying velocity. In the other method, the sedimentation method, followed by Osborne, Knop, Schloesing, and Hall, the soil is suspended in water and allowed to stand, the separation being effected either by the times required for the particles to settle down through a fixed distance, or by the distance fallen in a given time.

The hydraulic method requires special apparatus.

The coarser the grains of which a sand is composed the more rapid the current of water required to move

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[1] The scale at the side of p. 227 will enable the analyst to substitute the corresponding English measures of length for those of the metric system given in the text.

the particles. With a diameter of ·5 mm., the velocity of current required is 66 mm. per second; a velocity of 32 mm. will move particles ·3 mm. in diameter; and velocities of 16, 8, 4, 2, 1, and ·5 mm. per second correspond, respectively, with grains of the diameters ·16, ·12, ·072, ·047, ·036, ·025 mm.

One form of the apparatus employed in carrying out this operation is represented in Fig. 27. 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 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

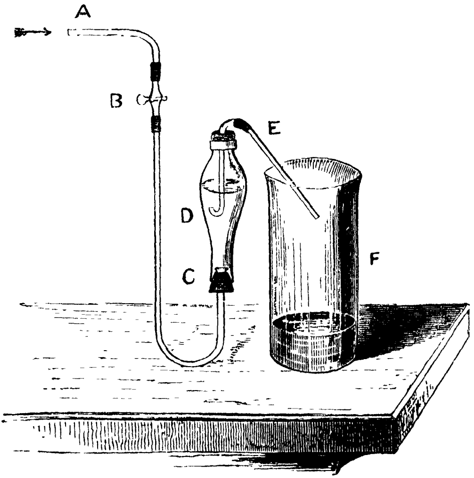

FIG. 27.

"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 to take 30 grams of fine soil, boil it with 150 c.c. of water for half an hour; the boiled mixture of soil and water is then poured into the vessel D, and 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 continuous thread into the beaker F. When the difference of water-level in the reservoir and the separator is about 57 cm., and the distance between the inflow and outflow in the separator is 13 cm., 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 a 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 cm., 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 cm. across its broadest part, and having an extreme length of 22 cm., 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 $\frac{4}{5}$ full.

The following sedimentation method, due to A. D. Hall, is one of the best, though it requires about three weeks for its completion and the evaporation of about twenty litres of water.

Ten grams of the air-dry fine earth are treated with 100 c.c. of $\frac{N}{5}$ hydrochloric acid, in a beaker or basin, the acid being renewed if not sufficient to dissolve all the calcium carbonate present. The soil is rubbed up for some time with a soft pestle, made of an indiarubber bung fixed on the end of a glass rod; the rubbing is continued until all lumps of clay are broken up. This pestling may be made easier by the aid of a small water-turbine. The undissolved material is thoroughly washed until free from acid, collected on a filter, dried, and weighed, to ascertain the loss of dissolved matter (carbonates and some humates) and hygroscopic water. The soil is then transferred to a sedimenting vessel and rubbed up with water containing ammonia, which completes the dissolution of the humates. A lipped beaker, about 10 cm. high and 7 cm. in diameter, with marks 7·5 cm. and 8·5 cm. from the bottom, is used. Into this beaker the soil is washed with water, through two sieves; the first having round holes 1 mm. in diameter, and the second being of woven brass wire cloth, 100 meshes to the inch. The soil material arrested by the sieves is dried, ignited, and weighed. To the soil and water in the beaker about 2 c.c. of strong ammonia is added, water added to the top mark, and the whole left undisturbed for twenty-four hours. The turbid liquid is then decanted from the sediment, which is rubbed up again with dilute ammonia water with the rubber pestle, water added to the mark, and again allowed to stand for twenty-four hours. This process is repeated day by day until the supernatant liquid is clear after twenty-four hours' standing: that is, until all particles which will not fall 8·5 cm. in twenty-four hours are removed. Usually, about eight decantations are sufficient; but with some soils double this number may be required.

The turbid liquid poured off is evaporated in a tared porcelain basin, the residue dried in a steam-oven, weighed, ignited, and again weighed; it is "clay."

The sediment remaining in the beaker is worked up again in a similar way, distilled water only being used, and the beaker filled up to the depth of 7·5 cm. This is left to stand two hours five minutes, and the water with its suspended matter then poured off; the process is repeated until all the material remaining suspended for one hundred and twenty-five minutes is removed. The decanted liquid is evaporated, the residue dried in a steam-oven, weighed, ignited, and reweighed.

A third series of decantations follows with a water column 7·5 cm. in height, and the time of settlement of 12·5 minutes. Finally, a series of decantations with a water column 7·5 cm. and a time of settlement of seventy-five seconds.

The fine earth is thus divided into seven fractions, the two coarsest by sieves, and the five finest by settlement from water.

The approximate size of the particles separated by following this method is as under:—

	Diameter in Millimetres. Maximum.	Diameter in Millimetres. Minimum.
First Sieve (Fine Gravel)	3·0	1·0
Second Sieve (Coarse Sand)	1·0	·2
First Sediment (Fine Sand)	·2	·04
Second Sediment (Silt)	·04	·01
Third Sediment (Fine Silt)	·01	·004
Fourth Sediment (Finest Silt)	·004	·002
"Clay"	·002	——

The height of water column and times of settlement here used are purely arbitrary, and may be varied at will to secure fractions of other and intermediate sizes of particles, the size being determined by actual measurement under a microscope. Worked as above, it was found that the fractions contained some smaller particles than belonged to their sediment, but that the bulk was within the specified limits.

The groups of particles obtained in the mechanical analysis of a soil do not possess any definite chemical individuality; but in the coarser-grained fractions quartz predominates, mixed with increasing quantities of hydrated aluminium silicate and ferric oxide, as the size of the particles becomes less. Even the finest sediment contains some free silica (quartz), very commonly about 10 per cent., sometimes more.

The results of the mechanical analyses of several Rothamsted soils are given in the *Journal of the Chemical Society*, 1904, pp. 950-963.

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 all 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 subsequently 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 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.)

Other physical characters of soil may be determined by experiment. Such are the amounts of moisture which 50 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, etc., 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 3 mm. 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 on 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; and available phosphorus pentoxide and potash by the citric-acid method. Qualitative testings are likewise made for sulphur trioxide, chlorine, nitrogen pentoxide, and iron in the ferrous condition.

ORGANIC MATTER AND COMBINED WATER.—Four grams of the prepared fine earth are heated gradually to low redness, and thus maintained till all blackening has disappeared; the residue, when cold, is moistened with ammonium carbonate, again dried and heated for a minute or two, in order to drive off excess of ammoniacal salt, and then weighed. The loss is organic matter and combined water.

SOLUBLE SALTS.—Ten 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 an excessive and probably 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. The total nitrogen should be determined by Kjeldahl's method (p. 164), using 10 to 20 grams of soil. 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 disk of copper-gauze laid over the opening, and on this two disks 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 indiarubber 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 Schloesing's method, given on p. 213. If there be any ammonia-salts present they must first be removed by distillation with sodium hydroxide.

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 p. 207).

PHOSPHORUS PENTOXIDE.—About 10 grams of the soil are employed for the determination of the phosphorus pentoxide and the potash; also for sand and insoluble silicates and for lime. 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 on the sand-bath at a temperature rather above 100° C., to render the whole of the silica insoluble. With some soils it is necessary to again moisten with strong hydrochloric acid, and again evaporate and heat. The mass, after cooling, is to be moistened with concentrated hydrochloric acid and allowed to stand fifteen minutes or longer; a little water is then added and the whole heated to the boiling-point. If the residue be grey, or white, or black, through the presence of much carbon, the liquid may be filtered and the residue well washed on the paper with hot water. If the residue be red, it must be again boiled with hydrochloric acid. 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 boiled with a few drops of strong nitric acid, precipitated by a slight excess of ammonia, the precipitate washed by decantation with hot water and then collected on a large filter-paper. In the filtrate the lime, magnesia, and potash are contained; in the precipitate the phosphorus pentoxide. To estimate the latter, the precipitate is redissolved in a small quantity of nitric acid, and the molybdate 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.

Molybdate 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 small.

To the solution about 30 c.c. of an acidified solution of ammonium molybdate are added; the mixture is heated on a steamer or water-bath to 70° C. for fifteen minutes; cooled, washed, first by decantation, and then on the filter, with 1 per cent. nitric acid solution. 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, after washing with 1 per cent. nitric acid, is treated on the filter with just enough cold 2 per cent. solution of ammonia to dissolve it completely; the clear solution, which contains the whole of the phosphorus pentoxide, is cooled, a few drops of citric acid are added, and finally some magnesia mixture. After twelve hours the precipitate of ammonium-magnesium phosphate is collected and treated exactly as before described, p. 156. 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.

For very small quantities of phosphoric acid the following modification of the molybdic-acid method may be adopted with advantage. Concentrate to a small bulk the nitric acid solution (see page 239) which contains the phosphoric acid. When cold, add excess of the acid ammonium molybdate solution and allow the mixture to stand *in the cold* for forty-eight 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 the contents of the capsule just to dryness, and dry till constant in the water-oven. One part of the residue will contain ·035 part of P_2O_5. Or the volumetric molybdate method, p. 184, may be used.

LIME.—The filtrate from the ammonia precipitate (see page 239, line 10) is boiled and treated with *pure* ammonium oxalate as long as a precipitate is produced; the whole is filtered; the lime is determined by collecting this precipitate of calcium oxalate, washing, drying, igniting, and weighing as carbonate, or as oxide, with the usual precautions.

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* loses 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 filter, and washed with alcohol till the washings are colourless. The precipitate is dissolved in hot water, the solution and washings collected in a weighed platinum dish, evaporated to dryness, dried in the water-oven, and weighed. For its composition see p. 159. The potassium in a soil should be calculated into K_2O.

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.

AVAILABLE PHOSPHORIC ACID AND POTASH

For the "fractional analysis" of a soil, solvents which have been used are: a saturated solution of carbon dioxide in water, dilute acetic acid, ammonium oxalate solution, dilute hydrochloric acid, and others. A dilute 1 per cent. solution of citric acid is found to give the best results for estimating the readily available potash and phosphoric acid in soils ; the method is due to Dr Bernard Dyer.

A weight of air-dried fine earth corresponding to 200 grams of the completely dried soil is placed in a Winchester quart bottle with two litres of distilled water in which are dissolved 20 grams of pure citric acid. The bottle used should be one in which strong acid has been previously stored, so as to minimise the possibility of dissolving potash from the glass, and should be filled with water and allowed to rest for some days, and then thoroughly rinsed before use.

The mixture of soil and dilute citric acid is kept in the bottle for seven days, with frequent shaking as often as possible after the soil has settled down. After the seven days' treatment the solution is filtered, and two portions of 500 c.c. each, representing 50 grams of soil, evaporated to dryness in a platinum basin, gently incinerated at a low temperature to get rid of the citric acid and other organic matters.

The residues are treated with hydrochloric acid, evaporated, heated to 105° C. to render silica insoluble, again dissolved in a little acid, and filtered. The portion in which potash is determined is taken up with dilute hydrochloric acid, that in which phosphoric acid is determined is taken up with dilute nitric acid.

For the determination of the PHOSPHORIC ACID, the nitric acid solution, which must be of small bulk, say 30 c.c., is treated in the *cold* with an equal volume of a solution of ammonium molybdate in nitric acid, containing 60 grams of molybdic acid to the litre. After standing forty-eight hours, the liquid is filtered, the precipitate washed, first with ammonium nitrate solution, then with dilute nitric acid, and finally with distilled water in small doses, till free from excess of acid. The yellow precipitate, ammonium phosphomolybdate, is then dissolved in ammonia into a tared basin, evaporated to dryness on a water-bath, and dried until the weight is constant in a water-oven. It contains 3·5 per cent. of its weight of phosphorus pentoxide.

This method of determining very small quantities of phosphoric acid gives more accurate results than by conversion into ammonium magnesium phosphate, if the conditions are closely observed; the solution must not be hot, or molybdic acid may crystallize out; gentle warming up to 35° C. hastens the precipitation, but must be done with care.

For the estimation of the POTASH, to the hydrochloric acid solution is added 5 to 10 c.c. of a solution of platinum chloride containing 5 milligrams of platinum per c.c. and the whole *slowly* evaporated on a water-bath until *nearly* dry. The precipitate is washed on to a filter-paper with a solution of platinum chloride, and afterwards with alcohol. The precipitate is dissolved off the filter-paper with a little hot water into a tared basin, evaporated, dried, and weighed as K_2PtCl_6.

This process can be used for determining small quantities of potash in the presence of a large excess of iron, aluminium, calcium and magnesium salts.

When a soil contains very much calcium or magnesium carbonate, this treatment with 1 per cent. citric acid gives rather uncertain results; but in the majority of cases it may be regarded as giving valuable information as to the amount of potassium and phosphorus in the soil which is immediately available as plant food.

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 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 oxide.

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 ammonia containing 5 per cent. NH_3. The liquid is filtered through glass wool after four 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. 238. 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. 238); 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. 238). 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 hydroxide. 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 hydroxide 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 hydroxide 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 rather strong sulphuric acid till dissolved, and a determination of iron in the solution is made according to the directions previously given at p. 189. The alumina will then be found by difference. The phosphorus pentoxide is present in the precipitate with the ferric oxide and alumina.

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 bromine 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, reprecipitated with ammonia, filtered, washed, and redissolved in dilute sulphuric acid; in this solution the ferric oxide is determined by the volumetric method: the difference is alumina.

MANGANESE OXIDE.—The filtrate and washings from the above are concentrated to about 180 c.c., a considerable amount of 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 bromine-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.

Manganese in soils, in the ashes of plants, in manures, in waters, etc., when in very *small quantities*, can be detected and estimated after conversion into permanganic acid in a nitric acid solution by ammonium persulphate in the presence of silver nitrate. The material, which should not contain more than about ·001 gram of manganese, is burnt at a dull red heat if organic matter be present; the residue heated on a water-bath with strong hydrochloric acid, a little sulphuric acid added and evaporated to dryness, and the residue gently heated. The residue is treated with nitric acid [1 : 4], filtered if necessary, and the residue washed with nitric acid. To the solution add 5 drops of 10 per cent. silver nitrate solution and then powdered ammonium persulphate (about ·5 gram), and the mixture warmed on a water-bath to near the boiling-point. The colour of the permanganic acid should quickly develop, and after some minutes reach a maximum. The solution may be heated to boiling. The solution should be diluted to 50 c.c. or 100 c.c., and the colour compared with that of a standard solution made either from potassium permanganate, or by oxidizing a standard solution of double sulphate of manganese and ammonium with nitric acid, silver nitrate, and ammonium persulphate.

The process is only applicable to very small quantities of manganese.

$$\mathrm{Mn} \times 1{\cdot}388 = \mathrm{Mn_3O_4}.$$

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.—Ten 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 ignited, is to be moistened with a drop of strong nitric acid, dried, again ignited, and weighed.

CHLORINE.—Thirteen 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 after ignition in a small porcelain or silica crucible: the latter operation is conducted according to the directions given at p. 181.

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 cm. 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 cm. 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 (Fig. 28). The apparatus is now weighed. After weighing, the apparatus is slowly 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 indiarubber 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

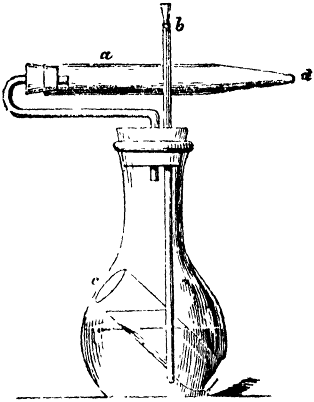

FIG. 28.

apparatus, when quite cold, weighed: the loss in weight is carbon dioxide.

$$CO_2 \times 2{\cdot}2727 = CaCO_3.$$

Some practice is needed to get fairly exact results with this carbon-dioxide apparatus. Other contrivances, in blown glass, as Fig. 29, may be substituted; the forms devised by Schrötter and by Rohrbeck leave nothing to be desired.

For the estimation of small quantities of carbonates, see A. D. Hall, *Trans. Chemical Society*, 1902, p. 81.

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.

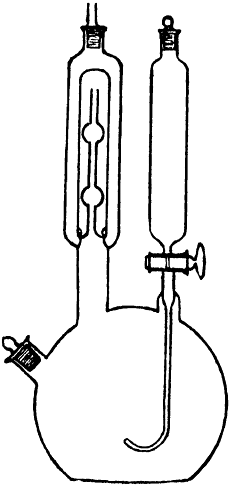

FIG. 29.

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. Three 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 should not be more than one-third full, 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.

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. 238). 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.

LIME is precipitated in the united filtrates and washings from the above, by an excess of ammonium oxalate. If the limestone be magnesian, decant the clear liquid from the calcium oxalate on to a filter, wash once by decantation, then redissolve the oxalate in hydrochloric acid, dilute with water, add ammonia in excess, and some ammonium oxalate, and collect and weigh in the usual manner.

MAGNESIA is determined by means of sodium phosphate and free ammonia in the filtrate from the lime.

If it is desired to determine the amount of alkalies, manganese dioxide, sulphur trioxide, and phosphorus pentoxide present, it may be done as follows:—

Seven grams, or more, of the limestone are dissolved in dilute hydrochloric acid, and the silica separated by evaporation. The residue is moistened with hydrochloric acid, and, after standing some time, dissolved in hot water, and the solution boiled and filtered. The residue on the filter will contain not only silica, but iron pyrites and organic or bituminous matter. By treatment with nitric acid the pyrites may be dissolved, and then estimated from the amount of SO_3 which it yields.

SULPHUR TRIOXIDE is precipitated from a boiling solution by a slight excess of barium chloride.

PHOSPHORUS PENTOXIDE.—The excess of free acid is removed as far as possible by the evaporation of the filtrate; it is afterwards diluted and treated in the cold with an excess of barium carbonate (used mixed with water to a thin cream), the whole being stirred at intervals during the course of an hour; the precipitate, which contains the whole of the phosphorus pentoxide, is collected and washed with cold water. It may be used for the estimation of phosphorus pentoxide, but this is best determined by the molybdic-acid method: six to ten grams of the limestone are dissolved in acid, the silica separated by evaporation, and the filtered solution treated as directed at p. 239.

MANGANESE DIOXIDE.—The filtrate from the barium carbonate is acidified with acetic acid, some ammonium acetate added, and a considerable amount of chlorine or bromine water; the further process is conducted as at p. 248. The washing of the precipitate must be continued till no *trace* of barium is found in the washings. The wash-water may be slightly acidified with acetic acid to facilitate the removal of the barium.

ALKALIES. — The filtrate from the manganese dioxide is boiled, precipitated by ammonium oxalate, and filtered; the filtrate is evaporated to dryness, and the residue gently ignited to expel ammonium salts; pure oxalic acid is then added and a little water, and the whole again evaporated and ignited. The residue is dissolved in a little hot water, and the solution filtered. A little hydrochloric acid is then added and the whole evaporated to dryness, ignited, and weighed. The alkalies are now in the state of mixed chlorides; for their separation see p. 241.

CARBON DIOXIDE.—In an accurate analysis of limestone, a determination of carbon dioxide should be made; for, the silica being in part, though to an unknown extent, combined with lime, the percentage of CO_2 does not admit of exact calculation from the ascertained percentage of lime.

BURNT LIME AND SLAKED LIME.

To determine the amount of free lime in quicklime or of calcium hydrate in slaked lime, weigh out ·5 gram of the finely powdered sample, place in a porcelain dish, and add an excess of water. Add a few drops of phenolphthalein solution, and heat to boiling. Then add standard sulphuric acid from a burette until the colour is just discharged. This will give, by calculation, the amount of lime or of calcium hydrate present; but not the calcium carbonate.

1 c.c. standard acid = ·028 CaO = ·037 CaH_2O_2.

To determine the total base, including carbonate present, add to the lime-water in the porcelain basin a few drops of methyl-orange solution, then an *excess* of standard acid, and titrate back with $\frac{N}{10}$ alkali solution until neutral, so as to estimate the excess of acid.

§ iv. The Analysis of Waters.

The impurities present in ordinary well- and spring-waters are principally derived from the soils (also turf and roots) through which the water passes, and from the infiltration of or contact with sewage and other refuse matter. A very small amount of impurity is derived from the gaseous and solid matters present in the air; but the carbon dioxide from that source 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 two or three times with some of the same water. The quantity of water required will vary greatly according to the object in view: a Winchester quart 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, nitrous, nitric, and silicic radicles, and chlorine, with occasionally the phosphoric radicle. Alumina, ferrous carbonate, and, rarely, arsenic, barium, lead, copper, manganese, zinc, etc., 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, etc.) before the other ingredients are estimated.

Detection of Lead, Copper, Zinc, Barium, and Arsenic in Waters.

Lead and copper.—To 50 c.c of the sample in a Nessler tube add a few drops of pure acetic acid and 10 c.c. of freshly prepared H_2S solution. If copper or lead are present the liquid will darken in colour. If either of these metals is suspected, evaporate a litre or more of the water to dryness and test the residue specially for the metals. The quantity present can be estimated by using a standard solution of a lead or copper salt, containing ·0001 gram of Cu or of Pb per c.c., and reproducing with this and distilled water the colour produced by H_2S with the sample, in Nessler's tubes.

Lead may also be detected by evaporating 500 c.c., after addition of 2 c.c. of acetic acid, to 50 c.c., filtering if necessary, and then adding 1 c.c. of a strong solution of potassium chromate.

A turbidity or slight precipitate is given at once if lead be present.

[Distilled water may contain traces of Cu from a copper still-head or condenser, or traces of Pb from a composition condensing pipe.]

Zinc is generally present as carbonate, and sometimes forms a dead white film on the surface of the water when exposed. It is derived from the zinc coating of tanks, cisterns, or pipes. The suspected film should be collected, washed with water, and heated on a platinum spatula. The ignited ash, if yellow whilst hot and white on cooling, contains zinc oxide.

The quantity present should be determined in a litre or more, evaporated to a small bulk after adding 2 c.c. of acetic acid, then adding ammonia in slight excess to precipitate any iron present, and precipitating the zinc as sulphide by the addition of ammonium sulphide.

Barium is detected by concentrating a litre of the water, adding a few drops of hydrochloric acid and then calcium sulphate solution.

Arsenic may be detected, and estimated, in the water by means of Marsh's test. [Arsenic may, through carelessness, be derived from arsenical sheep dips.]

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 cm. in diameter, and 60 cm. in length. The lower ends are closed with disks of colourless plate glass, covered with white enamel on the upper surface: these disks 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

The reaction of the water with delicate litmus paper should be noticed.

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, *i.e.*, Free and Saline Ammonia.
6. Ammonia producible from organic nitrogen compounds, *i.e.*, Albuminoid Ammonia.
7. Nitrogen existing as nitrates and nitrites.
8. Total and Permanent hardness.

1. TOTAL SOLID RESIDUE.

Evaporate 250 c.c. of the water to dryness in a platinum dish over the water-bath, dry the residue in a water-oven at 100° C. till constant in weight. Note the colour and appearance.

2. ORGANIC MATTER.

The dry residue is heated to low redness until all blackening has disappeared. The residue is treated with ammonium carbonate solution, dried, gently ignited, and again weighed : the loss gives approximately the amount of organic matter and combined water. 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. The nature of the fumes and odour evolved should also be observed: much nitrates may be indicated by reddish-brown fumes.

It is then to be tested for phosphorus pentoxide. Moisten with nitric acid, and evaporate to dryness to render the silica insoluble. Then take up with a little nitric acid, water being added, and lastly, filter 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 molybdate test and gently warmed for fifteen 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.

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, nitrites, sulphides, and 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 and made up to 100 c.c. with distilled water.

3. 100 c.c. 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. 2 or 3 decigrams of pure white starch is placed in a test-tube two-thirds filled with distilled water, well shaken, and heated to the boiling-point; then rapidly cooled under a watertap. This "starch water" should always be made fresh when wanted; it is used as an indicator 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. flasks, which have been rinsed with sulphuric acid and then with the water. Put 250 c.c. into each flask, then add to each flask 10 c.c. 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 flasks must be removed from the bath, and two or three drops of the solution of potassium iodide added to remove the pink colour. After thorough admixture, run from a burette the standard solution of sodium thiosulphate, 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 1 drop of potassium permanganate solution will restore the blue colour. At the end of four hours remove the other flask, 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 and acid must be added from time to time so as to keep it markedly pink. Note the volume of permanganate solution added.

The thiosulphate solution must be standardized, not only at first, but each time a determination is made, in a flask kept side by side with the flask in which the water being tested is kept, thus:—To 250 c.c. of distilled water add 2 or 3 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.

Thus, if a = the amount of thiosulphate used with the distilled water, and b that with the water under examination, a corresponds with the amount of permanganate added to the water, and b with the amount of permanganate in excess of that which the organic matter has destroyed.

$$a - b = \text{amount actually consumed.}$$

Since the amount of available oxygen in the 10 c.c. of permanganate added is ·001 gram, and 250 c.c. of water was used:—

$$\frac{a-b}{a} \times \cdot 001 \times 4 = \text{amount of oxygen required by 1 litre of water.}$$

If it is desired to estimate the mineral matters other than chlorine and nitrogen-compounds, it will be necessary, if the water is tolerably pure, to evaporate a larger quantity than a ¼ 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. 241.

SULPHUR TRIOXIDE is determined by precipitation with barium chloride in half 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 p. 211) in 100 c.c. of the water.

A convenient strength for the silver nitrate solution is 4·79 grams of pure silver nitrate per litre; 1 c.c. of this = ·001 Cl. It should be standardized against a solution of pure sodium chloride, 1·649 grams to a litre; 1 c c. contains ·001 Cl.

Waters containing an abnormal quality of chlorides 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 chlorides 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. 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 [Nessler glass, Fig. 30] about 18 cm. 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 ammonia-free distilled water run into it, and then 5 c.c. of standard ammonium chloride solution, containing ·00001 gram NH_3 per litre, and well mixed with the water by stirring with a glass rod. This water should have been previously freed from ammonia by distillation of distilled water from a retort with a little sulphuric acid, 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. 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

FIG. 30.

100 c.c. and diluting it to 1 litre, when 1 c.c. will be equal to ·00001 gram of ammonia.

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.

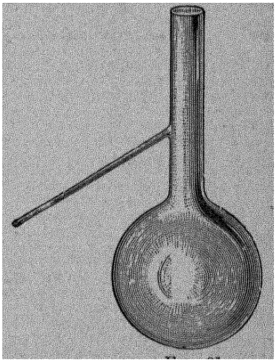
Fig. 31.

Ordinary distilled water, especially if made from river water, frequently contains much free ammonia. The following is a rapid process for preparing ammonia-free distilled water:—Take a round-bottomed Jena glass distillation flask (Fig. 31), of about 2 litres capacity, nearly fill it with ordinary distilled water, add 3 or 4 drops of bromine water, which should distinctly colour the water a brownish tinge. Boil briskly for five minutes until the free bromine has disappeared, then connect the flask with a glass condenser, and distil; reject the first few c.c. of the distillate which washed the condenser; the remainder of the distillate will be free from ammonia.

Into a clean 40-oz. stoppered retort, or flask, place 500 c.c. of distilled water, and distil until 50 c.c. of the distillate gives no colour on standing five minutes with 2 c.c. of Nessler's test. The apparatus will now be free from ammonia. Empty the retort, and when cool add 500 c.c. of the water to be tested with a few decigrams of freshly ignited sodium carbonate.

Distil, not too rapidly, and collect three quantities of 50 c.c. each. As each 50 c.c. is distilled add 2 c.c. of Nessler's test and put on one side. From the colour developed in the second and third 50 c.c. it can be judged whether it is necessary to distil a fourth or further quantities of 50 c.c. each. Generally the first 150 c.c. of distillate will contain all the free ammonia.

The water in the retort is cooled and the Albuminoid Ammonia determined in it.

6. ALBUMINOID AMMONIA, that is, 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 $\frac{2}{3}$ 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 hydroxide in 550 c.c. of pure distilled water. Boil the solution in a retort until 50 c.c. of the distillate gives no colour with 2 c.c. of Nessler's test, and keep it in a well-stoppered bottle.

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, freshly ignited pumice, or of a few short pieces of capillary glass tube, each sealed at one end.

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, etc., 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 quantity of free ammonia in the three or four distillates of 50 c.c. each, and the quantity of albuminoid ammonia in the several 50 c.c. distilled and collected after the addition of the permanganate solution, is determined as follows:—

Take ten Nessler tubes, marked 1 to 10, and fill to the 50 c.c. mark with ammonia-free water. Now measure with great care from a narrow burette, and place in the tubes the following quantities of standard ammonium chloride solution:—

Tube No.	Ammonium chloride solution. c.c.	Ammonia, NH_3. gram.
1	0·5	·000005
2	1·0	·00001
3	1·5	·000015
4	2·0	·00002
5	2·5	·000025
6	3·0	·00003
7	4·0	·00004
8	5·0	·00005
9	6·0	·00006
10	7·0	·00007

Add 2 c.c. of Nessler's test to each, stir well, and allow to stand five minutes. Wipe the stirring rod with a clean duster between each stirring.

By comparing the colours of the distillates containing the free ammonia and the albuminoid ammonia, after addition of 2 c.c. of Nessler's test, with the standards so prepared, the amount of ammonia in each tube is rapidly determined.

Should the colour of any of the distillates with Nessler's test be darker than the standard tube No. 10, the distillate must be diluted with 50 c.c. of ammonia-free water, and the colour of 50 c.c. of the diluted distillate be compared with the standards.

The quantities of free ammonia found in each tube are added together, and represent the amount in half a litre of water.

Similarly the quantities of albuminoid ammonia in each distillate are added together. From the totals the amounts of ammonia and albuminoid ammonia per 100,000 or per 1,000,000 of the water are calculated.

The estimation of ammonia by Nessler's process must be carried on in a room quite free from ammoniacal fumes.

As a check, 250 c.c. or more of the water may be introduced into the retort after the distillation, and the distillation repeated; the ammonia obtained should equal the sum of the free and albuminoid ammonia.

The process is best performed in bright sunlight. Ordinary gaslight, or electric incandescent light, is unsuitable.

The best artificial light is that from a Welsbach incandescent mantle that has been in use for some days.

7. NITROGEN AS NITRATES AND NITRITES

Nitrites should be tested for by taking 50 c.c. of the sample in a Nessler tube and adding 1 c.c. of a colourless solution of metaphenylenediamine (5 grams to a litre of water made acid with sulphuric acid) and 1 c.c. of dilute sulphuric acid (1 to 2 of water). If nitrites are present, a brown colour will develop. If the solution of metaphenylenediamine is coloured it can be decolorized by shaking up with freshly ignited animal charcoal, and filtering.

The nitrites can be estimated with these solutions, by comparing the depth of colour produced in 50 c.c. of the water with that produced in pure water to which a known amount of standard solution of potassium nitrite has been added. This solution should contain ·01 milligram of N_2O_3 per litre. To prepare it, take ·406 gram of pure dry silver nitrite, dissolve in hot water, and decompose with a slight excess of potassium chloride. Cool and make up to 1 litre, allow the silver chloride to settle, and dilute 100 c.c. of the clear liquid to 1 litre.

Nitrates may be determined by means of the nitrometer (p. 214). Evaporate 250 c.c. of the water, if free from nitrites, in a porcelain dish on a water-bath. Extract the residue with a very small quantity, about 2 c.c., of water, and pour the extract into the cup of a nitrometer. Draw this into the nitrometer-tube and add 5 c.c. of strong sulphuric acid. Carbonates and chlorides will be at once decomposed; drive out the carbon dioxide and the hydrochloric acid from the tube. The mixed liquids are now well shaken in contact with the mercury for eight or ten minutes. Nitric oxide gas is given off. Let the apparatus cool for about half an hour; level the mercury in the tubes; note the volume of gas, the temperature, and the height of the barometer; and calculate the volume of NO, as described on p. 216.

If 250 c.c. of water were used, the calculated volume in c.c. multiplied by 2·5 gives the nitrogen in parts per 1,000,000 of water.

If the water contains more than 12 grains of common salt per gallon, it should be removed before the nitrates are determined by this method. To the water (250 c.c.) add a saturated solution of silver sulphate in sufficient quantity to precipitate nearly all the chloride present. Filter, wash the precipitate with distilled water, and evaporate to dryness, and proceed as above.

If *nitrites* are present, evaporate the 250 c.c. of water in a porcelain dish with a slight excess of pure caustic soda, and treat the residue as above. The caustic alkali is added to decompose any ammonium nitrite present and convert it into sodium nitrite. Ammonium nitrite would be decomposed in evaporating the water with the evolution of nitrogen. By treating the water as above mentioned the nitrites and nitrates are determined together.

Several other methods may be used for the estimation of nitrates or nitrites in water; of those we give two of the best:—

Indigo Method.

This is a modification of a method devised by R. Warington. Two standard solutions are required, and pure sulphuric acid quite free from nitrogen compounds.

(1) Standard potassium nitrate solution, $\frac{N}{1000}$ strength, made by dissolving ·1011 KNO_3 in a litre of distilled water.

(2) Indigo-carmine (sodium sulphindylate) solution, 1 gram in half a litre of dilute (1 : 20) sulphuric acid. Keep this solution in the dark.

Pure sulphuric acid, specific gravity 1·84.

To standardize the indigo solution, 10 c.c. of the standard nitrate solution are run into a thin wide-mouthed 150 c.c. flask, then 10 c.c. of indigo solution, and from a graduated measure 20 c.c. of strong pure sulphuric acid; a rotatory motion is given to the flask to mix the liquids, and the flask held over a spirit lamp. If the indigo is at once decolorized, more is run in until, after heating for thirty seconds, the blue colour is just discharged and a greenish tint remains. The indigo solution should be diluted with 5 per cent. sulphuric acid to a strength the same as that of the potassium nitrate. Fresh trials are then made, and the exact strength of the indigo solution determined and noted. In determining nitrates in water, the amount present must be approximately that equal to the $\frac{N}{1000}$ potassium nitrate.

A trial titration is made with 10 c.c. of the water, adding indigo and then strong sulphuric acid equal in volume to the united volumes of indigo and water, and heating, and, if necessary, adding more indigo. This will show if the water needs dilution, and to what extent. After the water has been diluted, if necessary, with distilled water to the required strength, 10 c.c. are taken and fresh titrations made until the exact number of c.c. of indigo decolorized by the water is known. It is necessary always to heat for the same time, thirty seconds, and to work to the same shade of green as in standardizing the indigo. In the absence of large amounts of chlorides, accurate results can be obtained.

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 hydroxide 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 three or four 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 oz. 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. 268 ; but it may need dilution with pure distilled ammonia-free water. 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 pp. 268-270. 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.

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:—Fifty 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 $\frac{1}{10}$ 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. 279. 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 freshly boiled but cold distilled water, and the number showing the hardness multiplied according to the amount of dilution; thus if 25 c.c. were used, multiply by 2, etc. 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 100 c.c. 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 100 c.c., filtered, and the hardness estimated in 50 c.c. as before.

The temporary hardness is the difference between the total and permanent hardness.

It will be evident from the table on p. 279 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 specific gravity ·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.

TABLE OF HARDNESS

(50 c.c. of Water used)

A degree of hardness indicates 1 grain of $CaCO_3$ per gallon.

Soap sol. c.c.	$CaCO_3$ per 100,000.	Degrees of Hardness	Soap sol. c.c.	$CaCO_3$ per 100,000.	Degrees of Hardness.	Soap sol. c.c.	$CaCO_3$ per 100,000.	Degrees of Hardness	Soap sol. c.c.	$CaCO_3$ per 100,000.	Degrees of Hardness.
0·7	0·00	0·00	4·6	5·43	3·80	8·5	11·05	7·74	12·4	17·06	11·94
0·8	0·16	0·11	4·7	5·57	3·90	8·6	11·20	7·84	12·5	17·22	12·05
0·9	0·32	0·22	4·8	5·71	4·00	8·7	11·35	7·95	12·6	17·38	12·17
1·0	0·48	0·34	4·9	5·86	4·10	8·8	11·50	8·05	12·7	17·54	12·28
1·1	0·63	0·44	5·0	6·00	4·20	8·9	11·65	8·16	12·8	17·70	12·39
1·2	0·79	0·55	5·1	6·14	4·30	9·0	11·80	8·26	12·9	17·86	12·50
1·3	0·95	0·67	5·2	6·29	4·40	9·1	11·95	8·37	13·0	18·02	12·61
1·4	1·11	0·78	5·3	6·43	4·50	9·2	12·11	8·48	13·1	18·17	12·72
1·5	1·27	0·89	5·4	6·57	4·60	9·3	12·26	8·58	13·2	18·33	12·83
1·6	1·43	1·00	5·5	6·71	4·70	9·4	12·41	8·69	13·3	18·49	12·94
1·7	1·56	1·09	5·6	6·86	4·80	9·5	12·56	8·79	13·4	18·65	13·06
1·8	1·69	1·18	5·7	7·00	4·90	9·6	12·71	8·90	13·5	18·81	13·17
1·9	1·82	1·27	5·8	7·14	5·00	9·7	12·86	9·00	13·6	18·97	13·28
2·0	1·95	1·37	5·9	7·29	5·10	9·8	13·01	9·11	13·7	19·13	13·39
2·1	2·08	1·46	6·0	7·43	5·20	9·9	13·16	9·21	13·8	19·29	13·50
2·2	2·21	1·55	6·1	7·57	5·30	10·0	13·31	9·32	13·9	19·44	13·61
2·3	2·34	1·64	6·2	7·71	5·40	10·1	13·46	9·42	14·0	19·60	13·72
2·4	2·47	1·73	6·3	7·86	5·50	10·2	13·61	9·53	14·1	19·76	13·83
2·5	2·60	1·82	6·4	8·00	5·60	10·3	13·76	9·63	14·2	19·92	13·94
2·6	2·73	1·91	6·5	8·14	5·70	10·4	13·91	9·74	14·3	20·08	14·06
2·7	2·86	2·00	6·6	8·29	5·80	10·5	14·06	9·84	14·4	20·24	14·17
2·8	2·99	2·09	6·7	8·43	5·90	10·6	14·21	9·95	14·5	20·40	14·28
2·9	3·12	2·18	6·8	8·57	6·00	10·7	14·37	10·06	14·6	20·56	14·39
3·0	3·25	2·28	6·9	8·71	6·10	10·8	14·52	10·16	14·7	20·71	14·50
3·1	3·38	2·37	7·0	8·86	6·20	10·9	14·68	10·28	14·8	20·87	14·61
3·2	3·51	2·46	7·1	9·00	6·30	11·0	14·84	10·39	14·9	21·03	14·72
3·3	3·64	2·55	7·2	9·14	6·40	11·1	15·00	10·50	15·0	21·19	14·83
3·4	3·77	2·64	7·3	9·29	6·50	11·2	15·16	10·61	15·1	21·35	14·95
3·5	3·90	2·73	7·4	9·43	6·60	11·3	15·32	10·72	15·2	21·51	15·06
3·6	4·03	2·82	7·5	9·57	6·70	11·4	15·48	10·84	15·3	21·68	15·18
3·7	4·16	2·91	7·6	9·71	6·80	11·5	15·63	10·94	15·4	21·85	15·30
3·8	4·29	3·00	7·7	9·86	6·90	11·6	15·79	11·05	15·5	22·02	15·41
3·9	4·43	3·10	7·8	10·00	7·00	11·7	15·95	11·17	15·6	22·18	15·53
4·0	4·57	3·20	7·9	10·15	7·11	11·8	16·11	11·28	15·7	22·35	15·65
4·1	4·71	3·30	8·0	10·30	7·21	11·9	16·27	11·39	15·8	22·52	15·76
4·2	4·86	3·40	8·1	10·45	7·32	12·0	16·43	11·50	15·9	22·69	15·88
4·3	5·00	3·50	8·2	10·60	7·42	12·1	16·59	11·61	16·0	22·86	16·00
4·4	5·14	3·60	8·3	10·75	7·53	12·2	16·75	11·73	..	..	.
4·5	5·29	3·70	8·4	10·90	7·63	12·3	16·90	11·83	.	..	..

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 distilled 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.

Hehner's Process.

The hardness of water can also be estimated, without the use of standard soap solution, by Hehner's process For this we require two standard solutions, $\frac{N}{50}$ sulphuric acid and $\frac{N}{50}$ sodium carbonate. One c.c. of this acid neutralizes ·001 gram of $CaCO_3$, and 1 c c. of alkali precipitates 1 milligram of $CaCO_3$, or its equivalent in magnesium salts.

A suitable indicator is also wanted; for this purpose alizarin paste (1 gram to 200 c.c. water) or lacmoid answer best.

One hundred c.c. of the water are placed in a porcelain dish, tinted with the indicator, heated nearly to boiling, and standard acid cautiously added till the change of colour indicates neutrality. The number of c.c. of acid used represents the number of Clark's degrees of temporary hardness per 100,000.

The permanent hardness is found by taking 100 c.c. of the water, adding to it a known excess of the standard sodium carbonate solution: *i.e.*, more than enough to decompose the nitrates, chlorides, and sulphates of calcium and magnesium present; usually a volume equal to that of the water will suffice. Evaporate to dryness in a platinum dish, extract the soluble portion with small quantities of distilled water, filter through a very small filter-paper, and titrate the filtrate with the standard acid: this gives the excess of sodium carbonate, which is deducted from the amount used when the difference represents the permanent hardness.

If the water contains alkaline carbonates, the total and temporary hardness will be shown to be greater than it really is owing to neutralization of acid of the alkaline carbonate. But the estimation for permanent hardness will show more sodium carbonate than was actually added. If the excess so found is deducted from the temporary hardness, as first found, the remainder will be the true temporary hardness.

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 twelve hours ; $\frac{1}{5}$ 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-oz. bottles half full, the strips rising above the level of the water. The liquid is to be poured off after twenty-four 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.

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 should always be given :—

Description and origin of sample.
Date when drawn.
Temperature when drawn.
Appearance in 2-foot tube.
Smell when heated to 38° or 40° C.
Chlorine calculated as Common Salt.
Phosphoric Acid.
Nitrogen in Nitrates and Nitrites.
Nitrogen as ready-formed Ammonia.
Nitrogen obtained as Ammonia from albuminoid matter.
Oxygen absorbed in fifteen minutes at 27° C.
Oxygen absorbed in four hours at 27° C.

Total Hardness.
Permanent Hardness.
Temporary Hardness.
Total solid matter, dried at 100° C., in parts per 100,000.
Appearance, under the microscope, of deposit.
Action of the water on lead.
Poisonous metals.

§ v. Analysis of Foods.

OILCAKE.—FEEDING-MEAL

The constituents of oilcake are—proteins or albuminoids, mucilage and other soluble non-nitrogenous substances, oil, cellulose and fibre, mineral matters, and water.

In the case of oilcakes, the sample for analysis should be taken right across the middle of the cake, a strip an inch or two in width being sawn out. The sample is prepared by grinding it in a small hand coffee- or spice-mill, sifting the product, and again grinding the remainder left on the sieve and thoroughly mixing the whole.

Oil and nitrogen can be best determined in a finely ground sample.

WATER is determined by drying 2 grams in the water-oven until constant. The intervals between the weighings should not be too long, as the substance in most cases begins finally to gain weight from the oxidation of the oil.

OIL.—From 2 to 4 grams, according to its probable richness in oil, of the finely powdered cake, first dried, are introduced into a very convenient form of extraction-apparatus which has been introduced by Soxhlet. A vertical section of its main portion is shown in Fig. 32, of one-fourth the real size. To complete the apparatus, an upright glass tubular condenser, through which a current of cold water passes (such as is shown in Fig. 33. The condenser shown in Fig. 34 is even more effective, as it has two cooled surfaces on which the ether may condense), 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.

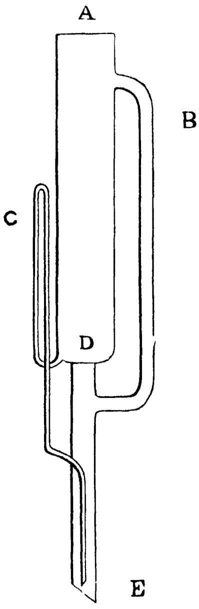

FIG. 32.

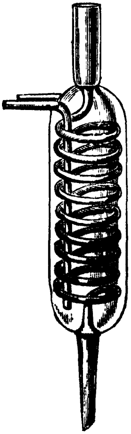

FIG. 33.

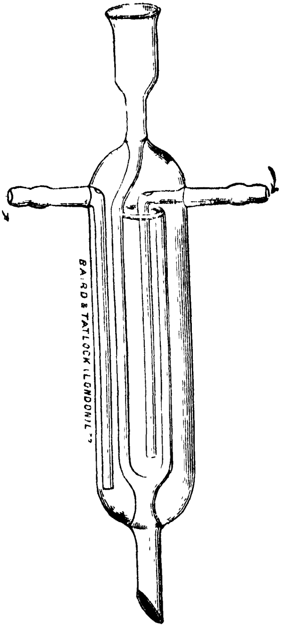

FIG. 34.

In order to commence a quantitative estimation of oil in an oilcake, about 25 c.c. of pure, washed, and redistilled ether (or of light petroleum ether) are put into a flask, which should be short, 7 cm. high, wide-mouthed, strong, and not over 20 grams in weight: this flask, which must have been weighed after drying and cooling, is then attached to the Soxhlet extractor (Fig. 32). 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. Extraction cups, or thimbles, of specially prepared oil-free paper are made for use with Soxhlet's apparatus, and are most convenient for holding the cake. The solvent is now introduced in sufficient quantity. 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 to D 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

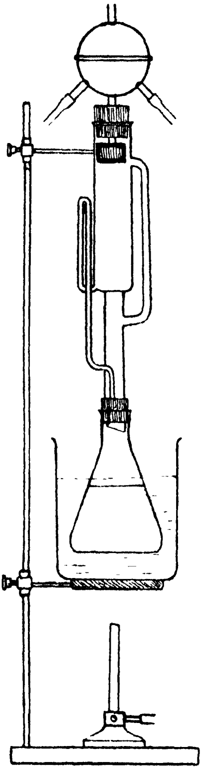

FIG. 35.—Shows the apparatus with the flask in a bath of hot water and the condenser, a metallic ball condenser, which is very effectual and occupies less space than the glass condensers.

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 as liquid through C, until a drop, tested as it falls from E, will no longer contain a trace of oil. When the oil is all extracted most of the ether may be recovered by attaching the flask to a small condenser and receiver and distilling over most of the solvent.

The flask is then kept in a warm place (*e.g.*, on the top of the water-oven) for a short time, and then heated to 100° until its weight is constant.

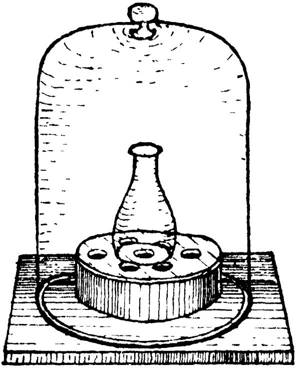

FIG. 36.

The drying should be conducted as quickly as possible, to avoid oxidation of the oil and consequent increase in weight. A convenient arrangement in which to cool the flask after taking from the water-oven, and before weighing, is shown in Fig. 36.

The oil from some meals lose considerably in weight in the water-oven. For instance, the oil from palm-nut kernel meal contains some volatile constituent which is lost unless the drying be conducted at the ordinary temperature, best over oil of vitriol and *in vacuo*, or under a reduced atmospheric pressure.

Where only a small quantity of material is available for an oil determination, it may be mixed with pure, coarse, quartz-sand before introduction to the oil-extractor. The whole scale of the apparatus may be reduced in size. Traces of chlorophyll and of resin, which very often accompany the oil, may generally be disregarded.

The Board of Agriculture Official Regulations read thus:—

DETERMINATION OF OIL

. (*a*) A weighed quantity of the sample shall be placed in a Soxhlet thimble, which shall then be placed in the Soxhlet extraction-tube and extracted with washed, redistilled ether. At the end of three to four hours the thimble shall be removed from the Soxhlet tube, dried, and its contents finely ground in a small mortar previously rinsed with ether. The substance shall then be returned to the thimble, the mortar being washed out with ether, and the extraction continued for another hour.

After evaporation of the solvent the oil shall be dried at 100° C. and weighed. The oil shall be redissolved in ether, and any undissolved matter shall be weighed and deducted.

(*b*) In the case of samples containing saccharine matter, *e.g.*, sugar meals, the weighed portion in the Soxhlet thimble shall be washed twice with water, and then dried, previous to the extraction.

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 specific gravity 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, etc., 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. The process usually adopted in commercial analyses for the estimation of fibre is that given below, under the heading Acid and Alkali method.

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. If the original cake be used, the fibre, after washing with acid and alkali, should be washed twice with alcohol and then with ether, to remove oil.

Acid and Alkali Method.

Three grams of the coarsely powdered sample are placed in a large beaker, 150 c.c. of hot 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 half an hour, the normal volume 200 c.c. (best marked by an ink line or a scratch with a diamond 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. 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 water. Fifty c.c. of a 5 per cent. sodium hydroxide solution are next added, and the beaker filled up with hot water to the mark indicating 200 c.c. The mixture is boiled for half an hour, some cold water added, and the whole allowed to rest. The residue collected once more on the calico filter, is washed with a 1 per cent. solution of ammonium hydrate until the filtrate is colourless. 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. When the fibre has been perfectly washed on the calico filter, 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.

ALBUMINOIDS or PROTEINS.—A Kjeldahl determination is made with about 1 gram of the finely powdered cake: 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.

This determination also includes the nitrogen in any amides, amino-acids, and organic nitrogenous adulterants.

The Board of Agriculture Official Regulations read thus:—

DETERMINATION OF ALBUMINOIDS

The percentage of albuminoids shall be ascertained by multiplying the percentage of nitrogen by 6·25.

The determination of nitrogen shall be as follows:—

A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 grams of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless or of light straw colour, is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, 1 gram of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in this control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.

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. 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, etc.—The various non-nitrogenous combustible constituents (other than oil and fibre) of cakes are usually determined by difference. They include mucilage, digestible cellulose, starch, pentosans, pectose, and other less important carbonaceous substances.

N.B.—A genuine linseed cake, made from properly ripened seed, contains no STARCH; if this be present, except in traces, 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, etc.), 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 linseed 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 hydroxide. 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. Immature linseed also contains starch. 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, etc., 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 recognise 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 rape seed and Indian linseed; for hydrocyanic acid in Java beans, or in red Rangoon beans.

Cakes, especially cotton cake, should be tested for boric acid, common salt, and other preservatives.

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 c.c. 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.

Microscopic examination of cakes.[1]—Besides examining the cake with a good hand lens the student should prepare specimens of the husk for examination with a higher power.

Digest 5 grams of the cake with 2 per cent. sulphuric acid on a water-bath for about one hour, and wash thoroughly with hot water; then digest for a similar time with 2 per cent. sodium hydroxide solution, and wash thoroughly. This makes the husks of the majority of the oil seeds and of the impurities and adulterants in them sufficiently transparent to be readily studied and recognised under the microscope. A 1-inch objective is sufficient for most seeds, though a higher power will be found better for some. For simple identification the husks after treatment may be viewed on a slide in water under a cover-glass. For permanent mounts the prepared husks should be soaked first in dilute alcohol, then in 50 per cent. alcohol, and afterwards in absolute alcohol to remove the water, then soaked in oil of cloves, and finally mounted in Canada balsam liquified with a little toluene or xylene. Permanent mounts of the oil seeds and impurities should be kept for reference.

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. One hundred c.c. of water and 1 c.c. of pure hydrochloric acid (of 1·125 specific gravity) 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

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[1] Cf. *Microscopy of Vegetable Foods*, A. L. Winton; or *Mikroskopie der Nahrungs und Genussmittel aus dem Pfanzenreiche*, von Josef Moeller.

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 dextrose. 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 hydroxide solution. Finally, the liquid is made up to an exact volume, say 200 c.c., and the dextrose 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 dextrose 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. Fifty 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. Fifty c.c. are taken and heated with 20 c.c. of 5 per cent. 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. Neutralize the two inverted solutions with sodium hydroxide, 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.

Wheaten flour used in breadmaking is sometimes bleached with nitrous fumes. The presence of *nitrites* in flour can be detected by shaking up the flour with *cold* water, allowing it to settle, filtering, and examining the filtrate with metaphenylene diamine as in water analysis. *Alum* and other mineral matter in flour may be detected by well shaking up 50 to 100 grams of the flour with chloroform in a stoppered separating funnel. The flour will float on the top and alum fall to the bottom, and can, after settling, be drawn off through the tap and identified.

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, ETC.

The chief constituents of these plants are water, cellulose, pectose, gum, sugar, proteins, 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.

A very convenient arrangement for drying slices of roots and tubers, and also succulent leaves, is shown in Fig. 37. 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.

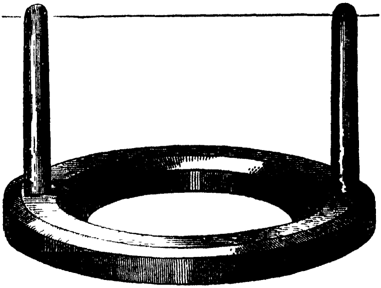

Fig. 87.

PROTEINS or ALBUMINOIDS.—A nitrogen determination by Kjeldahl's method (p. 164), is made in 1 gram, and the percentage of nitrogen multiplied by 6·25; the product, though often regarded as the percentage of proteins, requires a correction for that portion of the nitrogen which exists as nitrates, amides, ammonia salts, and other non-protein 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. 276).

Other plans of obtaining a fairly accurate approximation to the amount of nitrogen really existing as protein or flesh-forming substances in roots, etc., 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 fifteen minutes a little boiling phenol 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 treated by Kjeldahl's method for nitrogen determination, the filter-paper itself being cut up into fine shreds and introduced into the flask.

In this process the proteins, being coagulated and rendered insoluble, remain on the filter, while the nitrates, amides, amino-acids, 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, etc., an alcoholic solution of phenol may be advantageously substituted for an aqueous one in the first instance.

Copper-Hydrate Method.

Moist copper hydrate unites with protein 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 glycerol have been added. To this solution 1½ litres of very dilute sodium hydroxide 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. glycerol 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 per cent. solution of glycerol: 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 glycerol, 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 treated by Kjeldahl's method. 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 previously to the addition of the copper hydrate.

In turnips, often but one-half of the total nitrogen is protein; in mangolds heavily manured and quickly grown, even a less proportion of the nitrogen may be proteins.

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 a 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 proteins, 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 protein 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 most other 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 p. 86, 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, $C_6H_{10}O_5$; or ·0678 of lactose.

Previously to use, the exact strength of the solution must be found by titration, with a solution of pure sugar diluted to about ½ per cent. The analytical process is conducted as follows:—Ten c.c. of the copper solution are measured into a white porcelain basin 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 one-tenth of its volume of sulphuric acid for ten minutes, made alkaline with caustic soda, and diluted to a known volume, so as to contain between ½ and 1 per cent. 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 hydroxide.

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 hydroxide. 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.

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 filter-pump, 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 consist of an ordinary small paraffin lamp-glass. The narrow lower end of this is fitted with a perforated indiarubber cork; upon it is placed a piece of muslin and 12 mm. of clean sand; through the perforation a glass tube passes into a receiver below. This receiver (which may be a wide-mouthed Winchester quart, with ground neck and having an indiarubber stopper) is kept partially exhausted of air by being placed in suitable connection with an exhausting syringe or pump. 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 hydroxide in excess added, and the solution diluted to a known volume.

A convenient weight of beet-root to take is 100 grams, one-half the evaporated extract from which can then be diluted to a litre; this will give a solution containing the sugar from 5 parts of beet in 100 of water, and generally the right strength for titration. The remainder of the operations have been already described.

A much quicker method of estimation of sugar, which is practically essential when a large number of determinations have to be made in a limited time, is with the aid of a polarimeter. For instructions on the construction and use of this instrument other books must be consulted, e.g., *Handbook of the Polariscope*, by H. Landolt (Macmillan & Co.).

The STARCH in potato-tubers, parsnips, etc., may be approximately 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 hydroxide 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 twenty 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

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

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.

In many roots there occur considerable quantities of the substances known as PECTOSE, pectin, and pectic acid. It is rarely necessary to attempt 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 twelve 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 a 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 two 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, burned, 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 CaC_2O_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, ETC.

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 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 fixed oils and fats, wax, essential oils, free fat-acids, together with a part of the chlorophyll and some active principles.

2. *Ether*, free from alcohol and from water. This extracts resins, some organic acids, and chlorophyll.

3. *Alcohol*, which must be nearly absolute. This extracts tannin, glucosides, bitter principles, and alkaloids.

4. *Water*. This extracts sugars, dextrin, mucilage, many organic acids and their alkaline salts, calcium sulphate, soluble albuminoids, ammonium salts, nitrates, and amides.

5. *Sodium hydroxide solution*, containing ·1 to ·2 per cent. This extracts albuminoids with some kinds of gummy and pectous bodies.

6. *Water* at 100°. This extracts starch.

7. *Hydrochloric acid*, dilute, containing 1 per cent. This extracts calcium oxalate, manganese and iron oxides, and some gummy substances.

The final residue, remaining after the above treatment, will consist chiefly of cellulose and lignose with silica and other mineral matters. It, as well as the several groups of substances which have been removed by the several solvents successively used, will have to be further examined by special methods.

In ordinary cases, where the feeding value of green fodder is the chief point to be ascertained, the determinations described below will generally suffice.

WATER.—Whole leaves, to the amount of 100 grams, or more if the leaves be large, are dried slowly and carefully (on bibulous paper), if possible, in a current of warm dry air. If a large number of leaves have to be dried for any special purpose, it will be found convenient to tie them up one by one along strings stretched across a room: a warm temperature and free movement of the air assist the drying process greatly. When the dried leaf is required for the subsequent examination of certain ingredients alterable by light (chlorophyll, for instance), the room should be kept as dark as possible. Sometimes leaves may be advantageously dried by means of the same arrangement as that previously recommended for sliced roots.

NITROGEN.—When the total nitrogen merely is required, it may be determined in the dried and powdered leaf in the usual way. If afterwards the ammonia be determined by distillation with magnesium carbonate and Nesslerizing the distillate, if the nitrates be determined by the copper-zinc couple method; and if the true albuminoids be determined by the phenol or the copper-hydrate method, we are then in a position to calculate the amount of nitrogen existing in the form of amides and other bases, and of nitrogenous acids, by subtracting the amounts of nitrogen existing in the three known combinations from the total amount. There will, however, be a difficulty in stating the results in percentages, as we do not know the nature and consequently the centesimal composition of the amides, etc., in question. Were we dealing with asparagin only, it would suffice to multiply the percentage of residual nitrogen by 4·7.

ASH may be determined in the dried and broken (but not powdered) leaf in the usual way. Where particular accuracy is desired, the leaves should be calcined by the process described further on under the heading "Ashes of Plants."

FAT is to be determined in a rather coarsely powdered sample of the dried leaf by extraction with ether, petroleum-spirit, or carbon bisulphide in the usual way. Much of the matter extracted by these solvents will, however, not be fat, but leaf-green, or chlorophyll and xanthophyll. These colouring-matters may be removed from the solution by filtering it through freshly ignited animal charcoal. In the case of silage, lactic and other organic acids will be found in the ether extract. Use petroleum-spirit for choice. In stating the results, the nature of the solvent should be named.

ACIDS.—In silage the acids volatilized on distilling with water, mostly acetic acid and butyric acid, and the non-volatile acids, mostly lactic acid, should be determined.

CELLULOSE may be determined by carefully bruising in a mortar about 70 grams of whole leaves till a tolerably smooth paste is formed, and then exhausting with water, as before described in the case of roots. A determination of fat, as well as of nitrogen and ash, must be made in the crude cellulose.

Beet-root pulp from sugar manufactories or distilleries is analysed as directed for roots; a sugar determination is sometimes requisite.

FERMENTED LIQUORS, BEERS, ETC.

An adequate description of the examination of liquids containing alcohol would occupy too much space in the present elementary volume. We here confine ourselves to some points to which attention should be chiefly directed.

ALCOHOL.—This is estimated by distilling a known quantity of the liquid made alkaline with sodium carbonate in a suitable flask fitted air-tight to a good condenser (Fig. 38). When the last distillate no longer contains any spirit, all the previous distillates are mixed together, made up to the original volume with distilled water, heated or cooled, as the case may be, to the temperature of 15·5° C. (60° F.), and the specific gravity taken in the proper specific gravity bottle or tube, or by means of a hydrometer. A table showing how much absolute alcohol is contained in distillates of different densities may be found in most manuals of chemistry: we give a few extracts from such a table here (see p. 313). From the amount of alcohol present in the amount weighed, the amount in the whole measured distillate is calculated.

Absolute alcohol is here taken as having the specific gravity ·7938 when compared with water at the same temperature, 15·5° C.

Proof spirit has the specific gravity ·9198, and contains

49·24 per cent. of absolute alcohol by weight. When a sample of spirit is said to be 30° over proof, it is meant that 100 measures of it, after dilution with water, would

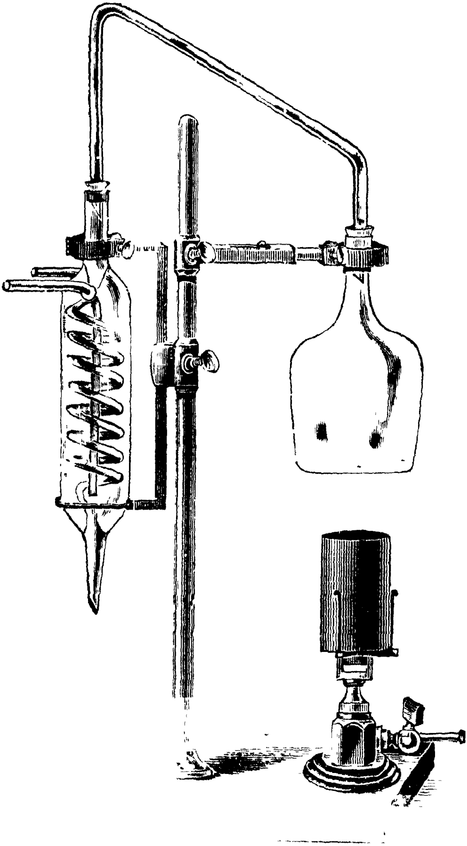

FIG. 38.

measure 130 of proof spirit. A sample 22° under proof

Specific Gravity of Distillate at 15·5° C.	% Absolute Alcohol by Weight.	Absolute Alcohol by Volume	Proof Spirit.
·9991	0·47	0·60	1·04
·9981	1·0	1·26	2·25
·9972	1·5	1·88	3·32
·9963	2·0	2·51	4·40
·9954	2·5	3·14	5·52
·9946	3·0	3·76	6·52
·9937	3·5	4·42	7·66
·9928	4·0	5·00	8·81
·9920	4·5	5·63	9·88
·9912	5·0	6·24	10·96
·9896	6·0	7·48	13·15
·9881	7·0	8·72	15·31
·9867	8·0	9·95	17·41
·9853	9.0	11·17	19·53
·9839	10·0	12·40	21·70
·9828	11·0	13·62	23·87
·9815	12·0	14·84	26·00
·9802	13·0	16·05	28·13
·9789	14·0	17·26	30·26
·9777	15·0	18·48	32·56
·9765	16·0	19·68	34·66
·9753	17·0	20·89	36·61
·9741	18·0	22·09	38·71
·9728	19·0	23·28	40·81
·9716	20·0	24·48	42·90
·9578	30·0	36·20	63·43
·9395	40·0	47·35	83·02
·91984	**49.24**	**57·079**	**100·00**
·9180	50·0	57·84	101·36
·8956	60·0	67·69	118·63
·8721	70·0	76·91	134·84
.8483	80·0	85·49	149·82
·8228	90·0	93·29	163·48
·79384	**100·0**	**100·00**	**175·25**

contains in 100 measures 100 − 22, or 78 measures of proof spirit. The last column of figures in the table serves to show the volumes of proof spirit to which the 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, etc., the water, alcohol, acetic acid, and traces of ethers present are volatilized, while the sugars, the glycerol, the proteids, colouring-matters, gums, pectin, etc., 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 proteids 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 $\frac{N}{10}$ soda solution used in nitrogen determinations, and methyl-orange or litmus, as an indicator. Vinegar 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 $\frac{N}{10}$ soda solution will neutralize:—

·0049	gram	H_2SO_4,	Sulphuric acid.
·0060	,,	$C_2H_4O_2$,	Acetic acid.
·0188	,,	$C_4KH_5O_6$,	Hydropotassium tartrate.
·0075	,,	$C_4H_6O_6$,	Tartaric acid.
·0090	,,	$C_3H_6O_3$,	Lactic acid.
·0077	,,	$C_4H_6O_5$,	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, 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 farther 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 then 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

p. 250) 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.

Part of the chlorine in the plant substance is always volatilized when the substance is burnt alone in the usual way. To estimate the total chlorine the substance must be burnt at a low temperature with an excess of pure lime, or of sodium carbonate, and the residue extracted with water; any incompletely burnt particles are burnt with more lime; the aqueous extract is then acidified with nitric acid and the chlorine precipitated as silver chloride with silver nitrate.

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 morning's milk is generally poorer than that of the evening. The length of time that has elapsed since calving, the character and the quantity of the food given, the temperature and moisture of the air, as well as the breed and 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 specific gravity of good milk is about 1·0325, *i.e.*, 100 c.c. of good milk will weigh about 103·25 grams; or, 1 gallon will weigh 10·325 lbs.

The quality of milk may best be determined by means of chemical analysis, the indications of the lactometer and creamometer alone being too often fallacious.

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 (caseinogen), albumin, lactose or sugar of milk, and mineral matters rich in phosphates. The phosphates are intimately associated with the casein, 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 proteins 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.

WATER.—As it is impossible to secure the perfect desiccation of a considerable quantity of milk, it is best to use a very small quantity for the purpose of ascertaining the amount of water and of total solids present. About 5 c.c. of the well-mixed sample of milk are poured into a flat platinum or porcelain basin 3 inches in diameter, and quickly and carefully weighed. The basin 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 is calculated into percentage on the weight taken. It will average 13 per cent., and will rarely fall below 12 per cent. in a genuine milk; while, if the cows be properly and liberally fed, it may even exceed 13·5 per cent. 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 made by the *Kieselguhr* method or Adams' Paper Coil method, to be described presently. The amount of fat 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 9·0 up to 9·6 per cent. It may usually be concluded that the milk has been watered should the figure fall under 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 8·5 per cent. of solids-not-fat. This limit is that adopted by the Board of Agriculture. Suppose, for example, that the analysis of a sample has given but 6·2 per cent. of solids-not-fat, we multiply that figure by 100 and divide it by 8·5, and so obtain 72·9 as the quotient, representing the percentage present of real milk:

$$\frac{6{\cdot}2 \times 100}{8{\cdot}5} = 72{\cdot}9.$$

The sample is therefore calculated to contain 27·1 per cent. of added water.

Kieselguhr Method.

FAT.—Ten c.c. of the milk is dropped into a porcelain basin which contains some Kieselguhr, stirred up, dried in the water-oven, turned into a mortar, and ground up. The residue is transferred to a paper thimble and extracted with ether in a Soxhlet's apparatus.

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, previously extracted with ether, 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 1 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. Coils of sufficiently absorbent paper from which all fat has been previously extracted can now be purchased ready for use.

Werner-Schmid's Method.

To carry out this method, which is peculiarly useful in the case of sour-milks, special calibrated tubes are made, such as Figs. 39 and 40. 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 basin or flask. After evaporation of the ether the fat left is dried for twenty 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.

Fig. 39.

Fig. 40.

A drawback to this method is the formation of a flocculent layer between the ethereal and aqueous layers; this renders the reading of the volume of the ether-layer difficult. By a modification of the process, 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. Twenty 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 upturned 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.

Various centrifugal volumetric methods for the rapid determination of fat have been devised. In these the milk is treated with strong acids to dissolve the casein, etc., warmed, and subjected to centrifugal action so as to bring about the separation of the fat in a fluid state, in an apparatus in which its volume can be read off.

One of the best of these machines is the Gerber Acid-Butyrometer. In using this for milk, 10 c.c. of strong sulphuric acid (sp. gr. 1·825) are placed in one of the special graduated butyrometer tubes, 1 c.c. of amyl alcohol (sp. gr. ·815 to ·818; B.P. 127° to 130° C.) carefully added, then 11 c.c. of milk, the tube closed with an indiarubber cork, the contents mixed by shaking, warmed, if necessary, to about 65° C., and whirled in the machine for about two to three minutes. Separated milk should be whirled for at least five minutes. After taking out the tubes from the centrifugal machine they may be kept in a water-bath at 65° C. for a minute before reading off the volume of the fat layer. Small machines are rotated by hand by means of a cord or a leather strap.

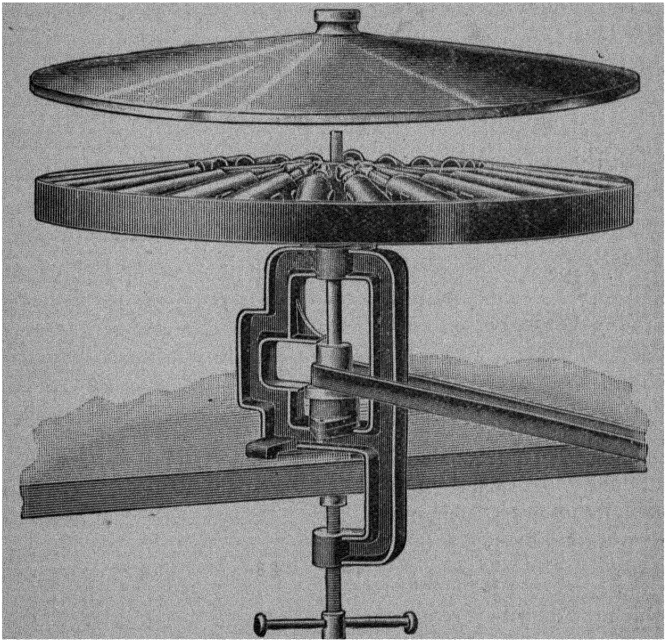

FIG. 41.

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 raises 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 per cent. of total solids and had the specific gravity 1032·2 yielded experimentally 3·62 per cent. of fat, while by calculation it was estimated to contain 3·59. For

$$\frac{5}{6}\left(12\cdot36-\frac{32\cdot2}{4}\right) = 3\cdot59.$$

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 (Fig. 42). In this instrument a glass plummet, suspended by a piece of thin platinum wire, is attached to one end of a graduated lever. On immersing the plummet 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 10 c.c. of liquid, and hence the weight required to restore equilibrium equals that of 10 c.c. of the fluid of which the density is required.

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—

$$\frac{1\cdot75 \times 100}{3} = 58\cdot3.$$

The sample is thus estimated to have lost by skimming 41·7 per cent. of its cream.

PROTEINS or ALBUMINOIDS.—The casein and other albuminoids of milk may be best determined in the dry residue of 10 c.c. of the milk by the Kjeldahl method. The milk may be measured directly into the Kjeldahl flask and evaporated therein, before adding the sulphuric acid. The percentage of nitrogen found may be multiplied by the usual factor, 6·25. Some chemists, however, employ the figure 6·3, on the supposition that the milk-albuminoids contain less than 16 per cent. of nitrogen, namely, 15·87 per cent. It is probable that the factor 6·3 yields results which are very near the truth.

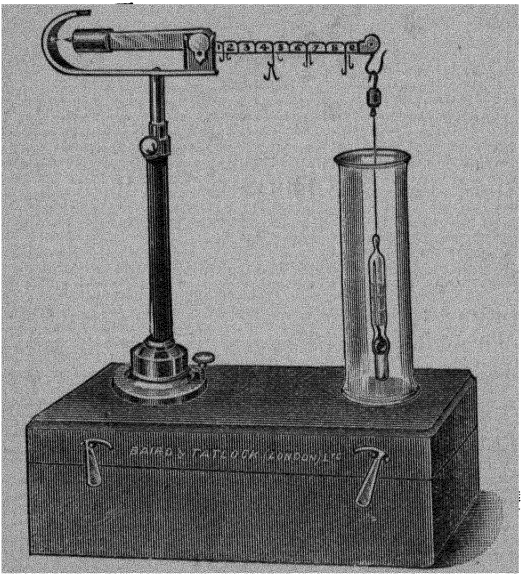

FIG. 42.

When the milk is evaporated directly in the Kjeldahl flask, on distilling with sodium hydroxide frothing sometimes takes place in a troublesome manner. This is due to a small quantity of insoluble volatile fatty acids condensing in the neck of the flask and afterwards saponifying with the caustic soda. The frothing may be prevented by rinsing the neck of the flask—after the digestion with sulphuric acid and cooling—with a little distilled water (about 100 c.c.) into the acid residue, then boiling till about 40 c.c. remain in the flask. Now make alkaline and distil in the usual way.

MILK-SUGAR.—A known weight of the milk, say 20 grams, is to be precipitated with 12 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 in a cylindrical graduated measure, and then diluted so as to measure 400 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 allowed to subside, and an aliquot part, representing 1 or 2 grams of the milk, rendered alkaline with sodium hydroxide, and titrated with Fehling's solution as directed on pp. 301 and 302. 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 very nearly ·7 part of ash in 100. The proportion in any sample may be determined by incinerating the total residue from 10 grams of milk. 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 ·7 and ·8—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, boric acid, phosphoric acid, or some other 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 1 or 2 drops of neutral potassium chromate solution, and titrate with centinormal silver nitrate (p. 211). 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 ·08 per cent. be found, it may fairly be inferred that common salt has been added to the milk.

Whey, buttermilk, and skimmed milk may be analysed as milk, but for the milk-fat determinations larger quantities must be taken.

Skimmed milk, or separated milk, should contain at least 9 per cent. of total solids.

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 complete success.

The Werner-Schmid method described on p. 321 is capable of yielding far more satisfactory results with stale milks than the Adams' method.

NOTE ON THE PROTEINS OF MILK.—Almost the whole of the nitrogenous matters in milk exists in the form of proteins. But caseinogen, generally known as casein, is not the only protein present, although it constitutes rather more than three-fourths of the total. Albumin is present, while there is a third substance of the same group which remains in solution when the casein and albumin have been removed. The albumin 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 albumin 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.

Dirt in Milk. — The sediment from as large a quantity as is available should be collected, washed with water by decantation, and a portion of it examined microscopically for straw, peat fibre, and dung. The main portion is collected on a small filter-paper, a strong solution of cane-sugar run through the paper, and the paper and sediment dried thoroughly at 100° C. Allow to cool, place a drop or two of strong sulphuric acid on the sediment, and run it off the paper. Hold the paper up to the light and examine the sediment with a pocket lens; if bile be present, a fine purple colour will be seen round the particles. [Modification of Pettenkofer's test for bile.]

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 proteins 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 twenty-four 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.

Cream should be tested for preservatives, especially for boron compounds, and for starch and gelatin.

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 16; 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 of 16 is the maximum allowed by the regulations of the Board of Agriculture in genuine *fresh* butter.

WATER.—Warm the sample in a bottle or jar until it just begins to melt, then beat it into the consistency of thick cream in order to thoroughly mix it. Weigh about 5 grams into a small flat porcelain dish containing clean dry sand, previously tared. 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 two or three 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 p. 211, 1 c.c. of which solution corresponds to ·00585 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 ignition 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 boric 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.

CASEIN.—Probably the simplest plan for determining the casein in butter, when it is not desired to make a direct determination of nitrogen, is the following:—

Five 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. 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, at as low a temperature as possible, 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 a 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. In the fourth method, a modification of the third by Polenské, the amounts of soluble and insoluble fatty acids in the butter are determined.

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 hydroxide 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 hydroxide 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 hydroxide 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 required. From this the saponification-equivalent, or the number of grams of fat capable of being saponified by 1 litre of normal alkali, may be calculated. The range in butter-fat varies from 241 to 253, in margarine from 285 to 290.

The result, however, is generally expressed in milligrams of potassium hydroxide required to saponify 1 gram of fat, thus:—No. of c.c. of normal $KHO \times 56{\cdot}1$, and divided by No. of grams of fat used.

Butter gives from 221·5 to 232·4; margarine, from 193·5 to 196·5; coco-nut fat, 246 to 260; lard, 195·4.

(56·1 = equivalent of KHO.)

Rapid Saponification Method.

Five grams of the clarified fat are weighed into a glass basin 4½ in. in diameter and melted on the water-bath. About 1 gram of stick sodium hydroxide 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 basin 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 basin 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 basin 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 ozs. of the filtrate, to which a few drops of phenolphthalein solution have been added, are coloured by the addition of not more than 0·2 c.c. of a decinormal solution of sodium hydroxide. 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 basin 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 basin 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 basin and filter; the result, multiplied by 20, gives the percentage of insoluble fatty acids yielded by the clarified butter-fat. The insoluble fatty acids in genuine butter-fat rarely exceed 88·5, but may reach 89. If the insoluble fatty acids exceed 89·5 the butter-fat is probably adulterated. If the soluble fatty acids fall below 5 per cent., the butter-fat is probably adulterated with margarine.

The Reichert-Meissl-Wollny Method.

5·0 grams of the clear fused butter-fat are introduced into a 300 c.c. flask of the form shown in Fig. 43—length of neck 7 to 8 cm., width of neck 2 cm. Two c.c. of a solution of sodium hydroxide in an equal weight of water, and 10 c.c. of alcohol, of about 92 per cent., are added. The soda solution must be free from carbon dioxide and preserved from the action of atmospheric carbon dioxide. The mixture is heated under a reflux condenser, connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water which have been kept boiling for at least ten minutes are added, and the flask heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of

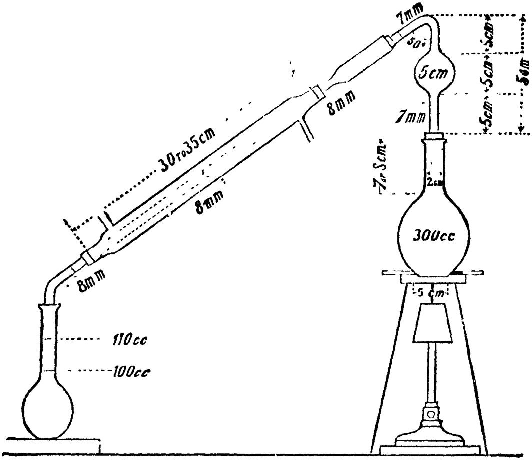

Fig. 43.

pumice or of broken clay tobacco-pipe are added, and the flask at once connected with a condenser by means of a glass tube 7 mm. wide and 15 cm. from the top of the cork to the bend. At a distance of 5 cm. above the cork is a bulb 5 cm. in diameter. The flask is supported on a circular piece of asbestos 12 cm. in diameter, having a hole in the centre 5 cm. in diameter, and is first heated by a very small flame, to fuse the insoluble fatty acids; but the heat must not at first be sufficient to cause the liquid to boil. The heat is gradually increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask; the distillation should take about thirty minutes (twenty-eight to thirty-two minutes). The distillate, which may be turbid, is shaken up, 100 c.c. filtered off through a dry filter-paper, transferred to a beaker, ·5 c.c. of an alcoholic solution of phenolphthalein (1 gram to 100 c.c. alcohol) added, and the filtrate titrated with decinormal alkali solution (sodium hydroxide or baryta). A blank experiment with the same reagents, but omitting the fat, should be made, and the amount of decinormal alkali required to neutralize the distillate found. This should not exceed ·3 c.c. The volume of decinormal solution of alkali used, less the amount obtained in the blank experiment, is multiplied by 1·1. The number so obtained is known as the "Reichert-Wollny number."

According to the recommendations of a Departmental Committee of the Board of Agriculture, a Reichert-Wollny number of 24 is the limit below which the presumption should be raised that the butter is not genuine. The number in pure butter may go up to about 32.

It is necessary, in order to secure accurate results in this process, that carbonic acid should be excluded particularly from the strong sodium hydroxide solution, and that the distillation of the volatile acids should proceed at the same rate and occupy the same time in all experiments.

Polenské's Method for determining Coco-nut Fat in Butter.

Butter frequently contains coco-nut oil as an adulterant; it may be detected and its amount estimated by a modified Reichert-Wollny process devised by Polenské, which estimates the soluble and insoluble volatile fatty acids contained in the fat.

The process is carried out as follows:—Five grams of the dry fat is placed in a 300 c.c. flask with 20 grams of glycerol and 2 c.c. of 50 per cent. sodium hydroxide solution. The mixture is heated over a free flame with constant shaking till the fat is saponified and the liquid suddenly becomes clear: this takes place in from three to five minutes; cool and add 90 c.c. of warm water (50° C.). If the soap is not all dissolved, warm the flask on a water-bath to a temperature of 50° C. The final solution must be clear, and if it is of a dark brown colour the test should not be continued. Now add to the hot soap solution about ·1 gram of powdered pumice [the fineness of ordinary sea-sand] recently ignited, and 50 c.c. of dilute sulphuric acid [25 c.c. of pure strong acid in a litre], and the flask at once attached to the bulb-tube and condenser.

The apparatus must agree in every detail as to the dimensions given in Fig. 44.

Heat the contents of the flask with a small flame until the fatty acids are all melted, then raise the temperature to the boiling-point and regulate the distillation so that 110 c.c. distil in twenty minutes. The condenser should be supplied with water at a temperature not exceeding 20° C. When 110 c.c. has been collected the flame is removed, and the receiving flask replaced by a 20 c.c. cylindrical measure.

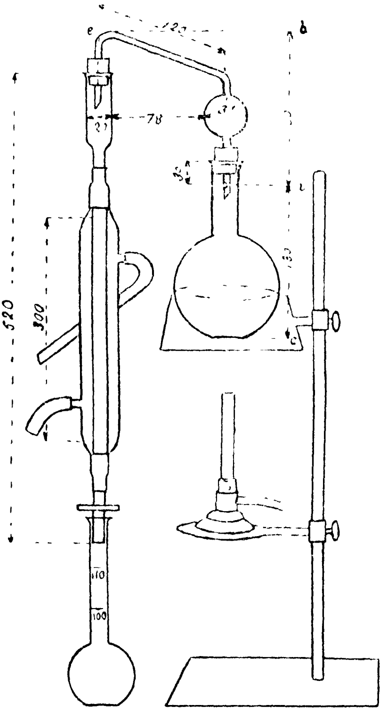

FIG. 44.

Cool the distillate by immersion in water to 15° C., and note the appearance of the insoluble fatty acids, whether in oily drops, semi-solid, or solid masses.

Mix the distillate by turning the flask upside down five or six times. Filter, through a dry, 8 cm. diameter filter-paper, 100 c.c. of the distillate, and titrate with $\frac{N}{10}$ NaHO solution, using as an indicator ·5 c.c. of phenolphthalein solution. The number of c.c. of $\frac{N}{10}$ soda solution used, multiplied by 1·1, gives the Reichert-Wollny number for the volatile fatty acids soluble in water.

The insoluble volatile fatty acids are next determined; wash away the soluble acids from the filter and apparatus by means of three successive lots of 15 c.c. of water which has been passed, severally, through the tube of the condenser, the 20 c.c. upright measure, and the 110 c.c. flask. These washings are not required. The insoluble volatile fatty acids which may be left in the condenser, 20 c.c. measure, 110 c.c. flask, and on the filter, are removed by rinsing these in succession three times with 15 c.c. of neutral 90 per cent. alcohol. [The alcohol is neutralized with $\frac{N}{10}$ NaHO, using phenolphthalein as an indicator.] The filter is the last to be rinsed, and care must be taken that each lot of alcohol passes through the filter before a new 15 c.c. is added.

The alcoholic filtrate containing the insoluble (in water) volatile fatty acids is titrated with $\frac{N}{10}$ NaHO, using ·5 c.c. of phenolphthalein solution as an indicator.

The number of c.c. of $\frac{N}{10}$ NaHO required for this neutralization is known as the Polenské New Butter Value.

Polenské's Values for Pure Butter-Fats.

Number of c.c. of $\frac{N}{10}$ NaOH required for the neutralization of the	
Soluble Volatile Fatty Acids. (Reichert-Wollny Value.)	Insoluble Volatile Fatty Acids (New Butter Value)
19·9	1·35
21·1	1·4
22·5	1·5
23·3	1·6
23·4	1·5
23·6	1·7
24·5	1·6
24·7	1·7
24·8	1·7
24·8	1·6
25·0	1·8
25·1	1·6
25·2	1·6
25·3	1·8
25·4	1·9
25·6	1·7
26·2	1·9
26·5	1·9
26·6	1·8
26·7	2·0
26·8	2·0
26·9	2·1
26·9	1·9
27·5	1·9
27·8	2·2
28·2	2·3
28·4	2·3
28·8	2·2
28·8	2·5
29·4	2·6
29·6	2·8
29·5	2·5
30·1	3·0

Butter-fats giving Reichert-Wollny figures of 24 to 30 for soluble volatile fatty acids require 1·5 to 3·0 c.c. $\frac{N}{10}$ alkali to neutralize the insoluble fatty acids.

Coco-nut oil gives Reichert-Wollny figures for the soluble volatile fatty acids from 6·8 to 7·7, and as much as 16·8 to 17·8 c.c. $\frac{N}{10}$ NaHO for the neutralization of the insoluble volatile fatty acids.

The amount of adulteration of butter with coco-nut oil may be determined approximately from the fact that the amount of $\frac{N}{10}$ NaHO required for the neutralization of the insoluble volatile fatty acids is increased by ·1 c.c. through each addition of 1 per cent. of coco-nut oil.

For example, a portion of the fat obtained from a sample labelled butter gave a Reichert-Wollny figure 25, and the insoluble volatile fatty acids required for neutralization 3 c.c. of $\frac{N}{10}$ NaHO. On referring to the above table, it is found that pure butter-fat with a Reichert-Wollny number of 25 requires only 1·8 c.c. $\frac{N}{10}$ NaHO for neutralization of the insoluble volatile fatty acids, therefore the excess 1·2 c.c. is to be calculated into coco-nut oil; *i.e.*, since ·1 c.c. of alkali is equivalent to 1 per cent., this sample is adjudged to contain 12 per cent. of coco-nut oil. This conclusion must be further tested and the presence or otherwise of phytosterol in the sample be determined.

The phytosterol in coco-nut cake given to milch cows does not pass into the milk.

Coco-nut oil contains from ·1 to ·5 per cent. of unsaponifiable matter composed in part of phytosterol. The presence of phytosterol in a fat is determined as follows.

The purified fat, obtained by melting the fat and sampling, is saponified by heating with alcoholic potash, the alcohol is removed by evaporation, and the remaining alkaline soap solution extracted with ether. Any dissolved soap must be removed from the ether extract by means of water.

The ether is then allowed to evaporate spontaneously when any unsaponifiable matter will be left as a residue. Dissolve such residue in absolute alcohol, filter, and evaporate to dryness on a water-bath in a small porcelain dish. To the residue add 2 c.c. of acetic anhydride, cover the dish and heat to the boiling-point, then evaporate to dryness on a water-bath. Warm the residue with a little absolute alcohol, cool, and allow to crystallize. The crystallized acetates are filtered off and washed with a little 95 per cent. alcohol, and then the melting-point determined. Phytosteryl acetate melts above 125° C. If necessary, further crystallizations should be made; and if the melting-point of the crystals is below 115° C., phytosterol is absent.

The specific gravity of the clarified fat at a temperature of 37·8° C. (100° F.) should be taken. It is necessary to use a pear-shaped specific gravity 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 ·91 to ·9138, assuming water to be 1, whereas oleomargarine and most other fats likely to be used as adulterants have actual densities varying between ·904 and ·907. The specific gravity of pure butter-fat, at a temperature of 15·5°, averages ·9307 when compared with water at the same temperature. The specific gravity of butter-fat, at any temperature above its melting-point up to 100° C., may be taken by means of Westphal's Hydrostatic Balance, and the bath shown in Fig. 45.

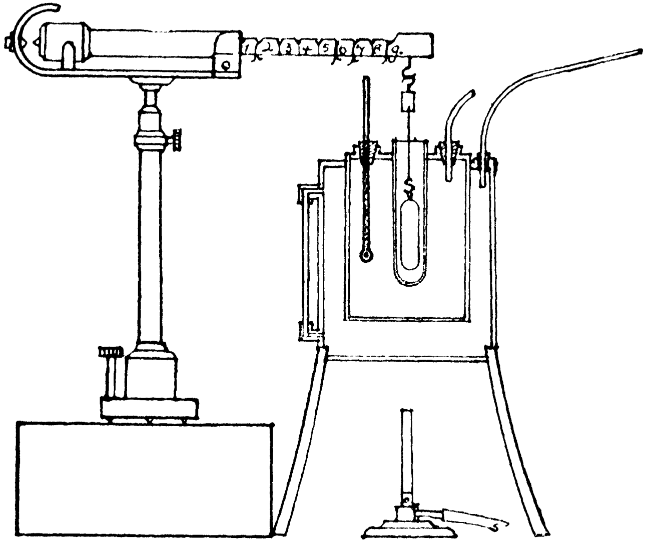

FIG. 15.

The specific gravity of coco-nut oil at 100° C. (water at 15° C. = 1·0) = 0·8736; the specific gravity of butter-fat at the same temperature = 0·865 – 0·868. Fig. 45 shows the apparatus which may be used for taking the specific gravity at the temperature of 100° C.

The *refractive index* of a fat gives useful indications as to its origin ; for this determination special apparatus is required.

The fat of butter contains glycerides of the soluble or volatile acids, butyric, caproic, caprylic, and capric, the first being the most abundant and the last in smallest amount. It also contains glycerides of the insoluble and non-volatile acids, lauric, myristic, palmitic, stearic, and oleic—of these, oleic and palmitic are most abundant and stearic least. The fats used to adulterate butter contain none, or but traces only, of the volatile and soluble acids, and upon this mainly depends the methods used in detecting adulterations of butter with foreign fat.

True butter-fat contains on an average about 88 per cent. of insoluble acids, whilst margarine contains over 95 per cent. Butter-fat contains 5 to 7 per cent. of soluble acids.

But the composition of the fat of genuine butter is liable to variations dependent on the climatic conditions (wet and cold winds in the autumn tend to diminish the volatile acids), on the period of lactation (with increase in length of period the volatile acids diminish), on the nature and amount of the food, on the breed of the cow, and on her idiosyncrasy.

In using the Reichert-Wollny method, about nine-tenths of genuine butter gives a figure between 24 and 32, and the greater part between 26 and 31. In a few cases the number may go up to 35, and in a very few may be as low as 18·4, but the butters yielding these numbers are produced under abnormal or exceptional conditions.

Other fats which are used to adulterate butter (such as margarine, the softer parts of beef-suet) contain practically no volatile acids, and proportionately a higher percentage of insoluble fatty acids. Coco-nut fat may give a Reichert-Wollny figure as high as 7.

The chief determinations which should be made in butter-fat in order to find whether it has been adulterated are: (1) its specific gravity; this at 37·8° C. (= 100° F.) should be near ·9130, the specific gravity of beef-fat is lower and that of coco-nut fat higher. (2) Its refractive index by means of a Zeiss Butyro-Refractometer (see Winter Blyth's Foods) or similar instrument; this often gives valuable indications of adulteration, though the refractive index of genuine butter is between that of two of its commonest adulterants, beef-fat and coco-nut fat. (3) Its saponification value by Koettstorfer's test; and (4) the proportion of volatile acids by the Reichert-Wollny test; this is the most important of all. The results of these tests must be considered together, for by skilful blending of adulterants the detection is made difficult, if not impossible, by the use of one or two tests alone, but a consideration of all will rarely let a case of fraud escape.

The more volatile acids are present the higher will be the specific gravity and the higher the saponification value, but the lower the refraction ; there must be a correlation between these data.

Borax and boric acid are frequently found in samples of fresh butter. They are best tested for in the ash contained in a porcelain basin (p. 56). Salicylic acid is sometimes used to preserve butter. To detect it, shake the butter with twice its volume of 20 per cent. alcohol and add a few drops of dilute ferric chloride solution ; a violet tint indicates salicylic acid.

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 half an hour before drying it in the water-oven

FAT.—Five 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 proteins in cheese are estimated by means of a nitrogen determination, ·5 gram of the dried substance being taken. In decayed cheese, however, the nitrogen exists in other forms than proteins; it may therefore be desirable to adopt the phenol method (see p. 299) for determining the 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 basin, 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. 326. 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 phenolphthalein, and then titrating with the alkali solution employed in nitrogen determinations until a faint pink colour is produced: 1 c.c. of that solution corresponds to ·009 gram of lactic acid. The acid present is assumed to be lactic, although butyric acid is also present in old cheeses.

AMMONIA.—Besides the proteins and certain organic compounds derived from them (leucine, tyrosine, etc.), 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. 268).

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 an 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. 211).

The addition of margarine 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 50 grams are hung in a bag over a beaker on the water-bath, and the fat collected in the beaker. Or, take 40 grams of blue vitriol, make it anhydrous by gentle heat, and mix it well with 20 grams of the cheese; the mixture is 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. Two 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 hydroxide in alcohol of ·835 specific gravity (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 fifteen minutes. Ten c.c. of alcohol with a few drops of alcoholic phenolphthalein 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 222 milligrams of KHO per gram of fat. If, however, the KHO consumed lies below this limit, then a portion of the extracted fat should be examined by the Reichert-Wollny method.

The colouring of cheese is commonly 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.

Paraffin is sometimes present in adulterated margarine and butter. To detect it, use Holder's test. About 10 drops (·3 gram) of melted fat is saponified with 5 c.c. alcoholic potash ($\frac{N}{2}$ KHO); to the clear liquid cold water is slowly added, about 1 c.c. at a time; if paraffin be absent, the solution remains clear with the addition of water up to 5 c.c. If paraffin be present, the solution becomes turbid or a distinct precipitate is given, according to the amount present. An addition of about 1 per cent. of paraffin to the fat can be so detected.

To estimate the amount of paraffin, 10 grams of the fat are saponified with 4 c.c. of a 40 per cent. solution of caustic soda and 25 c.c. of 90 per cent. alcohol. The solution of soap is diluted with 15 c.c. of water, gradually added, and shaken up twice in a separating-funnel with its own volume of petroleum ether (B.P. under 60°). The petroleum ether after separation is shaken up with 25 c.c. of 50 per cent. alcohol, to remove any dissolved soap; the separated petroleum is then evaporated or distilled off, and the residue weighed and examined for paraffin wax.

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 1 part of the tincture is mixed with 3 parts of a saturated solution of ammonium carbonate, and the mixed solution diluted with three 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-lb. loaf, the sample will, after standing for half an hour, assume a dark violet-blue tinge, the colour becoming more marked on drying. 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. With sour bread the reaction is not trustworthy.

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:—One hundred grams of the bread are carefully burnt to ash in a platinum dish. This ash is fused with three or four 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 (free from alumina) 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 a little sodium phosphate, 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 and in the sodium phosphate 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 2 lbs. of the flour examined, or by multiplying by 1084 we obtain the number of grains of potash-alum contained in a 4-lb. loaf, which is the mode in which the results of the analysis are usually reported in this country.

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, and true proteins in bread may be readily determined by processes already given in the *Guide* (see pp. 284 *et. seq.*).

DECIMAL MULTIPLIERS

[*Calculated from Latest International Atomic Weights*]

$BaSO_4$ × ·343 = SO_3
,, × ·4202 = H_2SO_4
,, × ·7465 = K_2SO_4
,, × ·5661 = $(NH_4)_2SO_4$

CaO × 1·7845 = CaO_3
,, × 2·4275 = $CaSO_4$

$CaCO_3$ × 0·5602 = CaO
,, × 1·3604 = $CaSO_4$

$CaH_4P_2O_8$ × 1·3251 = $Ca_3P_2O_8$

$Ca_3P_2O_8$ × ·4578 = P_2O_5
,, × ·7544 = $CaH_4P_2O_8$

Cl × 1·6486 = $NaCl$

K_2PtCl_6 × ·1938 = K_2O
,, × ·3584 = K_2SO_4
,, × ·3067 = $2KCl$

K_2O × 1·538 = $2KCl$
,, × 1·85 = K_2SO_4
,, × 2·1467 = $2KNO_3$

K_2SO_4 × ·5405 = K_2O

$2KCl$ × ·6317 = K_2O.

N × 1·2158 = NH_3
,, × 4·498 = HNO_3
,, × 6·0678 = $NaNO_3$
,, × 7·2169 = KNO_3
,, × 6·25 = Albuminoids

NH_3 × 0·8224 = N
,, × 3·88 = $(NH_4)_2SO_4$

$NaCl$ × ·6066 = Cl

$2NaCl$ × ·5304 = Na_2O

Na_2SO_4 × ·4364 = Na_2O

P_2O_5 × 2·1844 = $Ca_3P_2O_8$

$Mg_2P_2O_7$ × 0·3619 = $2MgO$
,, × 1·0811 = $2MgSO_4$
,, × 1·0515 = $CaH_4P_2O_8$
,, × 1·939 = $Ca_3P_2O_8$
,, × 0·6379 = P_2O_5

SO_3 × 1·7 = $CaSO_4$
,, × 2·15 = $CaSO_4 2H_2O$

The Analyst's Laboratory Companion, by A. E. Johnston, published by J. A. Churchhill, gives a large number of arithmetical data and useful hints and information to the analyst.

COMPOSITION OF MANURES

Approximate Usual Percentage Contents in	N.	P_2O_5.	K_2O.
Ammonium Sulphate	20	..	..
Sodium Nitrate	15·5	..	...
Potassium Nitrate	13	..	43
Calcium Nitrate	13	..	..
Calcium Cyanamide	18	.	...
Soot	3	..	...
Shoddy	7	...	..
Hair, feathers, etc.	14	...	..
Dried flesh	8	...	...
Dried blood	10	1	...
Peruvian Guano (varies widely)	9	14	..
Ichaboe Guano	8	10	...
Bolivian Guano	1	33	..
Fish Guano	9	8	..
Meat Guano	11	3	..
Bone Meal	4	22	...
Steamed Bones	1	29	..
Animal Charcoal	0·5	29	..
Bone Ash	...	36	...
Bone Superphsophate	2	13	...
Mineral Superphosphate	...	13 to 18	...
Basic Superphosphate	...	12	...
Basic Slag (varies)	...	14 to 20	...
Coprolites, Phosphorite, etc.	...	25	...
Apatite	...	36	...
Precipitated Phosphate	.	35	...
Kainite	...	...	13
Sylvinite	.	..	12
Concentrated Potash Salts	..		50
Potassium Sulphate	..	...	45
Potassium Chloride (Muriate)	..	..	50
Wood Ashes	..	3	7
Rape Cake	5	2	1·3
Castor Cake	6	1·8	1
Farmyard Manure	0·5	0·3	0·6
Sewage Sludge	1	1	...

INDEX

APPARATUS

BESIDES the water-bath, water-oven, blowpipe-table, sand-bath, condensers, 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 (dilute).
Hydrochloric acid (dilute).
Hydrosulphuric acid
Nitric acid (dilute).
Sulphuric acid (dilute).
Sodium acetate.
Sodium carbonate.
Sodium hydroxide.
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. 79 to 91 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, etc., 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 basins (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).
Bunsen burner, or glass spirit-lamp.
Retort stand and clamp.
Retort, stoppered (6 oz.).
Quill-tubing.
Crucible-tongs.
Mouth-blowpipe.
Platinum foil and wire.
Square of wire gauze.
Round iron sand-bath.
Round file; triangular file.
Pair of scissors.
Triangle.
Scales with glass pans, and weights.
Corks.
Vulcanized caoutchouc tubing.
Test-papers.
Packets of cut filters (3), to fit the funnels.
Duster.

PART II

Qualitative Analysis

Beakers, a second small set.
Spirit of wine (4 oz.).
Square of dark-blue glass.
Swedish or German filter-paper.
Spatula.

PART III

Quantitative Analysis

Mohr's 50 c.c. burette and stand.
10 c.c. and 20 c.c. pipettes.
Stoppered tube for weighing filter-papers.
Platinum wire.
Platinum crucible and cover, *or*
Fused quartz crucible.
Iron-wire triangles covered with silica (2).

Filter-stands (2).
Stoppered bottles for standard solutions of acid and alkali.
Kjeldahl's flasks (2).
Wash-bottle for ammonia.
Beakers, large (4).
Funnels, large (4).
500 c.c. measure.
100 c.c. cylindrical measure.
Desiccator.
Carbon-dioxide apparatus.
Wide-mouth corked phials, 2 oz. (4).
Clock-glasses (4).
Cut-filters, assorted.
Sheet of glazed paper.
Camel's-hair brush.
Glass stirring-rods.
Pair of watch-glasses, with ground edges and clips.

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