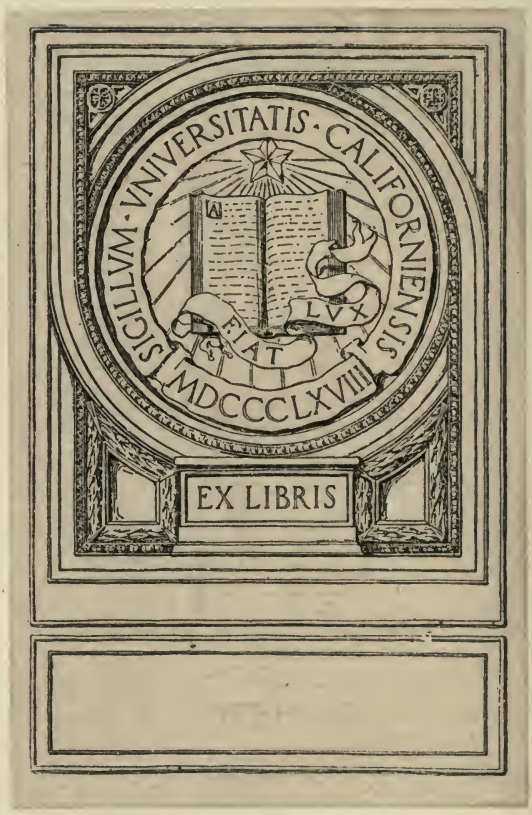
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AGRICULTURAL ANALYSIS

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A MANUAL OF QUANTITATIVE ANALYSIS FOR STUDENTS OF AGRICULTURE

BY

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PREFACE

THIS book is intended for those students of Agricultural Chemistry who desire a knowledge of commercial quantitative analysis.

The first two chapters deal with ordinary quantitative analysis, and may be omitted by those who have already received a general training in practical chemistry. The remainder of the book contains an account of those processes which the experience of many workers has shown to be the most useful to the agricultural analyst.

In this second edition the original arrangement of the book has been retained, but the chapters on the analysis of dairy produce and of water have been re-written.

It would be well-nigh impossible, in a volume of this size, to acknowledge all the sources to which I am indebted for assistance, but the mass of the information here given was acquired whilst working in the laboratory of the Royal Agricultural Society of

England. For the training received there, and for many courtesies shown since then, my most hearty thanks are due to Dr. J. Augustus Voelcker.

My thanks are also due to Dr. Clowes and Mr. J. B. Coleman, for permission to use several wood-cuts from their manual of quantitative analysis.

F. T. A.

St. George's Hospital, s.w., 1904.

CONTENTS

PART I

OPERATIONS USED IN QUANTITATIVE ANALYSIS

PART II

THE MORE COMMON ESTIMATIONS OCCURRING IN AGRICULTURAL ANALYSIS

SECTION I.—GRAVIMETRIC ESTIMATIONS

SECTION II.—VOLUMETRIC ESTIMATIONS

PART III

THE ESTIMATION OF NITROGEN

PART IV

SAMPLES AND SAMPLING

PART V

THE ANALYSIS OF FEEDING MATERIALS

PART VI

THE ANALYSIS AND VALUATION OF MANURES

PART VII

SOIL ANALYSIS

PART VIII

THE ANALYSIS OF DAIRY PRODUCE

PART IX

WATER ANALYSIS

AGRICULTURAL ANALYSIS

PART I

OPERATIONS USED IN QUANTITATIVE ANALYSIS

THE student who has hitherto confined his attention to general experiments and **qualitative** analysis, will find that **quantitative** work demands a new kind of skill.

It is really an art arising from the Science of Chemistry, and just as every other art has its own special technique, so the art of quantitative analysis can only be acquired by those who have mastered certain simple operations, and have become familiar with certain instruments. The chief of these operations are set out, and the principal instruments are described, in the following paragraphs:

1. The **balances** which are used in different laboratories vary so considerably that it is better to leave all explanation of their working in the hands of the teacher.

2. The **weights,** however, are generally of one description. In the assay of metalliferous ores the grain is usually taken as a standard of weight, but for all the purposes of the agricultural chemist the French or metric system will be found most convenient.

Fig. 1 represents a box of gram weights, which are arranged in the following order :

Brass.	Platinum.	Gold Wire.	Brass.	Platinum.	Gold Wire.
100	·5	·01	1	·01	—
50	·2	·01	1	·005	—
20	·1	·01	1	·002	—
10	·1	·01	—	·002	—
10	·05	·01	—	·001	—
5	·02	—	—	·001	—
2	·01	—	—	·001	—

Of these, the six smallest platinum weights are not as a rule used, their place being taken by one of the weights in the third column. These are known as 'riders' (paragraph 3).

Fig. 1.—Box of Weights.

In a laboratory where the balance is in constant use it is a very convenient plan to keep the weights most commonly used on a piece of cardboard, just inside the balance case. The

cardboard should be marked off as in fig. 2, each square being covered with the weight whose value is written upon it.

3. The **rider** is a piece of wire bent so that it may be placed on the graduated beam of the balance as shown in

50	20	10	10
5	2	1	1
·5	·2	·1	·1
·05	·02	·01	·01

FIG. 2.—Card.

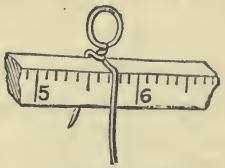

FIG. 3.—Rider.

fig. 3. Each division of the beam corresponds to a milligram (·001). The use of the rider, therefore, obviates the troublesome work of using very small platinum weights.

DIRECTIONS FOR WEIGHING

4. A few minutes' instruction from a teacher will be found more valuable than written advice. The following rules will, however, be of use :

(*a*) See that the scale pans are free from dust. If not, cleanse them with a large camel's-hair brush.

(*b*) Always test the balance before using by releasing the beam and allowing it to swing. The swings, as indicated by the pointer, should be equal in each direction. If the balance be not accurate, it must be adjusted.

The two most common attachments for effecting this adjustment are :

1. A small lever at the centre of the beam, which may be bent over towards the pan which is too light.

2. A nut running on a finely threaded screw at the end of the beam, which may be screwed towards, or away from, the centre as required.

(*c*) Place the substance to be weighed on the left-hand pan, reserving the right-hand pan for the weights.

(*d*) Always add the weights systematically in the order in

which they are placed in the box or on the card. If the weight on the pan be too heavy, remove it and add the next lighter weight. When you have thus arrived at a weight just too light, leave it on the pan and begin adding the weights belonging to the next decimal place, commencing, as before, with the heaviest. When all the weights on the card have been tried, get the final weight accurately with the rider.

(*e*) Always raise the beam from its bearings before adding or removing a weight.

(*f*) Never weigh out a substance by placing it directly on the scale pan, but place it in some weighed vessel of glass, porcelain, or platinum.

(*g*) Never weigh substances or vessels whilst they are either hotter or colder than the air inside the balance case.

EXERCISE I.—Carefully clean a pair of watch glasses fitted with a clip, and weigh them. Powder some oxalic acid. Place a small quantity—about a gram—in the watch glasses and weigh again.

Enter the results in your note-book, thus :

Watch glasses + clip + $H_2C_2O_4 2H_2O$	=
Watch glasses + clip	=
$H_2C_2O_4 2H_2O$	=

Place the watch glasses with the acid in a desiccator (fig. 4).

DESICCATORS

5. The **desiccator** (fig. 4) is an apparatus which is intended to prevent hygroscopic substances from gaining weight by absorption of water.

Substances which have been heated are apt to condense moisture on their surfaces when cooling, and thus to increase in weight. To prevent this a desiccator is used. The apparatus shown in fig. 4 is a very convenient form. It consists of a *nearly* air-tight vessel, the air of which is constantly kept dry

by either lumps of calcium chloride or pieces of pumice saturated with strong sulphuric acid. The latter is objectionable from the fact that in carrying the desiccator about the acid is apt to be splashed up on to the substances above it. A very convenient method of charging the desiccator is to put a couple of handfuls of dry washed sand in the bottom compartment, and pour just sufficient strong sulphuric acid on to the sand to form a firm mass which will not splash about.

Fig. 4.— Desiccator.

A large desiccator capable of holding larger vessels is made by placing a bell jar on a greased ground-glass plate. Inside the chamber thus formed is placed a glass dish containing some drying agent and covered with a piece of perforated zinc.

If a desiccator be quite air-tight, the air which has been heated by the introduction of a hot vessel will contract as it cools. When such a desiccator is opened the draught caused by the inrush of air will often displace light substances from the vessel in which they are contained, and thus spoil analyses at the last moment. This may be avoided by making a deep file-mark on the rim of the vessel, which, when the lid is replaced, will leave a fine communication between the outer and inner air. This will not render the desiccator any less reliable.

DRYING OF SOLIDS

6. The water contained in many solid bodies is of two kinds, viz. :—Adherent water or *moisture*, and combined water or *water of crystallisation*. Moisture may always be removed

by heating for a longer or shorter time at 100° C., but combined water often requires a very much higher temperature for its removal.

7. The apparatus used for keeping substances at a constant temperature of 100° C., or thereabouts, is shown in fig. 5. It is known as a *steam oven*, and consists of a copper oven with a double coating. The interval between the two coatings is

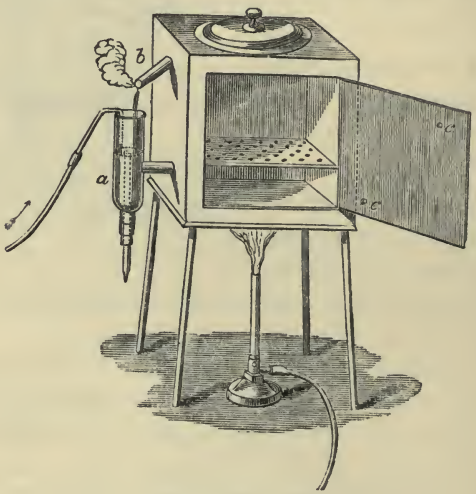

FIG. 5.—Steam Oven.

partly filled with water. At one side is an arrangement for keeping the water at a constant level in the oven.

EXERCISE II.—Place the watch glass containing the oxalic acid which has been weighed out in Exercise I. in the steam oven, leaving the clamp in the desiccator. After it has been heated for two hours, replace the clamp and allow the whole to cool in the desiccator; then weigh it. Again remove the clamp and restore to the oven for half-an-hour, allow to cool in the desiccator, and weigh. Repeat this process until two consecutive weighings do not differ by more than one milligram. It may now be presumed that all the moisture which can be driven off at 100° C. has gone.

Enter the results under those of the last example, thus :

After drying i. . .
,, ,, ii. . .
,, ,, iii. . .
Loss . . .

The loss is calculated by subtracting the last weighing from the weighing obtained in Example I.

Multiply this 'loss' by 100 and divide by the weight of acid used ; the quotient will give the percentage of water which has been lost.

8. For drying at temperatures between 100° and 200° C., an *air oven* is used. This is very similar to the steam oven. The space between the inner and outer coatings is occupied by air, whilst through a hole in the top is inserted a thermometer held in position by a perforated cork.

Should it be necessary to keep this bath at a constant temperature for any length of time, some form of *regulator* may be used. The one represented in fig. 6 is both simple and convenient. A is a bulb about $\frac{5}{8}$ inch diameter, blown at the end of a piece of $\frac{3}{8}$-inch glass tubing 5 inches long. An inch from the other end is a side tube (C). B is a piece of copper tube $\frac{1}{4}$ inch diameter, fitted into the bulb tube by a sound cork. The end of the copper tube D is slit up with a fine saw for about an inch. The bulb is filled with mercury, and the whole apparatus is fitted by a split cork into the top of the air oven. B is connected with the gas supply, and C with the burner which heats the oven. Should the oven become too hot, the mercury will rise and close the slit D through which

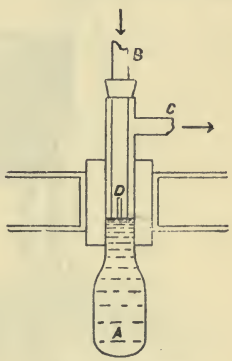

FIG. 6.—Regulator.

the gas passes. Thus after a while the temperature of the bath becomes constant. This constant temperature may easily be altered by sliding the tube B in or out of the bulb tube. If slid in, the gas supply is decreased, and *vice versâ*.

EXERCISE III.—Weigh out about 1 gram of barium chloride as before, and heat in the air bath at 120° C. until of constant weight. Calculate the percentage of combined water as in Exercise II.

FIG. 7.—Water Bath.

EVAPORATION OF LIQUIDS

9. In quantitative analysis it is usual to evaporate liquids at a temperature just below their boiling-point. This prevents loss by spirting. Figs. 7 and 8 show convenient forms of

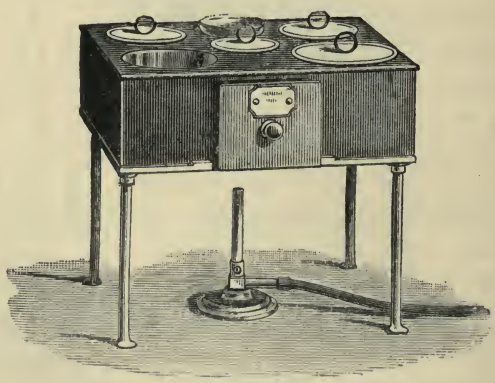

FIG. 8.

water bath, though should the bath be kept in work continuously it will be necessary to have some attachment to

keep the water at a constant level. Such an attachment is shown in fig. 5 on a steam oven.

Either porcelain, platinum, or nickel vessels may be used for evaporation, but the most generally useful is a beaker of the form shown in fig. 9. This may be generally procured of

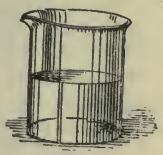

FIG. 9.

FIG. 10.

very thin glass, which allows the heat to pass freely from the water in the bath to the liquid in the beaker, and moreover its shape allows it to touch the water (see fig. 10), which keeps it at a higher temperature than is the case with a vessel simply immersed in the steam.

Another method of evaporation will be found in paragraph 339, fig. 49.

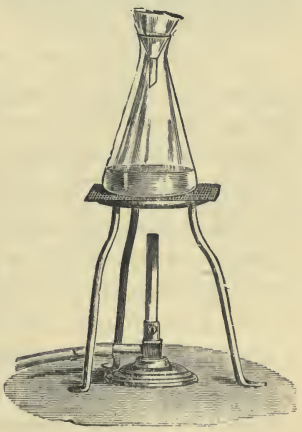

FIG. 11.

SOLUTION OF SOLIDS

10. Solution is usually accelerated by heat, therefore substances soluble in water should be dissolved by heating with water in a beaker over a Bunsen flame.

Should any gas be evolved during the process of solution—*e.g.*, when chalk or Iceland spar is dissolved in hydrochloric acid—precautions must be taken to prevent loss by spirting. Fig. 11 shows a very useful arrangement.

EXERCISE IV.—Weigh a clean watch glass, place upon it about half a gram of a mixture of sand and chalk, and weigh again. Enter the results in your note book. Place a funnel in the mouth of a conical flask, as shown in fig. 11, and wash the powder off your watch glass into the funnel with water from a wash-bottle jet. When all the powder has thus been transferred to the flask, pour dilute hydrochloric acid, a little at a time, through the funnel into the flask until effervescence ceases. Heat the liquid to boiling in order that all the carbonic acid may be expelled. Remove the funnel, and wash it, both inside and out, with the spray of a wash bottle, allowing the drops to fall into the flask. Cover the glass with a watch glass, and keep for Exercise VI.

PRECIPITATION

11. The student will be perfectly familiar with this operation after having studied qualitative analysis. Certain special precautions must, however, be taken when the contents of the filter have to be weighed.

(*a*) The precipitation must be complete. This is best explained by taking an example. Suppose that it were necessary to determine how much iron is contained in a certain solution of ferric chloride. The addition of ammonia will give a precipitate of ferric hydrate; but before this precipitate is weighed it is necessary to ascertain whether sufficient ammonia has been added to precipitate *the whole* of the iron. This may be done by allowing the precipitate to subside and adding a little more ammonia. If no further precipitate be formed, then the precipitation is complete.

(*b*) Large excess of the precipitant is to be avoided.

(*c*) The precipitate must be obtained in a condition which will not readily pass through the filter paper. In some cases this takes place naturally, as in the precipitation of $Fe_2(OH)_6$; but in others it causes considerable difficulty—*e.g.*, barium sulphate. In many cases a good granular precipitate may be

obtained by having *both solution and precipitant* at the boiling point when mixing them.

(*d*) Whenever hot water has no solvent action on the precipitate, it should be thrown down and filtered whilst the solution is hot.

(*e*) When pouring a liquid from one vessel to another, pour it down a wet glass rod one of whose extremities touches the side of the vessel (see fig. 12). This prevents loss by splashing.

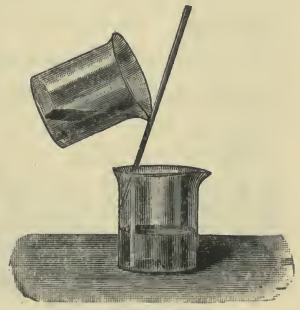

Fig. 12.

Exercise V.—Weigh out on a watch glass about ·5 gram of ammonia alum. Place this in an 8-oz. beaker, and pour upon it about 50 c.c. of boiling distilled water. Stir up the liquid with a clean glass rod until all the solid has dissolved. Now pour dilute ammonia carefully down the side of the vessel until precipitation is complete—*i.e.*, until, after stirring, the liquid smells of ammonia. It is easy to make a mistake in testing by the smell of ammonia, as it is quite possible that the air in the beaker may contain a little ammonia gas even before the liquid has become ammoniacal. It is therefore necessary to blow the ammonia fumes away before smelling; or a piece of red litmus paper may be added. When this has become blue the liquid contains excess of ammonia. Place the beaker over a Bunsen burner and heat just to boiling, keeping it covered the while with a clock glass. Place the beaker on one side to settle.

FILTRATION AND WASHING

12. These operations are exactly like the ones with which the student is familiar. More care, however, is required for quantitative than for qualitative analysis. The following instructions will show the principal precautions required:

(*a*) Special quantitative filter paper should be used. This

paper is very even in structure, and has been washed free from most of its mineral matter by acids. A 9-cm. filter paper when burned should not leave a milligram of ash.

(*b*) The precipitate should be allowed to subside, and the clear liquid poured down a glass rod into the filter (see fig. 13).

(*c*) The tip of the filter funnel should touch the edge of the beaker which is to receive the filtrate. This will prevent splashing.

(*d*) The precipitate should be washed, when possible, by decantation. When as much of the liquid as can be poured out without removing the sediment has been transferred to the filter, hot water is poured on to the precipitate which is still in the beaker, and it is allowed to settle. The clear liquid is again poured off as before, and the operation is repeated until the filtrate is pure water. Finally, the precipitate is transferred to the filter, the last portions being washed on to the paper by the wash-bottle spray. Should any portions adhere to the side of the beaker, they may be removed by rubbing with a glass rod tipped with a piece of india-rubber tubing.

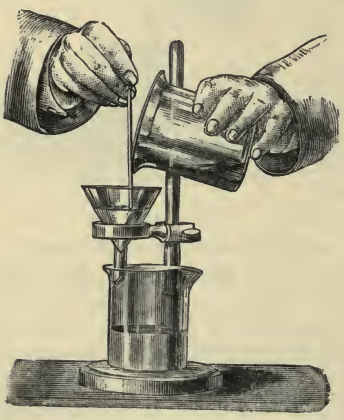

FIG. 13.—Filtration.

(*e*) Never use a glass rod tipped with india-rubber except for the operation above mentioned. If such a rod be placed in a liquid during precipitation, some of the precipitate may get in between the rod and the rubber and thus be lost.

(*f*) Never fill your filter with liquid, or some of the precipitate may escape over the edge of the paper.

(*g*) Allow each portion of washing liquid to drain away before adding the next.

(*h*) Always evaporate the final washings to see that no further impurity is being removed from the precipitate.

A general method of doing this is as follows : Take a piece of thin glass (cheap window glass will do) and cut it into strips about three inches long by half an inch wide. Thoroughly clean one of these strips, and collect a few drops of the filtrate on its surface. Next lay it across the mouth of an Argand burner which is burning with a very low flame, and allow the drop of liquid to evaporate. No residue should be left on the surface.

Of course this method does not apply in cases where the precipitate has to be washed free from acid, but this is easily shown by litmus paper.

It should be remembered that although a residue of acid or of ammonium salts left in a precipitate is entirely driven off in the subsequent ignition, still much harm may be done by the action of these substances on the filter paper, making it brittle and difficult to handle.

EXERCISE VI.—Filter the liquid contained in the flask after Exercise IV. through a 9 cm. filter, taking care to observe all the precautions above mentioned, washing with hot water by decantation until the filtrate is perfectly free from solid matter. Keep the precipitate for the following exercise.

WASH BOTTLES

13. From the student's work in qualitative analysis he will be familiar with the construction and use of the ordinary *wash bottle*. It will be found very convenient to keep two wash bottles for quantitative work, one for cold and the other for hot water.

14. Occasionally other liquids besides water are necessary for washing certain precipitates; for instance, ammonium phospho-molybdate must be washed with dilute nitric acid, and ammonium magnesium phosphate must be washed with dilute ammonia. In all cases where the washing liquid gives off objectionable fumes a *special form of wash bottle* is necessary. The stopper is drilled with three holes (see fig. 14) which contain respectively a short tube terminating both just inside and just outside the stopper (*a*, fig. 14), an ordinary tube with a jet (*b*, fig. 14), and a blowing tube with a trap to prevent the fumes from passing back into the mouth (*c*, fig. 14). This trap is very simple in its structure, consisting merely of a piece of india-rubber tubing stopped up at one end by a piece of glass rod, and having a longitudinal slit about half-an-inch long cut in one side of it. In using this wash bottle the operator must keep his finger on the tube *a* whilst blowing, and remove it when he wants the spray to cease, otherwise it will continue to run for some little time after the blowing has been stopped.

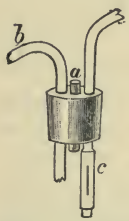

FIG. 14.—Ammonia Wash Bottle.

THE FILTER PUMP

15. In laboratories where a good pressure of water is obtainable filtration may be greatly accelerated by the use of the filter pump. A very convenient form of apparatus is shown in fig. 15. A is a Geissler's filter pump; B is a bottle with a good cork doubly pierced; and C is a stout flask having a tube sealed in one side of its neck. By means of the pump a partial vacuum is caused in C, so that the pressure of the air outside forces the liquid through the filter into the

flask. In using the filter pump the following precautions must be taken :

(*a*) Place a small platinum cone at the bottom of the funnel to prevent the breaking of the filter paper.

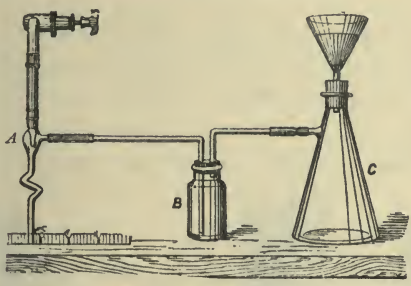

FIG. 15.—Filter Pump.

(*b*) See that the paper fits exactly into the funnel.

(*c*) Turn on the water in the pump very gradually.

(*d*) Never allow the filter to become quite empty.

DRYING PRECIPITATES

16. The method of drying depends on the treatment which is to follow. If, as is most usual, the filter paper is to be burned and the precipitate ignited and weighed, then the drying may be carried on rapidly in an air oven. A very convenient filter drier is easily made from an old biscuit tin. A line is drawn round the tin four inches from the top. Sixteen holes, four on each side, are made in the tin along this line. A piece of No. 16 B.W.G. copper wire is threaded backwards and forwards through these holes, so as to form a network inside the tin, with meshes parallel to its sides. The tin may now be placed on a large tripod in such a manner that the network of wires is in a horizontal plane. The funnel, covered with a piece of filter paper, is placed upright in one of the

meshes, and the cover placed loosely on the tin, which is heated by means of a Bunsen burner.

IGNITION OF PRECIPITATES

17. For this operation vessels made of porcelain, nickel, and platinum are used. Of these the platinum vessel is the most convenient, but unfortunately it tends to form fusible alloys with the heavy metals. The agricultural analyst, however, has so very seldom to ignite precipitates which are hurtful to

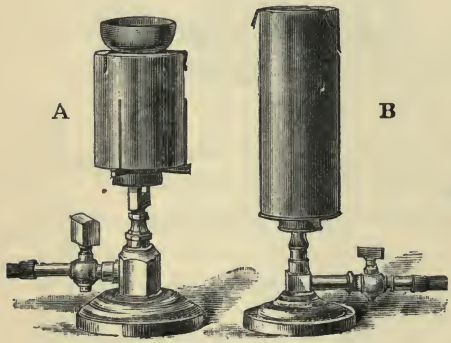

FIG. 16.—Argands.

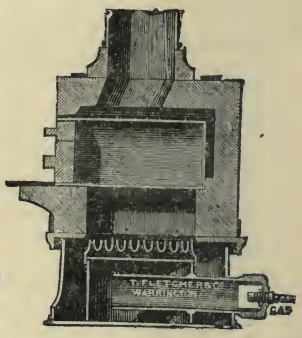

FIG. 17.—Fletcher.

platinum that he may use vessels of that metal almost exclusively. The most useful form is a capsule 1 inch deep by 2 inches diameter, as shown in fig. 16.

18. When a platinum vessel is frequently heated over a Bunsen flame it tends to blister, and a grey deposit forms where the flame has touched it. After a little while it begins to lose weight, and in time the capsule becomes worn out.

This may be avoided in a great measure by cleaning the vessel frequently with sea-sand, whose rounded granules smooth down the minute blisters which give the grey appearance.

19. A better plan is never to let a flame touch the platinum. Whenever a precipitate is to be ignited, an *Argand burner* should be used of one of the forms shown in fig. 16.

The support for the capsule is made either of platinum wire, or of iron wire round which has been fastened a strip of platinum foil. Should a higher temperature be required, as in the burning of $CaCO_3$ to CaO, a *Fletcher muffle furnace* may be used (see fig. 17).

BURNING THE FILTER

20. This operation is carried out in several ways, but for the purposes of this book only two need be described.

(*a*) When the burning of the filter has no action on the precipitate, the filter paper may be folded up whilst still wet, placed in a platinum dish, and ignited very gradually over an Argand.

(*b*) In other cases the precipitate, dried as described in paragraph 16, is removed as completely as possible from the filter paper to the dish, and the paper burned in a coil of platinum wire.

If the wire be wound carelessly about the paper, it will probably break after being used a few times, from being continually bent about in different ways. This is avoided by winding the wire in a spiral around a small cone of wood. When required for use the wooden cone is removed and the filter folded up and introduced into the spiral as in fig. 18.

FIG. 18.

The operation of burning is shown in fig. 19. The spiral of wire containing the filter is held over the platinum dish, which stands on a glazed tile. Should the precipitate be dark coloured, a white tile is used; should it be light, a red one is to be preferred. First the paper is ignited by the Bunsen burner,

and allowed to burn quietly until the last spark dies out. Then the burner is used to keep it red hot until all the carbonaceous matter is burned off. The ash is then shaken out into the

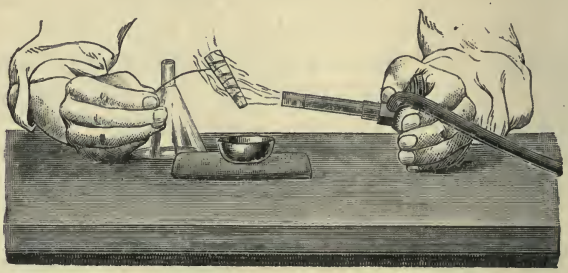

Fig. 19.

dish, and the last traces removed from the wire with a small camel's-hair brush. Finally, any portions of the ash which may have fallen on the tile are swept into the dish. The dish is then ready for ignition and weighing.

Exercise VII.—Carefully clean a platinum dish of the size described in paragraph 17. Place it over an Argand, as in fig. 16, until red hot. Remove it to a desiccator, and when quite cool weigh it. Place the wet filter paper containing the sand which has been washed in performing Exercise VI. in this dish, and heat over an Argand turned down until the flame is as small as possible. Whilst it is drying start Exercise VIII. When steam ceases to come off, turn up the burner until the dish becomes red hot. The paper will catch fire and burn. When nothing is left but the sand and the white ash of the filter paper, remove to a desiccator, and when cool weigh. Enter your results thus :

Dish + sand + ash	=	
Dish	=	_____
Sand + ash	=	
Filter ash	=	_____
Sand	=	

From this calculate what percentage of sand was contained in the mixture dissolved in Exercise IV.

EXERCISE VIII.—Whilst the ignition described above is going on, filter off the alumina precipitate obtained in Exercise V., washing it thoroughly by decantation. Dry in the arrangement described in paragraph 16, and burn it as described in paragraph 20 *b*, first weighing the dish as in Exercise VII. Finally, ignite the dish and precipitate, cool in a desiccator, and weigh. Enter the results just under the entry for Exercise V., and calculate the percentage of Al_2O_3 which you have precipitated out of the ammonia alum.

PART II

THE MORE COMMON ESTIMATIONS OCCURRING IN AGRICULTURAL ANALYSIS

21. No one can expect to attain proficiency in any branch of quantitative analysis unless he first acquire confidence in the accuracy of his work. The most simple way of acquiring confidence is to practise the different estimations on pure substances of known composition. The results are in this way easily checked. By working systematically through this section, using always the substance recommended, the student will gain the necessary confidence and at the same time acquire a knowledge of all the simpler operations used in agricultural analysis.

Always read through the whole of a paragraph before commencing the work described therein.

Section I.—GRAVIMETRIC ESTIMATIONS

ESTIMATION OF IRON

22. **Substance used.**—Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$.

Method employed.—The iron is precipitated as ferric hydrate and weighed as ferric oxide, Fe_2O_3.

Weigh out in a watch glass about ·5 gram of pure ferrous ammonium sulphate which has been finely powdered and pressed between folds of filter paper. Transfer this to a 10-oz. beaker, washing the last traces of substance from the watch glass by means of the wash bottle, and dissolve in about

30 c.c. of hot water, using a few drops of dilute H_2SO_4 to clear the solution. The water must be poured down the sides of the beaker to avoid all risk of splashing.

23. **Precipitation.**—Raise the liquid to boiling-point over a Bunsen burner, and add gradually 5 c.c. of strong nitric acid. The liquid, which has hitherto been only just coloured, will now acquire a deep-yellow tint from the oxidation of the ferrous to a ferric salt. After it has boiled for a few seconds remove it from the burner, and add dilute ammonia (3 of distilled water to 1 of strong ammonia) cautiously. Stir with a glass rod. Place a very small piece of litmus paper in the beaker. Continue adding ammonia until the litmus paper shows a distinctly alkaline reaction. A flocculent precipitate of ferric hydrate will be thrown down. Cover the beaker with a clock glass, replace it over a Bunsen flame, and allow it to boil for about a minute. Turn out the light, and allow the precipitate to settle.

It is very convenient to have a small wash bottle of about 8 oz. capacity containing ammonia, the jet of liquid being much preferable to the unmanageable stream which comes from the mouth of a bottle. The special form of wash bottle described in paragraph 14 is, however, necessary. The ordinary form would often fill the operator's mouth with ammonia fumes.

24. **Filtration and Washing.**—Whilst the precipitate is settling, fit a 9-cm. filter paper into a clean glass funnel, and moisten it with hot water. When the precipitate has settled smear the outside of the lip of the beaker with the smallest possible quantity of lard or vaseline, and pour the clear liquid down a clean glass rod into the filter paper. Wash the precipitate by decantation exactly as directed in paragraph 12 (*d*).

25. **Drying, Igniting, and Weighing.**—Cover the top of the funnel with a piece of filter paper, and dry it in the oven described in paragraph 16. Whilst it is drying clean a

platinum dish 2 inches in diameter by 1 inch in depth. Heat it to redness over an Argand. Allow it to cool in a desiccator and weigh it. Enter the result as shown below. Place the dish on a clean white glazed tile, and transfer into it as much as possible of the dried precipitate. Burn the filter paper in a spiral of platinum wire exactly as directed in paragraph 20. Shake the ash into the dish. With a small camel's-hair brush sweep into the dish every particle which has drifted over on to the tile. Place the dish with its contents over an Argand, and ignite at a red heat for two or three minutes, or until any scrap of charred filter which has escaped burning in the wire is completely reduced to ash. Allow to cool in a desiccator, and weigh.

26. **Entry and Calculation.**—The following example shows the method of entry in the laboratory note book. The weights are entered on the right-hand page, and the calculations made on the left:

$2Fe + 3O = Fe_2O_3$.
$112 + 48 = 160$.
$\therefore$ 160 Fe_2O_3 contains 112 Fe
1 ,, ,, 112
160

·0941 ,, ,, $\frac{7 \quad \cdot0941 \times 112}{160}$
10

·0941
·7
·06587 = Fe

4638) 6587 (14·20 % Fe
4638
19490
18552
9380
9276
104

Percentage of Fe found = 14·20
,, calculated = 14·29

Glass + $Fe(NH_4)_2(SO_4)_2 6H_2O$	= 6·0832
Glass	= 5·6194
$Fe(NH_4)_2(SO_4)_2 6H_2O$	= ·4638
Dish + Fe_2O_3 + Ash	= 16·1744
Dish	= 16·0798
Fe_2O_3 + Ash	= ·0946
Ash	= ·0005
Fe_2O_3	= ·0941

ESTIMATION OF SULPHURIC ACID (SO_3)

27. **Substance used.**—Copper sulphate, $CuSO_4.5H_2O$.

Method employed.—The SO_3 is precipitated by barium chloride and weighed as barium sulphate.

Weigh out about ·5 gram of pure crystallised copper sulphate on a watch glass. Transfer to a 10-oz. beaker, and dissolve as in the previous estimation, using HCl instead of H_2SO_4 to clear the solution.

28. **Precipitation.**—Add to the liquid in the beaker about 20 c.c. of ammonium chloride solution and bring it to the boil over a Bunsen. The reason for adding this NH_4Cl is that barium sulphate is thrown down in a more granular form in the presence of this salt than is otherwise the case. This minimises the risk of the precipitate being so fine as to pass through the pores of the filter paper, which is the chief difficulty with this estimation. As soon as the solution boils add excess of *boiling* barium chloride solution.[1] Cover the beaker with a watch glass, and boil for about half-a-minute; then allow the precipitate to settle completely. Add another drop of barium chloride to make sure that no sulphate remains in solution. Should a further precipitate be caused, the liquid must be stirred, reheated, and a further quantity of boiling barium chloride added.

If the above directions have been followed exactly, the barium sulphate will have settled in about ten minutes.

29. **Washing.**—The precipitate should be washed about five times by decantation (paragraph 12), then transferred to the filter and washed with hot water from the wash bottle until a few drops of the filtrate no longer give a cloudiness when tested with sulphuric acid. The test tube in which this

[1] For the estimation of sulphuric acid the ordinary barium chloride solution is not very satisfactory: a *saturated* solution should be used.

test is performed should be allowed to stand for about a minute, as it often takes that time before the cloudiness appears.

30. **Burning and Ignition.**—The precipitate is dried (paragraph 16) and transferred to a platinum dish, as in the estimation of iron. Great care must, however, be taken *thoroughly* to burn the filter paper *on the wire.* Any carbonaceous matter dropped into the dish tends to reduce a portion of the $BaSO_4$ to BaS. This, however, will not take place in a good current of air such as is kept up around the hot wire. Further, it should be mentioned that a shallow dish is preferable to a deep crucible for the ignition. A shallow dish will afford every opportunity for the free circulation of the air; a deep crucible will keep out the air. With these special precautions, the burning of the filter and subsequent ignition over an Argand may be performed as described in paragraphs 20 and 18.

31. **Entry and Calculation.**—The results should be entered in the note book as shown in paragraph 26, and the calculation made in much the same way. One molecule of $BaSO_4$ corresponds to one of SO_3; or 233 parts by weight of $BaSO_4$ correspond to 80 parts by weight of SO_3.

ESTIMATION OF POTASH

32. **Substance used.**—Potassic chloride, KCl.

Method employed.—The potassium is precipitated as K_2PtCl_6, and weighed as such.

Weigh out about ·3 gram of pure potassic chloride, and wash it off the watch glass into a wide-mouthed beaker 2 inches high by 2 inches broad, using as little water as possible. Add sufficient water to dissolve it, then two or three drops of dilute hydrochloric acid.

33. **Precipitation.**—Pour into the liquid 6 c.c. of a 10 per

cent. solution of platinum chloride, and evaporate on the water bath. Evaporation must be continued until, on removing the beaker from the water bath, the liquid sets to a pasty condition. If it has evaporated to *dryness* a few drops of water should be added, and evaporation continued until the pasty condition is reached. The beaker is then allowed to cool, and strong alcohol is added and gently swilled around the beaker until the liquid is of uniform colour.

34. **Filtration and Washing.** — Two pieces of filter paper are taken and placed one in each pan of the balance, and the heavier one trimmed with a sharp pair of scissors until the two are identical in weight. They are then folded together and placed in a funnel. The alcoholic liquor is poured through them, and the crystalline precipitate washed with alcohol by decantation until the filtrate is colourless. The precipitate is then transferred to the filter, and washed with alcohol until the filter papers appear quite white and the filtrate is no longer yellow. In this operation the flaky crystals of the precipitate should not be broken up. Further, the india-rubber tip to the glass rod must not be used, as the alcohol is apt to render it sticky. The filter papers are dried in the steam oven, cooled in a desiccator, and separated. The blank filter is put on the pan with the weights, and the one containing the K_2PtCl_6 on the other, and the difference is weighed.

By this method the two filters are both treated in the same way, and will therefore lose weight equally. The error which would creep in if the filter paper were simply weighed and its weight subtracted from the total weight of paper and K_2PtCl_6 is thus eliminated.

35. *Another method* of arriving at the weight of the precipitate—which, however, takes a slightly longer time—is as follows :

Filter off, and wash on an ordinary filter paper. Dry at 100°,

then transfer as much as possible of the precipitate to a weighed platinum dish. Replace the filter in the funnel, and wash it two or three times with small quantities of boiling distilled water, allowing the washings to run into the platinum dish. When the adhering precipitate has entirely disappeared from the filter, place the dish on the water bath until the water has evaporated. Remove it to the steam oven for a few minutes. Cool in a desiccator, and weigh.

36. **Calculation.**—From the weight of K_2PtCl_6 the weight of K may be obtained, or, as is more usual in agricultural chemistry, an equivalent quantity of K_2O may be calculated. (See paragraph 251.)

When a large number of analyses have to be made in a given time, it is of importance to make the calculation as short as possible. To this end 'factors' are usually employed. The factor for calculating how much K_2O is represented by a given quantity of K_2PtCl_6 is ·19308, or, as is more frequently used, ·193. Thus in calculating out the result of this estimation we use the following formula :

$$\frac{\text{Wt. of } K_2PtCl_6 \times 100}{\text{Wt. of substance taken}} \times \cdot 193 = \% \text{ of } K_2O.$$

ESTIMATION OF PHOSPHORIC ACID (P_2O_5)[1]

37. **Substance used.**—Sodium hydrogen phosphate, $Na_2HPO_4.12H_2O$.

Method employed.—The phosphoric acid is precipitated as $Mg.NH_4.PO_4.6H_2O$, which is ignited and weighed as $Mg_2P_2O_7$.

[1] When phosphatic manures are guaranteed to contain a certain percentage of phosphoric acid, P_2O_5 is usually meant. The one exception to this rule is liquid phosphoric acid, which is generally guaranteed to contain a percentage of H_3PO_4.

Before starting this analysis, a stock of magnesia mixture should be prepared as follows :

Preparation of magnesia mixture.—Dissolve 60 grams $MgCl_2$ and 80 grams NH_4Cl in 600 c.c. of distilled water. Add 400 c.c. strong ammonia (Sp.G. = ·880), and allow to stand twenty-four hours. Filter off any sediment.

$MgSO_4$ is sometimes used instead of $MgCl_2$, but is objectionable, as a basic sulphate of magnesia is often precipitated with the magnesium ammonium phosphate.

Weigh out about 1 gram of pure $Na_2HPO_4.12H_2O$. Transfer to a 12-oz. beaker, and dissolve in about 100 c.c. of distilled water.

38. **Precipitation.**—Measure off 30 c.c. of the magnesia mixture and pour it into the beaker. Stir well for a few seconds. Add 20 c.c. strong ammonia and stir again. Now cover the beaker with a clock glass and allow it to stand in a cool place for $2\frac{1}{2}$ hours, stirring it once every fifteen minutes. At the end of this time precipitation will be complete. Should it be found more convenient to allow the beaker to stand overnight, it will be advisable to add 10 c.c. strong ammonia next morning and stir well. When the precipitate has subsided it will be ready for filtering.

39. **Filtration and Washing.**—The precipitate in this case must not be washed by decantation, but must be got on to the filter paper at once. It is much quicker, however, to decant the clear liquid through the filter than to filter the turbid liquid. When all the clear portion has passed through, wash the pasty precipitate on to the filter with dilute ammonia (1 of ·880 NH_3 to 3 of H_2O), using the special form of wash bottle described in paragraph 14. Wash the precipitate six times with ammonia, allowing each portion to run through before adding the next. Test a few drops of the filtrate with excess of dilute HNO_3 and a drop of $AgNO_3$. No cloudiness

should appear. If this test shows that the precipitate is not yet free from chlorides, it should receive further washing.

40. **Ignition and Weighing.**—After the filter has been dried (paragraph 16), transfer as much as possible to a platinum dish. Burn the filter paper completely in the platinum spiral (see fig. 19). Place the ash in the dish, and remove it to an Argand which is turned down to the smallest possible flame. The flame is increased gradually until, in about forty minutes, the dish is at a dull red heat. Now watch it until a bright red glow passes suddenly over the precipitate and dies away again. Turn up the Argand until the dish is as hot as possible, and ignite for about five minutes. Cool in the desiccator and weigh.

41. **Calculation.**—One molecule of $Mg_2P_2O_7$ corresponds to one of P_2O_5, hence the quantity of P_2O_5 in the quantity of $Na_2HPO_4.12H_2O$ taken may be calculated, and from this the percentage. The factor for converting $Mg_2P_2O_7$ into P_2O_5 is ·64. Thus :

$$\frac{\text{Wt. of } Mg_2P_2O_7 \times 100}{\text{Wt. of } Na_2HPO_4.12H_2O} \times \cdot 64 = \% \text{ of } P_2O_5.$$

N.B. If this exercise has been carefully worked, the percentage of P_2O_5 found will be lower than that required by theory, as the magnesium ammonium salt is slightly soluble in dilute ammonia. For further discussion of this error see paragraph 200.

ESTIMATION OF CALCIUM

42. **Substance used.**—Calcium carbonate, $CaCO_3$.

Method employed.—The calcium is precipitated as calcium oxalate, and either heated gently and weighed as $CaCO_3$, or ignited strongly and weighed as CaO.

Weigh out about ·5 gram powdered Iceland spar, wash into a 12-oz. beaker, and cover with a clock glass. Insert the jet of a

wash bottle containing dilute HCl between the clock glass and the edge of the beaker, and blow the acid so that the spray may strike the opposite side of the vessel and descend gently upon the spar. When about 50 c.c. have been added, allow the beaker to stand in a warm place (on the top of the steam oven will be found very convenient) until all effervescence ceases. Should any of the substance remain undissolved, add a little more acid. Remove the clock glass, and wash any liquid adhering to it back into the beaker.

43. **Precipitation.**—The precipitate obtained when a solution containing calcium is mixed with one containing an oxalate is of such fine texture that it often passes through a filter paper and thus causes much annoyance. This difficulty may be overcome in the following manner :

Dilute the solution to about 150 c.c. ; make alkaline with dilute NH_3, and heat until it just boils. Whilst it is heating weigh out roughly a gram of pure finely powdered ammonium oxalate. Remove the beaker from the flame and add the *solid* ammonium oxalate a little at a time, stirring continuously. Replace the beaker over the flame and raise to a boil ; then stop heating, and allow the precipitate to settle. This will not take more than a minute or two.

In using this method care must be taken to remove the beaker from the influence of the flame before adding the oxalate to the solution. If this be not attended to, an effervescence will take place which may cause the loss of some of the solution.

The oxalate should be tested by placing about 2 grams in a weighed platinum crucible and heating to redness. The salt should volatilise entirely, leaving no residue—*i.e.*, the crucible should not gain in weight.

44. **Washing and Filtration.**—Wash about six times by decantation, then once or twice on the filter, testing the

final washings by means of a glass slip, as described in paragraph 12 (*h*).

45. **Ignition and Weighing.**—Dry the precipitate, and prepare it for weighing as follows: Remove as much of the precipitate as possible from the paper to a weighed platinum dish, keeping it well on one side of the dish. Burn the filter rapidly on a spiral of platinum wire, and *whilst still black* drop it into the dish, so that it may lie in direct contact with the platinum and not on top of the calcium oxalate. Place the dish on an Argand with the flame turned low, and gradually turn it up until, in about half-an-hour, it is just below a red heat. Now watch the filter paper carefully for a few minutes. If it should begin to burn, or if sparks appear on its surface, the flame must be lowered. If in the course of half-an-hour the paper is still perfectly black, the flame must be turned up a little. When the right temperature is obtained in this way the paper will gradually crumble down to a light-grey coloured mass. As soon as all the black of the filter has gone, which should take place in about forty minutes from commencing, the dish may be cooled down in a desiccator and weighed.

A very little practice is sufficient to enable the analyst to hit the right temperature for this reaction, but a second weighing is generally advisable after heating at the same temperature as before for ten minutes longer. The second weighing should not be more than half a milligram different from the first.

N.B.—It is frequently recommended that the $CaCO_3$ obtained in this manner be moistened with ammonium carbonate solution, and re-heated before weighing. This is to bring back any CaO which may have been formed to $CaCO_3$. Any additional accuracy gained by this method is more than made up for by the chances of loss by spirting.

46. When the weight of the $CaCO_3$ has been verified, the dish may be placed in a Fletcher muffle furnace and kept at

a bright red heat for twenty minutes, cooled in a desiccator, and weighed again. This gives the weight as CaO.

When only small quantities of lime are to be estimated (less than ·1 gram), the CaO method should be used. For larger quantities the $CaCO_3$ method is sufficiently accurate.

47. **Calculation.**—The calculation is very simple; it is either

$$\frac{\text{Wt. of } CaCO_3 \times 100}{\text{Wt. of spar taken}} \times \cdot 56 = \% \text{ CaO},$$

or

$$\frac{\text{Wt. of CaO} \times 100}{\text{Wt. of spar taken}} = \% \text{ of CaO}.$$

ESTIMATION OF CARBON DIOXIDE IN CARBONATES

48. **Substance used.**—Iceland spar, $CaCO_3$.

Methods.—(*a*) By difference. The carbon dioxide is driven off by means of an acid, and the loss of weight caused thereby is estimated

(*b*) By direct weighing. The carbon dioxide given off on treatment with an acid is absorbed and weighed.

49. (*a*) This method, although capable of giving very good results in the hands of a skilled analyst, is somewhat difficult for a student. Still, since it is frequently used both in commercial practice and in technical examinations, it is well that the agricultural student should be familiar with it.

Several kinds of apparatus are used for this determination, but all are the same in principle. Two are described; one which is readily fitted up in any laboratory, and a second which must be made by a professional glass blower, but which is obtainable from any manufacturing firm.

50. **Apparatus required.**—1. The apparatus is readily

understood from fig. 20. A wide-mouthed 4-oz. flask is fitted with an india-rubber stopper, through which are bored two holes. Through one is fitted a tube, A A, reaching close to the bottom of the flask; through the other is placed another tube, B B, which terminates at one end just inside the stopper and at the other after being bent three times at right angles, inside a calcium chloride tube, C. The outer ends of these two tubes are closed by pieces of india-rubber tubing, into which fit stoppers of glass rod.

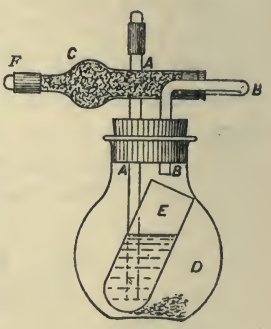

FIG. 20.

The apparatus is completed by placing a portion of a test tube, E, inside the flask. This must be just so long that it cannot lie down in the flask, but so short that the india-rubber stopper may be inserted without touching it.

The tube C is filled with small pieces of fused calcium chloride, and the test tube, E, is filled three-quarters full of hydrochloric acid, 1 part strong acid and 1 part distilled water, and the apparatus is ready for use.

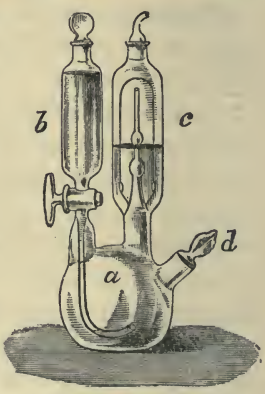

FIG. 21.

51. **Schroeder's Apparatus.**—2. Should this form be used, the cistern *b*, fig. 21, is filled with hydrochloric acid 1 to 1, and the cistern *c* is half filled with strong sulphuric acid, which dries the effluent gas just as the calcium chloride does in the first apparatus. The apparatus, whichever of the two it may be,

is first of all weighed, care being taken that no moisture adheres to its exterior. About 1 gram of finely ground Iceland spar is then introduced into the apparatus, and it is weighed again, the difference giving the weight of spar added.

If the first apparatus be used, care must be taken that none of the added substance fall into the test tube of acid. To avoid this it is desirable to remove the tube whilst pouring the substance into the flask. If Schroeder's apparatus be used, the carbonate may be poured through the opening *d*.

The next operation is to drive off the carbon dioxide.

52. If the apparatus in fig. 20 be used, F is unstoppered, and the flask is tilted on one side so as to allow the acid in E to run over on to the substance below. As soon as effervescence ceases a little more acid is run over. This operation is continued until the whole of the substance is dissolved. The flask is then placed on top of the water oven for about ten minutes to expel any CO_2 which may be dissolved in the liquid. Finally, the stopper at A is removed, and air slowly aspirated through the apparatus (by attaching F to an air-pump or by sucking a tube attached to F) until all CO_2 is expelled from the flask. The stoppers at A and F are then replaced, and the apparatus is weighed.

53. **Calculation.**—

Weight I. = Apparatus.
Weight II. = Apparatus + Substance.
Weight III. = Apparatus + Substance − CO_2.
∴ Weight II. − Weight I. = Iceland spar,
and Weight II. − Weight III. = CO_2.

From this the percentage of CO_2 in the Iceland spar may be readily calculated.

54. If Schroeder's apparatus be used, the acid is let in gradually as before by the tap at the bottom of the cistern *b*,

and the CO_2 evolved, after bubbling through the H_2SO_4 in *c*, is allowed to escape into the air. The apparatus is warmed and the air expelled as before, the stopper and tap on *b* of course being opened. The apparatus is then weighed, and the percentage of CO_2 calculated as before.

55. **Method *b*. By direct weighing.**—Several forms of apparatus are used for this estimation, perhaps the simplest

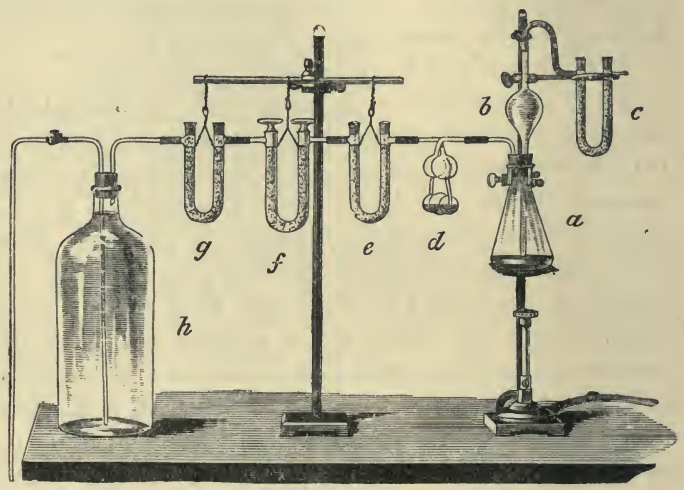

FIG. 22.

being that recommended in Crookes's 'Select Methods of Chemical Analysis.'[1]

[1] For the benefit of those who wish to try this method, I quote the following:

H. T. S. Gladding uses an apparatus for the estimation of carbonic acid by absorption. It consists of the ordinary generating flask, followed by an empty U tube to retain condensed water vapour; this is succeeded by four potash bulbs of the Geissler form. The first of these contains concentrated sulphuric acid to dry the gas. The next two contain potash solution of Sp. G. 1·27 for absorbing the carbonic acid; the last contains concentrated sulphuric acid to absorb the moisture given up by the potash

For use by students, however, the apparatus shown in fig. 22 is to be recommended.

a is an 8-oz. conical flask, into which the weighed quantity of carbonate is placed. Through the stopper of the flask pass two tubes, one communicating with a reservoir of dilute hydrochloric acid, *b*, and the other with a series of tubes, *d*, *e*, *f*, and *g*, intended to purify and absorb the CO_2 formed.

At the end of this series of tubes is some form of aspirator, by means of which a current of pure dry air may be caused to pass through the whole apparatus.

Preparation of the apparatus:

First of all, the different U tubes must be carefully cleaned and filled as follows:

Tube f. This is the tube which is destined to absorb the CO_2 evolved in the flask *a*. The form of tube shown in the figure is very convenient, as the two stopcocks enable the operator to shut off its contents from the air whilst weighing. When the tube is perfectly clean and dry, a loose plug of cotton wool is pushed down one side to the position 1, fig. 23. The part 3, fig. 23, is filled with granulated soda lime which has been sifted free from dust, and the part 2, fig. 23, with granular calcium chloride. Two little plugs of cotton wool are then placed at the ends, 4, 4, fig. 23, and the glass stopcocks inserted.

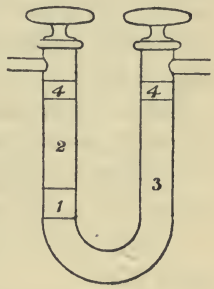

FIG. 23.

solution. Then comes a U tube containing soda-lime, and serving as a guard.

The last three Geissler bulbs constitute the weighable portion of the apparatus. Perfectly dry air plus carbonic acid enters these, and perfectly dry air alone escapes. The increase in weight gives the amount of carbonic acid.

Tube e. This tube must have a plug of cotton wool driven down until it divides the tube into equal portions. One limb is filled with granulated $CaCl_2$, and the other with small pieces of pumice which have been soaked in a saturated solution of $CuSO_4$, then dried at 200° C. until they have become colourless.

Tube g is filled with $CaCl_2$. The remaining tube (*c*) is to purify the air which is passed through at the end of the operation. It is filled with soda lime. When all the different pieces of apparatus shown in the figure have been got together, the Liebig's bulbs (*d*) must be filled about half full of strong sulphuric acid, and the absorption tubes joined together with india-rubber tubing. Especial care must be taken that the different reagents with which the CO_2 comes in contact after leaving the flask are arranged in the correct order, as it is very easy to get some of the tubes turned the wrong way round. The correct order is as follows:

Strong sulphuric acid to dry the gas, and contained in the bulbs *d*.

Calcium chloride to complete this drying, and contained in the limb of *e* next the bulbs.

Anhydrous copper sulphate and pumice, to absorb any HCl which may come over, and contained in the limb of *e* next to *f*.

Soda lime to absorb the CO_2, contained in the limb of *f* next to *e*.

Calcium chloride, contained in the limb of *f* next to *g*. When the soda lime begins to absorb CO_2 it gets warm and loses a little moisture. This $CaCl_2$ is to absorb any such moisture.

Calcium chloride, contained in *g*, to prevent any moisture from diffusing back into *f*.

Having made the absorption apparatus and got it correctly in position, the pipette, *b*, is fitted into the stopper so that its

tip reaches nearly to the bottom of the flask *a*. Above, the pipette is joined to the tube *c* by about 6 inches of india-rubber tubing which is closed by a clip.

56. **The Determination.**—Weigh about a gram of the pure Iceland spar, and transfer it to the flask *a*. Next weigh the tube *f*, and replace it in its position. Fill the tube *b* with dilute hydrochloric acid, and close the clip so that no acid may drop from the tip of the pipette. Replace the stopper in the flask, and the whole apparatus will appear exactly as in the figure, excepting that the aspirator will not be in position. Loosen the clip above *b*, so that the acid may flow down slowly upon the spar. When all effervescence has ceased, close the clip and bring the acid to a boil by placing a Bunsen beneath it ; next, lower the flame, attach *g* to the aspirator or to a pump (fig. 15), loosen the clip, and allow air to pass through the apparatus for fifteen minutes. The speed of the air current should be so regulated that the bubbles may be counted as they pass through the sulphuric acid bulb. When the air has been passing for the prescribed time, stop the aspirator, turn off the stopcocks in *f*, and remove the tube : weigh it. The amount which it has gained will represent the amount of CO_2 which has been given off from the spar.

Section II.—VOLUMETRIC ESTIMATIONS

57. In *volumetric* analysis the balance is to a great extent replaced by instruments which measure volumes.

The principle of volumetric analysis is best explained by taking an example. Suppose that we had a solution of sulphuric acid of which we knew the exact strength, every c.c. containing a certain weight of pure H_2SO_4. It is required by means of this solution to find out how much pure KHO exists

in a solution of this substance. The method would be to measure out a quantity of the KHO solution, mix with it a few drops of litmus solution, and add the sulphuric acid until the liquid became neutral.

If we could measure the volume of H_2SO_4 solution added, we should know the weight of pure H_2SO_4 required to neutralise the KHO in the KHO solution. From the weight of H_2SO_4 it would be easy to calculate the weight of KHO.

A solution of known strength, such as the sulphuric acid in the above example, is called a standard solution.

A substance which tells when the reaction is completed, as the litmus in the example, is called an indicator.

The instrument by which the amount of sulphuric acid is added is a burette.

58. **Standard Solutions.**—For convenience in calculating, standard solutions are generally made up to certain strengths known as normal (N), seminormal $\left(\frac{N}{2}\right)$, and decinormal $\left(\frac{N}{10}\right)$.

A *normal solution of a monobasic acid*, or of a monacidic alkali, is one of which 1 litre contains the molecular weight in grams of the acid or alkali.

A *normal solution of any other acid* is one of which 1 litre will exactly neutralise 1 litre of normal monacidic alkali solution. In the same way, a normal solution of any other alkali would be one of which 1 litre will exactly neutralise 1 litre of normal monobasic acid solution. Thus, a litre of a normal solution of caustic potash, KHO, would contain 56 grams of potash, and, according to the equation

$$\begin{aligned} HCl + KHO &= KCl + H_2O \\ 36{\cdot}5 + \ 56 &= 74{\cdot}5 + 18, \end{aligned}$$

a litre of normal potash would exactly neutralise 36·5 grams

of HCl, and if this amount be made up to a litre with water it will constitute a normal solution of HCl.

On the other hand, should a dibasic acid be used, only half its molecular weight will be required to make a litre of normal solution, as may be seen from the equation

$$H_2SO_4 + 2KHO = K_2SO_4 + 2H_2O$$
$$98 + 56 \times 2 = 135 + 2 \times 18$$

Ninety-eight grams (or the molecular weight in grams) of H_2SO_4 will neutralise 56×2 grams of KHO, or 2 litres of normal KHO.

In the same way, a normal solution of oxalic acid, $C_2H_2O_4.2H_2O$, will contain $126 \div 2$, or 63 grams per litre.

As normal solutions are often too strong for delicate work, solutions of half normal strength (seminormal), or one-tenth normal strength (decinormal), are frequently used.

Very little practice will soon show the student that the great advantage which solutions of normal strength, or some simple fraction of this strength, have over all others is in the facility with which results may be calculated from them.

59. **Indicators.**—The following are the principal indicators used :

Litmus. The solution is not often used in agricultural work, but litmus paper is sometimes necessary. This is bought in small strips made up into the form of books, and will be familiar to students who have done any qualitative analysis.

Cochineal. This indicator is not affected in colour by carbonic acid. It may be prepared by dissolving 1 gram of powdered cochineal in 20 c.c. of methylated spirit, diluting with 80 c.c. of water, and allowing to settle. The clear liquid is yellow, but is changed to a deep wine-red by alkalis. It should not be used in presence of iron, aluminium, or acetic acid, or their compounds.

Phenol-phthaleïn. Must be dissolved in alcohol. Colourless when acid or neutral red when alkaline. It should not be used with ammonia, but is very useful in the titration of weak organic acids.

Lacmoid. Dissolves in water, and gives the same colour effects as litmus, but is more sensitive.

Methyl orange. Is a most convenient indicator and strongly to be recommended, its colour being bright yellow with alkalis and red with acids. It should be made up by dissolving a gram in a litre of water. It is not affected by carbonic acid.

In using indicators to determine the end of a reaction, the solutions should always be used in the same way. For instance, if methyl orange be used to determine when a certain amount of H_2SO_4 is neutralised by running in alkali from a burette, a slightly different result will be obtained from that which would be got by running the acid into the alkali.

PREPARATION OF SEMINORMAL SULPHURIC ACID

60. Half fill a litre flask with distilled water. Measure out 35 c.c. of strong sulphuric acid in a graduated 100-c.c. cylinder, and pour it, a little at a time, into the water in the flask, shaking the liquid round after each addition. The acid need not be measured very exactly, as the solution has to be standardised afterwards. When all the acid has been added, cool the flask, either by allowing it to stand over night or by placing in a current of cold water, as shown in fig. 24. The beaker placed over the mouth of the flask prevents any water getting into the liquid. Next fill up to the litre mark with water, and mix thoroughly.

FIG. 24.

N.B.—When large quantities of standard acid have to be prepared, this mixing becomes a matter of some difficulty. The best method is to

pour the liquid into a large bottle, and force a rapid stream of air through it. This may be done by means of the blowpipe bellows.

61. **Standardising.**—Carefully clean a burette, washing it first with distilled water, then with a portion of the acid which has just been made up. Allow it to drain for a minute, then fill it with the acid. Drop an Erdmann's float into the top of the burette, and allow the liquid to run from the tap, or pinch-cock, until the mark on the float stands at the 0 c.c. mark on the burette. Now allow exactly 10 c.c. to run out into a clean 12-oz. beaker; dilute to about 50 c.c., and determine the amount of H_2SO_4 exactly as described in paragraphs 28 to 30. As soon as this is started, take another 10 c.c. from the burette, and make a duplicate determination in the same way. Should the two determinations agree pretty closely, then their mean may be taken as the true quantity of H_2SO_4 contained in 10 c.c. of the solution. The next thing is to calculate, from this result, how much water must be added to make the solution exactly seminormal.

62. A normal solution (see paragraph 58) contains 49 grams of pure H_2SO_4[1] per litre. Therefore a seminormal solution such as is being prepared, should contain $\frac{49}{2} = 24{\cdot}5$ grams per litre, or ·245 gram per 10 c.c.

Now, by experiment we have found how much H_2SO_4 10 c.c. of our solution contains. Call this x.

If x grams of H_2SO_4 are contained in 10 c.c.,

then 1 gram ,, is ,, $\frac{10}{x}$,, ;

$\therefore$ ·245 gram ,, is ,, $\frac{{\cdot}245 \times 10}{x} = \frac{2{\cdot}45}{x}$.

[1] On page 23 a method was described for the estimation of sulphuric acid, where the result was calculated as SO_3. The use of the formula H_2SO_4 in volumetric and of the anhydride SO_3 in gravimetric analysis is merely a matter of convenience which will be better understood by the

If, therefore, we wish to have our acid seminormal, we must dilute every $\frac{2{\cdot}45}{x}$ c.c. until it becomes 10 c.c.; or, multiplying these quantities by 100, we must dilute $\frac{245}{x}$ c c. to a litre.

To do this pour the calculated quantity of the dilute acid $\left(\frac{245}{x} \text{ c.c.}\right)$ into a stoppered, graduated litre cylinder, and fill up to the litre mark with distilled water. Mix well by shaking. The solution so prepared should be accurately seminormal.

Keep this standard solution in a well-stoppered Winchester quart bottle, taking care that it is quite clean and dry before pouring in the liquid. If it be not quite dry, wash it out with a little of the standard acid; throw away the washings, then pour in the rest of the acid.

PREPARATION OF SEMINORMAL CAUSTIC POTASH SOLUTION

63. Weigh out on a rough balance 10 grams of solid caustic potash; place this in a 20-oz. beaker, together with about 300 c.c. of distilled water, and allow it to dissolve. When all the solid has disappeared, pour the liquid into a clean litre flask and make up to the litre mark with distilled water. Caustic potash gives out considerable heat on dissolving, so that the solution will be distinctly warm. Before proceeding farther it must be cooled (fig. 24). After cooling, the solution will be found to have shrunk slightly. Make up again to the litre mark, and mix thoroughly.

64. **Standardisation.**—Fill a burette with seminormal

student when calculating the results of the more complex analyses described later on.

sulphuric acid, as described in the last article, and another with the caustic potash solution just prepared. Run out 10 c.c. of the acid into an 8-oz. beaker. Stand the beaker on a white tile under the KHO burette; add a drop of methyl orange solution (paragraph 59), stir with a glass rod, and run the alkali solution from the burette, drop by drop, into the beaker, stirring continually until the colour changes from red to yellow. When the solution is just neutralised one drop of alkali should make the change from red to yellow. Read off the amount of alkali used and repeat the experiment several times. Take the mean of your readings as accurate.

The next operation is to dilute your solution to seminormal strength.

Suppose that the amount of alkali which neutralises 10 c.c. of $\frac{N}{2}$ H_2SO_4 is x.

Then x c.c. must be diluted to 10 c.c., or $100x$ c.c. must be diluted to a litre.

Measure out in a graduated litre cylinder $100x$ c.c. of alkali solution. Make up to a litre with distilled water, shake up well and store in a clean well-stoppered Winchester quart bottle.

The solution should now be seminormal—*i.e.*, it should contain $\frac{56}{2}$ grams of KHO per litre.

A fresh experiment should be made with this seminormal solution to see that 10 c.c. of the $\frac{N}{2}$ sulphuric acid is exactly neutralised by 10 c.c. of the $\frac{N}{2}$ alkali.

65. The two solutions whose preparation has just been described are used very largely in the estimation of nitrogen (see Part III.). Greater accuracy is, however, obtained by using a $\frac{N}{5}$ *solution of caustic potash.* To prepare this it is

only necessary to measure out 200 c.c. of the seminormal solution into a litre flask and fill up to the mark with water. Of course the new solution must be thoroughly mixed. The seminormal solution of H_2SO_4 is of very convenient strength for nitrogen estimations, so that it must be remembered that 50 c.c. $\frac{N}{5}$ potash solution correspond to 20 c.c. $\frac{N}{2}$ sulphuric acid solution.

ESTIMATION OF CHLORINE IN SOLUBLE CHLORIDES

66. **Method.**—A solution of silver nitrate is made of known strength, and the volume required to precipitate the whole of the chlorine as AgCl is noted.

67. **Preparation of Standard Silver Nitrate Solution.**—Two watch glasses having ground edges and a clip are weighed, and into one of them is introduced as nearly as possible 17 grams of powdered pure silver nitrate. This watch glass is then placed in the steam oven for half-an-hour, allowed to cool in a desiccator, and then clipped to the other watch glass. The two watch glasses, with clip and dry nitrate of silver, are then weighed accurately. A glass filter funnel is placed in the neck of a graduated litre cylinder. The clip is taken off the watch glasses, and the silver nitrate is washed with cold water down the funnel into the cylinder. The glasses and funnels are well washed to free them from any adhering silver nitrate, and the washings, which should not exceed 300 c.c., allowed to run into the cylinder. The solution is left standing until all the solid is dissolved. The cylinder is then filled up to the 1000-c.c. mark with distilled water.

If exactly 17 grams have been taken, then the solution will be decinormal ; but if it should be more or less, then a certain

factor will have to be used with it—that is to say, the number of c.c. used in any operation will have to be multiplied by a number or factor to tell us how many c.c. would have been used had the solution been accurately decinormal.

This must be calculated from the weight taken in the following manner :

Suppose the actual weight taken to have been 16·9545 grams.

Now, 17 grams $AgNO_3$ are contained in 1000 c.c. $\frac{N}{10}$ $AgNO_3$,

$\therefore$ 1 gram „ is „ $\frac{1000}{17}$ „ „

and 16·9545 grams $AgNO_3$ are „ $\frac{1000 \times 16{\cdot}9545}{17}$ „

This fraction works out to 997·3.

But 16·9545 grams $AgNO_3$ are contained in 1000 c.c. of our solution,

$\therefore$ 1000 c.c. of our solution = 997·3 $\frac{N}{10}$ $AgNO_3$,

or 1 c.c. „ „ = ·9973 „

That is to say, if we multiply the number of c.c. of our solution used in any operation by ·9973, the product will be the number of c.c. which would have been used had the solution been decinormal. Therefore ·9973 is the factor for this solution.

68. **Potassic Chromate Solution.**—A 2 per cent. solution of pure neutral potassic chromate is made. This should be perfectly free from chlorine. It may be tested by adding a drop of nitric acid to a small quantity, and then a drop of silver nitrate solution. If it remains perfectly clear, chlorides are absent.

69. **The Estimation.** — Weigh out accurately about 1 gram of pure common salt (NaCl) into a small beaker ; dissolve this in 50 c.c. of cold water, transfer into a 250-c.c.

measuring flask, rinsing out the beaker well with cold distilled water and adding the rinsings to the solution in the flask. Fill up with distilled water to the mark, and shake up the solution so as to mix thoroughly. Measure out 25 c.c. of this solution with a pipette into an 8-oz. beaker, and add one drop of the K_2CrO_4 solution.

Fill up a burette with the standard silver nitrate solution, add an Erdmann's float, taking care that there are no bubbles of air either attached to the float or in the stopcock. Note the position of the mark on the float. Stand the beaker containing the NaCl on a white tile, and allow the silver solution to run into it, drop by drop, stirring continuously with a glass rod. As each drop of $AgNO_3$ enters the liquid in the beaker a bright-red precipitate of Ag_2CrO_4 is momentarily formed, but this immediately becomes white as it is turned by the salt into AgCl. When the white precipitate begins to curdle and settle, add the $AgNO_3$ more slowly, stirring after each drop until the red colour entirely disappears. As soon as the red colour remains permanent, leaving the solution just faintly coloured, close the stopcock of the burette and note down the new position of the float. The difference between the two positions gives the amount added. Make two or three determinations in this manner, using the mean of your readings as the true result.

70. **Calculation.**—First multiply the factor by the number of c.c. used. This will give the number of c.c. which would have been used had the solution been decinormal—*i.e.*, had it contained 17 grams of $AgNO_3$ or 10·8 of Ag per litre. By inspecting the equation

Ag	+	Cl	=	AgCl
108	+	35·5	=	143·5

we see that 108 of silver are equal to 35·5 of chlorine,

$\therefore$ ·0108 Ag precipitates ·00355 Cl, but 1 c.c. $\frac{N}{10}AgNO_3$ contains ·0108 Ag $\therefore$ we multiply the number of c.c. of $\frac{N}{10}$ $AgNO_3$ used by ·00355, which will give the number of grams of chlorine in the 25 c.c. of the NaCl solution; this multiplied by 10 gives the total weight of chlorine, and this multiplied by 100 and divided by the weight of NaCl taken gives the percentage of Cl in the NaCl solution.

VOLUMETRIC ESTIMATION OF IRON

71. This estimation depends upon the fact that ferrous salts may be oxidised by either $K_2Mn_2O_8$ or $K_2Cr_2O_7$ in the presence of acids to ferric salts by one of the equations:

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$
$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

From these equations it will be seen that one molecule of $K_2Mn_2O_8$ will oxidise ten of $FeSO_4$ or 316 grams of $K_2Mn_2O_8$ will oxidise 10 × 56 grams of iron from the ferrous to the ferric state. Thus a normal[1] solution of $K_2Mn_2O_8$ would contain 31·6 grams per litre. In the same way it may be calculated that a normal solution of $K_2Cr_2O_7$ will contain 49 grams per litre.

72. **Preparation of Standard Bichromate of Potash.**—This solution, although slightly more troublesome to use than permanganate, has the advantage of permanency. It may be kept in a well-stoppered bottle almost indefinitely, without suffering any change of strength.

Weigh out exactly 4·91 grams of powdered $K_2Cr_2O_7$ which

[1] It will be noticed that the word *normal* is here used in a manner which is not included by the definition given on page 38, as $K_2Mn_2O_8$ is neither an acid nor an alkali.

has been dried in a desiccator, dissolve in water, and make up to a litre exactly as described in the case of $AgNO_3$; mix well.

73. **Estimation of Iron in Solutions of Ferrous Salts.** It is necessary that all the iron in the solution shall be in the ferrous state. If any ferric salts be present, they must be reduced before titration as described in the next article. To acquire proficiency in the actual estimation, $Fe(NH_4)_2(SO_4)_2.6H_2O$ may be used. Weigh out about a gram of this salt, dissolve it in water, add 2 drops of strong H_2SO_4, and make up to 250 c.c. in a flask of that capacity. After shaking up well, remove 25 c.c. with a pipette into a beaker. In another beaker make up a very dilute solution of *potassic ferricyanide*, $K_3Fe(CN)_6$, by dissolving a piece of this salt, about the size of a hemp seed, in 50 c.c. of distilled water. Place about a dozen separate drops of this solution on a white tile. This is most easily done by dipping a glass rod into the solution and touching the plate with it. A drop of any acid liquid containing iron in the ferrous state will turn one of these drops blue, whilst ferric salts will produce no visible change.

Warm the beaker containing the ferrous solution to about 60° C. Run in the decinormal bichromate solution from a burette, half a c.c. at a time, stirring well after each addition. After stirring, take out a drop on the end of a stirring rod and touch one of the $K_3Fe(CN)_6$ drops on the tile. As soon as no colour is formed read off the amount added. This gives a rough estimate of the quantity required ; but, seeing that we have added half a c.c. at a time, this reading may be ·4 c.c. out, as the liquid is apt to absorb oxygen from the air. Throw away the liquid, wash out the beaker, and measure out another 25 c.c. Warm up to about 60° C. as before. This time the bichromate may be run in until ·5 c.c. less than before has been added. Then add the solution, drop by drop, testing after each addition, until the exact amount is discovered.

Afterwards check your work by taking another 25 c.c. and running in the exact amount, all but a drop or two, finishing up as before

74. **Calculation.**—For each operation one-tenth of the amount of ferrous salt weighed out has been used. Therefore, the total amount of iron in the 250 c.c. of solution is obtained by multiplying in $10 \times \cdot 0056$ by the number of c.c. of $K_2Cr_2O_7$ used.

75. **Estimation of Iron in Solutions containing Ferric Salts.**—The first thing necessary is to reduce the iron to the ferrous state. Several methods have been devised for performing this operation, and these may be found in text books on general quantitative analysis. The one here given is easily and rapidly worked, and gives good results.

76. Make up a solution of *stannous chloride* by dissolving about 10 grams of the salt in 25 c.c. of hot dilute hydrochloric acid (equal parts of strong acid and distilled water), dilute to 100 c.c., and keep in a bottle whose stopper is very slightly smeared with vaseline. This prevents the salt from creeping up and cementing the stopper into the bottle. It will not vitiate the solution, because that is always taken out by a pipette as shown in the sequel. A few pieces of pure tin should be kept at the bottom of the liquid.

Make up a saturated solution of *mercuric chloride* in 100 c.c. of water.

77. **The Estimation.**—Measure out 10 c.c. of a dilute solution of ferric chloride[1] into a 4-oz. conical flask, add about 40 c.c. of water, and heat to boiling. Suck up into a 5-c.c. pipette some of the stannous chloride solution and add it, drop by drop, to the boiling liquid in the flask. Continue adding until the liquid becomes quite colourless.

[1] If it be desired to check this estimation the iron should be determined in another 10 c.c. by the gravimetric method given in paragraph 22.

Remove the flame, and add 1 c.c. of $HgCl_2$ to oxidise the excess of $SnCl_2$. Boil for a few seconds. If the operation has been carefully conducted, only a faint precipitate of Hg_2Cl_2 will be formed. Now cool down the flask, by running cold water round it, to 60° C., and titrate, exactly as with the ferrous salt, using the whole of the solution in the flask and making a separate reduction for each titration until the exact quantity of bichromate solution required is found.

78. *Permanganate of potassium*, as before stated, may be substituted for bichromate. The solution of this substance has a very deep purple colour, and as that colour is destroyed by reduction no indicator is required.

To prepare a decinormal solution of $K_2Mn_2O_8$, dissolve about 5 grams of this substance and dilute to a litre. Standardise it by means of oxalic acid solution. The action of oxalic acid on permanganate is as follows :

$$5H_2C_2O_4.2H_2O + K_2Mn_2O_8 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 18H_2O.$$

Dissolve 63·01 grams of dry crystals of oxalic acid in water and make up to a litre. Measure out 10 c.c. into a beaker by means of a pipette ; add 5 c.c. of dilute H_2SO_4 and dilute with about 50 c.c. of water. Heat this solution to 60° C., and run in the $K_2Mn_2O_8$ solution from a glass-tapped burette, stirring after each addition. As soon as a faint permanent colour is produced, read off the amount that has been added. From this result the amount of $K_2Mn_2O_8$ per c.c. may be calculated.

In using $K_2Mn_2O_8$ solution the following precautions should be remembered :

Always acidify with sulphuric acid.

No HCl must be present, as it is liable to be oxidised and evolve chlorine.

Organic matter must be absent.

Nitric acid should be present only in very small quantities.

ESTIMATION OF SUGAR

79. There are many sugars which occur in the vegetable kingdom, but in this article only two are dealt with—viz., cane sugar and glucose. All the determinations which have been described up to this point are dependent on definite chemical reactions

which can be represented by equations and calculated from atomic and molecular weights. The determination of the quantity of sugar in any substance is an operation of a different order. No calculation can be made from equations. The test for grape sugar known to elementary students (red precipitate of Cu_2O on boiling with Fehling's solution) is not strictly quantitative, as a slight variation of the conditions under which the test is made will entirely alter the results obtained. Certain sugars, when heated with an alkaline solution of copper tartrate, give red precipitates of cuprous oxide. The *quantity* of that precipitate varies greatly not only with the quantity of the sugar, but also with its chemical constitution and with the conditions of temperature and strength of the solution.

It is therefore evident that however carefully the standard solution of copper tartrate may be made, it will be useless unless carefully standardised by the especial sugar and under the especial condition of temperature and dilution which will apply when the actual estimation is carried out.

The two sugars dealt with in this article are *cane sugar* and *glucose*. Glucose is estimated by the method described below, but cane sugar must first be 'inverted' by boiling with an acid which converts it into *invert sugar*. This (dextrose and laevulose) has practically the same action on Fehling's solution as glucose (dextrose).

80. **Preparation of Fehling's Solution.**—Weigh out exactly 34·64 grams of copper sulphate which has been ground finely and pressed between folds of filter paper. Dissolve with the usual precautions in about 300 c.c. of distilled water, preferably in a 500-c.c. flask. Make up to the 500-c.c. mark, mix well, and keep in a well-stoppered bottle marked 'Fehling's solution I.' Next weigh out 173 grams of Rochelle salt (sodium potassium tartrate) and 160 grams of caustic potash. Dissolve

these together in about 300 c.c. of water. Decant into a 500-c.c. flask, and make up to the 500-c.c. mark. Bottle and label 'Fehling's solution II.' [1]

81. **Preparation of Sugar Solution.**—Weigh out exactly 2·375 grams of pure crystallised cane sugar. Dissolve in about 50 c.c. of water in a beaker, add 2 c.c. of dilute HCl, and place the beaker on the water bath for twenty minutes. This will convert the cane sugar entirely into glucose. Just neutralise with caustic soda, decant into a 500-c.c. flask, and wash the beaker, pouring the washings into the flask. Make up to 500 c.c. and mix well. If this solution has been correctly made, 10 c.c. will contain ·05 gram of glucose, which is equivalent to ·0475 of cane sugar.

82. **Standardisation of Fehling's Solution.**—For this purpose the sugar solution just prepared may be considered accurate. In fact, for the reasons set forth in article 79 it is far more likely to be accurate than the Fehling's solution. Fill two burettes, one with sugar solution and the other with Fehling's solution I. Place the burettes in clamps which support them at such a height that their taps are about 8 inches above the bench. Run 5 c.c. of solution I. into an evaporating basin 4 inches in diameter. With a pipette add 5 c.c. of solution II. Stir with a glass rod until the solution becomes quite clear, then place the basin on a tripod and heat it just to boiling. It is most convenient to have a Bunsen burner about a foot away from the burette containing the sugar solution. This enables the operator to slide the tripod with the basin either under the burette or over the burner. When the solution boils, slide it under the burette

[1] Fehling's solution II., like all other strong solutions of potash and soda, is apt to give trouble by fixing the stopper of the bottle tightly. This difficulty may be overcome by rubbing the stopper lightly with vaseline.

and run in 5 c.c. of the sugar solution, then bring it back over the burner. A red precipitate will form. After boiling about thirty seconds, slide away from the flame and allow the precipitate to settle. If the liquid be still blue, more sugar must be added; if colourless, too much has been added already. The colour of the liquid is best seen by allowing the precipitate to settle completely, and then tilting the basin up sideways so that the white side of the basin may be seen through the liquid. In this case, however, the liquid will be still blue. Add another c.c. of sugar solution. Boil for half-a-minute, and allow to settle again. Repeat this operation until the blue colour has nearly gone, then add the solution, a drop or two at a time, boiling after each addition and testing a drop of the liquid for copper by placing it on a porcelain tile together with a drop of potassium ferrocyanide solution in dilute HCl. A brown colouration shows that there is still excess of copper. In this case add more sugar, boil, and test again.

To tell when the reaction is complete without the aid of $K_4Fe(CN)_6$ requires considerable practice, therefore the student is advised to use it always.

When the reaction is complete, read off the amount of sugar solution which has been added. Now, the probability is that this result will be higher than the truth. The reason for this may be seen by allowing the basin to stand for about five minutes after the determination has been finished, when the solution will have become distinctly blue again from the re-oxidation of the Cu_2O.

It is necessary, therefore, to do the estimation as rapidly as possible. After having got an idea of the quantity which is necessary by the preliminary operation just described, clean out the dish, take a fresh 5 c.c. of solution I. and another of solution II. as before. Mix with the rod. Heat to boiling,

and run in the requisite amount of sugar, all but ·5 c.c. Boil, and see whether the liquid is blue; if in doubt, test with acid $K_4Fe(CN)_6$. Then add sugar, drop by drop, boiling after each addition until no copper is left in solution. Read off the result again.

A third determination is necessary for accuracy. This time run in the whole amount of sugar solution except ·1 c.c. The operation will thus be done very rapidly, and hence very accurately. Take this last result as correct.

When the Fehling's solution has been thus standardised, calculate what weight of glucose was contained in the quantity of solution used, and label the Fehling's solution bottles. Five c c. solution I. and 5 c.c. solution II. $= x$ glucose, where x is the weight calculated.

83. It has already been pointed out that different results may be obtained by using solutions of different strength. This necessitates that the solution we work with shall always be of nearly the same strength as the solution used in standardising. Should a preliminary determination show it to be much stronger, it must be diluted to approximately the right strength.

84. **Gravimetric Method.**—The volumetric method described above is rapid and, in practised hands, good, but is always a stumbling block to students. Messrs Clowes and Coleman, in their 'Text-book of Quantitative Analysis,' describe a gravimetric method which the author has found very satisfactory, and which students will be able to carry out without much difficulty.

Filter paper absorbs a certain amount of copper sulphate which obstinately refuses to be washed out. It is therefore necessary to prepare an asbestos filter, and it is on the preparation of this filter that the accuracy of the determination depends. A 'calcium chloride' tube of the shape shown on the

apparatus in fig. 20 (page 32), 4 or 5 inches long, is carefully cleaned and a tightly fitting disc of platinum foil which has been perforated is passed down the wider end to block up the thinner tube. A little good asbestos is carefully torn up, then reduced to a pulp with water, and poured into the tube; this is pressed down carefully, and then a little more pulp poured in until a felted mass about $\frac{1}{4}$ inch thick has been formed over the platinum. The tube is then connected with a filter pump and washed successively with dilute sulphuric acid, caustic potash, hot water, alcohol, and finally ether. It is then dried in a steam oven and weighed. When this is ready the estimation may be carried out as follows:

'Thirty c.c. of the copper solution and 30 c.c. of the tartrate solution [paragraph 80] are mixed with 60 c.c. of water in a beaker. The liquid is heated by immersing the beaker in boiling water. Twenty-five c.c. of the sugar solution, which must not contain more than 0·25 glucose, are then heated to boiling and added to the liquid in the beaker, and the beaker is heated in the boiling water for ten minutes longer.

'The liquid is then quickly filtered through the asbestos filter, using the filter pump, and the cuprous oxide is well washed in the filter with boiling water, then with alcohol, and finally with ether. It is dried in the steam oven and weighed.'[1]

The weight of cuprous oxide thus found, multiplied by 0·5045, equals the weight of glucose in the solution.

[1] Clowes and Coleman.

PART III

THE ESTIMATION OF NITROGEN

THE percentage of nitrogen affects the value of both feeding materials and manures to a greater extent than that of any other element The determination of nitrogen is consequently an operation of the greatest importance in agricultural work. It has therefore been thought well to devote a chapter entirely to describing the best methods at present in use for making this estimation.

85. **Permanent Apparatus.**—In all agricultural laboratories apparatus is kept permanently set up for the determination of nitrogen. It should be remembered, therefore, that although some processes—Kjeldahl's, for instance—may seem very long and tedious when only one estimation is required, they become comparatively simple when the apparatus is once set up and used frequently.

Fig. 25 is taken from a photograph of the bench used for nitrogen determination in the laboratory of the Notts County Council. The two bottles A and B contain respectively standard acid and alkali which may be run into the burettes beneath. The bottle C contains strong caustic soda, and is in connection with an arrangement for measuring out 100 c.c. at a time. On the lower shelf are bottles containing the various substances used in the different processes, and on the bench are different pieces of apparatus which are dealt with in detail in the descriptions of those processes for which they are used.

Other permanent apparatus is shown in figs. 27, 28, 29, and 30.

The student should make himself thoroughly expert in those forms of nitrogen estimation described in paragraphs 86 *to* 96

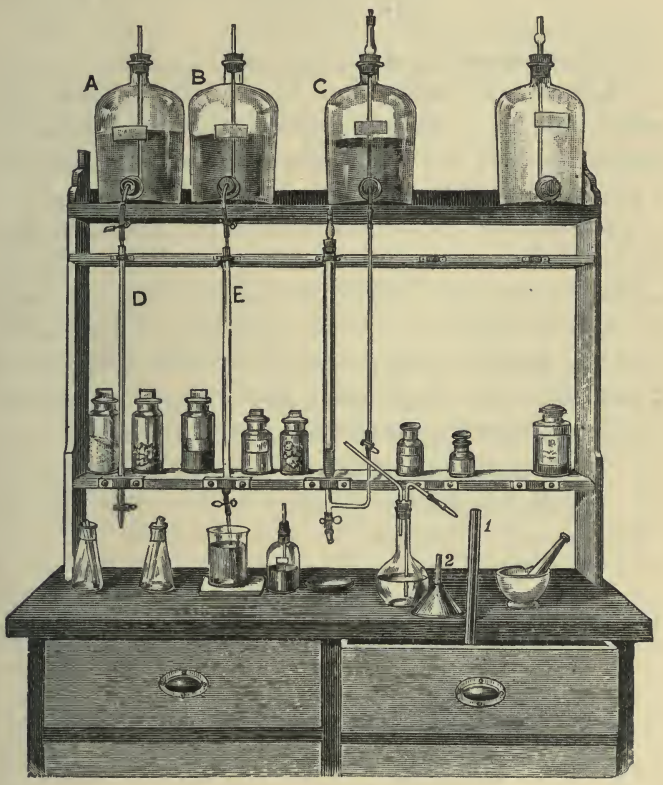

Fig. 25.

before he proceeds to the analysis of feeding materials. The remaining methods, which include the estimation of nitrogen when nitrates are present, may be conveniently left over until the end of

Part V., but must be thoroughly mastered before attempting the analysis of manures.

THE SODA LIME PROCESS (WILL AND VARRENTRAP)

86. **Substance used.**—Urea, $CO(NH_2)_2$.

Method.—The substance is decomposed by contact with red-hot soda lime, and the ammonia thus evolved absorbed in standard sulphuric acid. The amount of acid thus neutralised is determined by titration with standard caustic potash.

87. This determination may be made in a hard glass tube which has been sealed at one end, but as this is very liable to accidents an iron tube of about $\frac{1}{2}$-inch internal diameter which has one end welded up is much preferable. In laboratories where this method is used a supply of these iron tubes, varying in length from 14 to 30 inches, is kept. For this experiment the following apparatus is necessary:

An 18-inch iron tube (1, fig. 25).
A copper funnel (2, fig. 25).
A mortar and pestle.
A spatula.
A Will and Varrentrap bulb (fig. 26).
Corks and cork borers.
A furnace (fig. 27).

Also the following substances:

Seminormal sulphuric acid.
Quinquinormal $\left(\frac{N}{5}\right)$ alkali.
Granulated soda lime.
A mixture of 3 parts sugar and 4 parts soda lime.
Asbestos.

88. **The Operation.**—First find a cork to fit the iron tube. Bore a hole through it large enough to take the end of the Will and Varrentrap bulb tube. Fix it as shown in fig. 26. Now run into the bulb 20 c.c. of the seminormal acid from a burette (D, fig. 25) and set it on one side.

Next weigh out accurately about ·3 gram of pure dry urea. Place the iron tubes in the staple fixed in the drawer, just as the tube stands in fig. 25. By means of the copper funnel introduce sufficient of the soda lime and sugar mixture to fill an inch at the end of the tube. Pour as much granulated soda lime as could be held on a penny into the mortar. Turn out the urea on to this, and just cover it with finely powdered soda lime. Then add about twice as much granulated soda lime as is already in the mortar, placing it first on the watch glass and pouring it thence into the mortar. This ensures that all the urea shall be removed from the glass. Now mix thoroughly with the steel spatula, and pour through the funnel into the tube. Rinse out the mortar with fresh granulated soda lime several times, pouring the rinsings into the tube, stopping when it is within 4 inches of the open end. Cover the soda lime with a plug of asbestos which fills about an inch of the tube when gently pressed down with a thick glass rod. Now close the tube with the cork through which passes the tube of the Will and Varrentrap bulb.

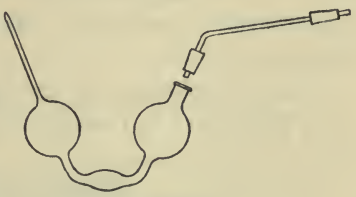

FIG. 26.

The tube is now ready for heating, which may conveniently be done in a Bunsen combustion furnace, as shown in fig. 27, but any tube furnace may be used. (A few of the tiles have here been removed to show the construction of the furnace.)

After placing the tube in the furnace, turn on and light the two taps *nearest the open end.* Gas will be seen to bubble through the bulbs. As soon as this ceases turn on the next tap. The bubbles will start again. When they have ceased, or nearly so, turn on another. Continue turning on the taps in this way until the whole tube is red hot.

The last few taps will, of course, only heat the mixture of soda lime and sugar which was introduced first of all. This gives off various gases which expel the last traces of ammonia from the tube.

When all bubbling has ceased, hold the tube firmly with a pair of glass pliers, and carefully draw the bulbs out. (The glass

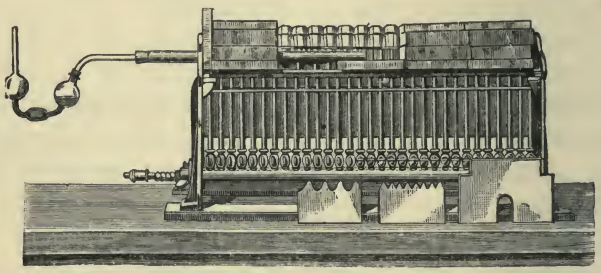

Fig. 27.

tube will come away, leaving cork adhering to the iron tube.) Empty the acid into a large beaker. Wash out the bulbs twice with distilled water, pouring the washings into the beaker which already contains the acid. Add a few drops of methyl orange solution, and titrate with the quinquinormal alkali, using burette E, fig. 25.

89. **Calculation.**—Divide the number of c.c. of potash run into the acid by 2·5, which gives the number of c.c. of acid which have been neutralised by it. Subtract this from 20, and you have the number of c.c. of acid which have been neutralised by ammonia.

Since the sulphuric acid solution is seminormal, one litre will neutralise $\frac{17}{2}$ grams of NH_3, or one c.c. will neutralise $\frac{\cdot 017}{2} = \cdot 0085$ gram of NH_3, which is equivalent to $\frac{\cdot 014}{2} = \cdot 007$ gram N. If, therefore, we multiply the number of c.c. neutralised by ammonia by ·007, we obtain the weight of N in the urea. From this the percentage of nitrogen may be calculated.

THE SULPHURIC ACID METHOD

This method was due to Kjeldahl, but the more accurate modification here described is known as Gunning's process.

90. **Substance used.**—Since urea does not require the full working of this process, a sample of linseed cake whose percentage of N is known should be used.

Method employed.—The substance is decomposed by hot strong sulphuric acid, whose boiling-point is increased by the addition of potassic sulphate. The ammonia so formed is expelled by means of caustic soda, and absorbed and estimated as before.

The general principle of this method was invented by Kjeldahl, and since the time when it was first made public a large number of modifications have been used. The original method decomposed any organic matter by means of sulphuric acid, mercuric oxide, and potassium permanganate. One writer recommends the use of manganese dioxide in place of permanganate. Others, again, have shown that these powerful oxidising agents occasionally oxidise some of the nitrogen, which thus escapes as an oxide of nitrogen. The method here described is used in some of the principal agricultural laboratories.

91. **Apparatus required.**—This is shown in figs. 28, 29, and 30, and described in the text.

Chemicals required.—Sulphuric acid free from nitrogen. Strong caustic soda solution. This is prepared by dissolving 357 grams of 98 per cent. caustic soda in the least possible quantity of water and making up to a litre. It is kept in the arrangement shown at C, fig. 25. The bottle has a soda lime tube above to prevent the access of CO_2. By opening the pinchcock, the solution is allowed to run into the tube, which has two marks upon it. When it is full up to the topmost mark, the cock is closed and the liquid is run out below into a beaker, until the level in the tube is that of the bottom mark. This measures out exactly 100 c.c.

Anhydrous potassium sulphate is also required.

92. **Heating with Acid.**—Weigh out about 1 gram of linseed cake, and introduce it into an 8-oz. flask, taking care that none adheres to the neck. Measure out 20 c.c. of strong H_2SO_4 free from nitrogen. Pour it on to the cake, and heat gradually up to the boiling-point of the acid.[1] A very convenient stand for this is shown in fig. 28. The stand itself is made of iron, and a piece of asbestos cardboard, A, pierced with four holes, each 3 inches diameter, is used as a rest for the flasks. A sheet-iron support, B, is fixed at the back of the stand, so that the flasks whilst heating may be tilted as in the figure ; this prevents loss by spirting. The heat is supplied by the four Argand burners C, C, C, C. The temperature obtained by this means is quite sufficient for the purpose, whilst the strong illumination of the flask and its contents supplied by the bright flame is a great advantage to the operator.

When the liquid has ceased frothing (from twenty to forty

[1] It need scarcely be mentioned that the heating of a carbonaceous substance with sulphuric acid will give off large quantities of sulphur dioxide This operation must therefore be carried out in a draught cupboard.

minutes) it will be quite black and impervious to the light, but also quite free from clots of carbonaceous matter. It is now necessary to clear the solution. Place the flask upright for a moment, throw into it about 8 grams of dry powdered K_2SO_4, and immediately return to the inclined position. The potash salt will very considerably raise the boiling-point of the acid, and at this higher temperature the carbonaceous matter in solution is readily oxidised, with evolution of SO_2. As the liquid becomes clearer the light of the Argand begins to pene-

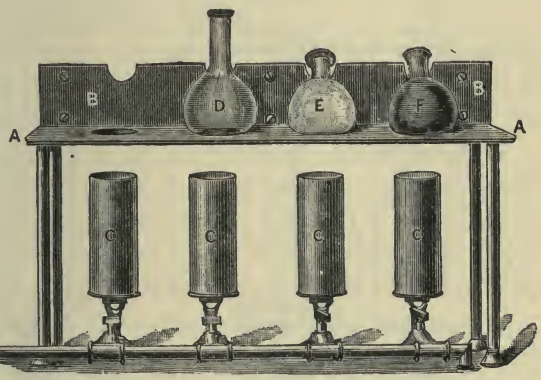

FIG. 28.

trate it, illuminating the white fumes in the flask. This makes the interior of the flask appear first dark red, which changes gradually to yellow and finally to white. It is then allowed to cool. In the figure the flask F shows the beginning of the operation, E is clearing, and D is cooling.

93. **The Distillation.**—The whole of the nitrogen being now in the shape of sulphate of ammonia, the next process consists of distilling off the ammonia after setting it free by caustic soda.

Fig. 29 shows a very convenient form of apparatus.

A is an ordinary half-gallon oil can fitted with a good cork pierced by two holes. Through one hole passes the straight tube K, which reaches to within an inch of the bottom of the can. Through the other passes the delivery tube M. This arrangement serves as a boiler for supplying steam. B is a 60-oz. flask fitted with an india-rubber stopper pierced by three holes. The tube M passes through one of these down to the bottom of the flask; the other two being occupied respectively

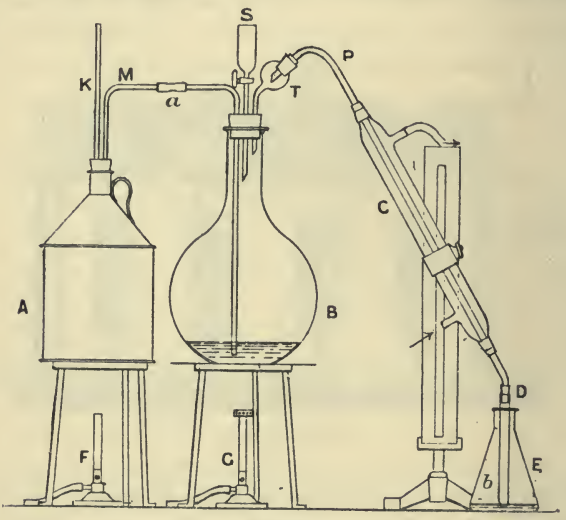

FIG. 29.

by the tap funnel S and the trap T. This trap is merely a device for preventing caustic soda from being mechanically carried over into the condenser. Its construction is sufficiently apparent from fig. 30.[1] C is a condenser of the usual form, but made of metal instead of glass, the inner tube being of block

[1] The trap may be left out if the tube leading from the flask E be continued straight upwards for a foot or so before it bends down to dip into the condenser.

tin. This substance, whilst not acted upon by ammonia, is a far better conductor of heat than glass, so that a 12-inch condenser is perfectly effective. D is a long test tube with a hole blown through its end at *b*. It is fixed to the end of the condenser by a cork, and dips to within half-an-inch of the bottom of the 8-oz. conical flask E.

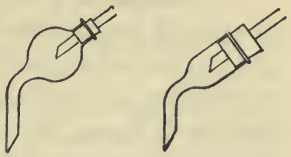

FIG. 30.

94. When the apparatus is ready, proceed with the estimation in the following manner:

(*a*) Run 20 c.c. of seminormal sulphuric acid from a burette into the flask E. Insert the test tube D and fix on to the condenser, as in the figure.

(*b*) Half fill the can A with water, and set it to boil.

(*c*) Pour about 100 c.c. of distilled water into the large flask B. Then pour into this water the acid liquid in which the linseed cake has been decomposed. Wash out the small flask three times with water, and add the washings to the liquid in B.

(*d*) Replace all the apparatus as in the figure.

(*e*) Measure out 100 c.c. of the strong caustic soda solution (357 grams per litre), and run it through the tap funnel, S, into the flask.

95. The *distillation* may now be proceeded with. Light the lamp under A, and turn on the water through the condenser. In a few minutes the liquid in B will be raised to the boiling-point. Allow the steam to pass for twenty-five minutes, then light the rose burner G. Let the steam pass for five minutes more, and the distillation will be completed.

Remove the test tube D and flask E from the condenser. Take the tube from the flask, washing back the adhering acid. Add a drop or two of methyl orange, and titrate with standard KHO.

The calculation is exactly the same as in the soda lime process.

96. **Comparison of the Two Methods.**—The soda lime process has the advantage of requiring little or no apparatus but what may be found in any laboratory, but it possesses the disadvantage that the acid in the bulb is often much discoloured during the operation, thus rendering accurate titration very difficult. Another disadvantage which is not at all shared by the acid process is that the substance for analysis must be very finely divided. When such materials as horn and dried blood have to be analysed, fine grinding is next to impossible, and very erroneous results are often obtained. In all cases where grinding is difficult, the substance should be ground finely enough to enable the operator to weigh out a good average sample, and the nitrogen estimated by the acid method.

ESTIMATION OF NITROGEN IN PRESENCE OF NITRATES

97. **Substance used.**—A mixture of three parts starch and one part ammonium nitrate, NH_4NO_3.

Method employed.—The substance is decomposed by sulphuric acid and salicylic acid, the N_2O_5 being reduced meanwhile to ammonia with zinc-dust. The ammonia is separated and estimated as before.

98. **Apparatus.**—This is exactly the same as is used in paragraphs 92–96.

Chemicals.—Sulphuric and salicylic acids, prepared by dissolving 2 grams of salicylic acid in 30 c.c. of sulphuric acid.

Mercury.

Sodium sulphide solution, 80 grams per litre.

Strong caustic soda and standard acid and alkali as before (paragraphs 87 and 91).

Zinc-dust.

99. **The Operation.**—Weigh out about a gram of the mixture of starch and ammonium nitrate. Transfer to an 8-oz. flask and moisten with the smallest possible quantity of water. Take especial care that no dry particles are left in the flask; for if such particles should float on the surface of the acid when it is poured into the flask, HNO_3 may be given off and escape. Pour into the moistened substance 30 c.c. of sulphuric acid in which 2 grams of salicylic acid has been dissolved. Heat on a stand (fig. 28) or sand bath until all frothing ceases. Whilst this preliminary heating is going on, weigh out roughly 2 grams of zinc-dust. As soon as the frothing has ceased add this zinc-dust, a little at a time; then add about 10 grams of K_2SO_4 and heat until the liquid becomes colourless. If, in an hour, the liquid is still black or contains carbonaceous matter, the clearing may be greatly assisted by the addition of a drop of mercury.

When the liquid is quite clear, all the nitrogen contained in the original substance will be in the form of ammonium sulphate. If the operation has been managed satisfactorily without the aid of mercury, the ammonia may be driven off by 150 c.c. of strong caustic soda, as described in paragraphs 93–95. Should it have been found necessary to use mercury, it must be removed from solution by adding 25 c.c. of the sodium sulphide solution together with the caustic soda. The reason for this is that mercury-ammonium salts are apt to be formed, which are not completely decomposed by the strong alkali, and hence some of the ammonia does not find its way into the standard acid.

TO DISTINGUISH BETWEEN 'NITRIC,' 'AMMONIACAL' AND 'ORGANIC' NITROGEN

100. The value of the nitrogen in manures varies considerably according to whether it is in a soluble or an insoluble state. Hence it is often of importance to discover in what state this element occurs. The three most common occurrences are:

'**Nitric,**' where it is in direct combination with oxygen, as in a nitrate or nitro-compound;

'**Ammoniacal,**' where it is in direct combination with hydrogen and may be driven off as ammonia by a caustic alkaline solution;

'**Organic,**' where it is in combination with some organic material and is not released as ammonia by caustic alkalis.

A convenient substance for practising on may be prepared by mixing linseed cake with ammonium sulphate and sodium nitrate.

To obtain an analysis showing the relative quantities of the different forms of nitrogen in this mixture, three operations are necessary.

Operation I.—Weigh out ·5 gram of the mixture. Place it in the large flask shown in fig. 29, add 200 c.c. of distilled water and 2 grams of calcined magnesia. Attach the absorption flask containing 20 c.c. of $\frac{N}{2}$ sulphuric acid, and distil exactly as described in paragraphs 93–95. Titrate the acid with $\frac{N}{5}$ caustic potash, and calculate the percentage of nitrogen which has been liberated by the magnesia. This will give the percentage of ammoniacal nitrogen.

N.B.—This is the ordinary method used to determine the amount of ammonia in ammoniacal salts.

Operation II.—Determine the nitrogen by means of the acid process (paragraphs 92–95). The sulphuric acid used, in this case, will drive off all the 'nitric' nitrogen in the form of HNO_3. Thus the percentage of ammoniacal + organic nitrogen will be obtained.

Operation III.—Determine the total nitrogen as explained in paragraphs 97–99.

101. **Calculation.**—By these three operations we obtain three results. The first gives the percentage of ammoniacal nitrogen. The difference between the second and the first is the percentage of organic nitrogen, and the difference between the third and the second is the percentage of 'nitric' nitrogen.

RAPID METHODS FOR THE DETERMINATION OF NITROGEN IN NITRATES

102. In cases where nothing but the percentage of 'nitric' nitrogen is required, as in alkaline nitrates, the above method would be very long and tedious. Therefore, three methods are here given, each of which has its special recommendations.

103. **Ulsch's Method.**—This method is the most generally applicable, and is of especial value in the analysis of alkaline nitrates, and mixed manures which contain nitrates *but not ammonium salts.*

Method employed.—The nitrate is reduced by iron and dilute sulphuric acid. Ammonium sulphate is thus formed. The ammonia is driven off and estimated as before.

Substance used.—Potassium nitrate, KNO_3. Weigh out accurately about 2 grams of pure potassium nitrate, and dissolve in a little water. Introduce the solution into a 100-c.c. flask, with all the precautions used in making up a standard solution.

Add distilled water to the 100-c.c. mark. Shake well. Measure out 25 c.c. of this solution with a pipette into an 8-oz. flask. Add 5 grams of reduced iron and 20 c.c. of dilute sulphuric acid (one volume of acid to three of water). Place the flask in an inclined position on the stand (fig. 28) and allow the reaction to continue *without heating* until effervescence ceases. Now heat to boiling for six minutes, then allow to cool. The nitrogen is now in the state of sulphate of ammonia, and may be estimated as in paragraph 100, operation I. Instead of magnesia, however, add 20 c.c. of caustic soda solution and two or three lumps of clean granulated zinc. The calculation in this case is similar to the one in paragraph 89; but it must be remembered that, whereas about 2 grams of the potassium nitrate were weighed out and dissolved, only one quarter of this solution was used.

104. **Schloesing's Method** (*modified*).—This is a very rapid method, and is generally used for the estimation of the nitrates in soils. It may, however, be advantageously used in the estimation of nitrogen in alkaline nitrates and manures.

Method.—The nitrate is decomposed by sulphuric acid and ferrous sulphate according to the equation

$$2NaNO_3 + 6FeSO_4 + 4H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + Na_2SO_4 + 4H_2O.$$

The nitric oxide is measured.

105. **Apparatus.**—Many forms of apparatus are used for this operation. Of the two described here, the first is in use at the laboratory of the Royal Agricultural Society of England, and has the great advantage that no other gas excepting the nitric oxide and a little water vapour is present in any part of the apparatus. The second one is more readily prepared but less easily worked.

106. The first apparatus is shown in fig. 31. A is a round-bottomed flask, in which the reaction is to take place. B is a

tap funnel by which the liquid may be introduced into A. C is a trap joint which prevents any of the solution from getting into the side tube D. The tube D, by which the gas is to escape, bends twice at angles of 135°, and is at least 36 inches in length from the second bend, G, to the lower outlet. The end N is recurved into a hook, so that the gas may pass into the measuring tube, K, which stands in a trough of mercury, F.

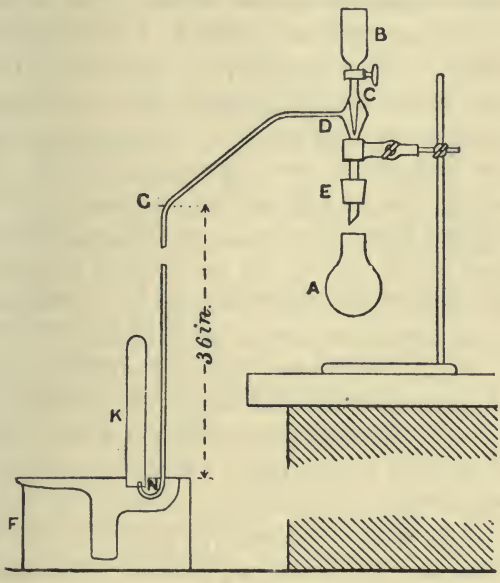

FIG. 31.

107. **The Experiment.**—Fix the tap funnel firmly in the clip of a retort stand, in the position shown in the figure, so that the side tube may fall over the side of the bench. Place the mercury trough beneath the outlet N. Fix the flask A in position, and the apparatus is ready for work.

Weigh out about 1 gram of pure KNO_3 and dissolve in a 100-c.c. flask, as directed in paragraph 103. Measure out 20 c.c.

with a pipette and run it into the flask A, washing it in with 20 c.c. of warm water. Next weigh out roughly a gram of pure ferrous sulphate and dissolve it in 20 c.c. of hot water to which a drop of sulphuric acid has been added. Whilst it is dissolving, close the stopcock of the funnel, see that the end of the evolution tube dips under the mercury, and boil the liquid in the flask until it is reduced to about half its bulk. This will drive all air out of the apparatus, and on allowing it to cool the mercury will rise in the side tube nearly to the barometric height. If the mercury does not rise freely, then there is some leak in the apparatus. Should all go well, heat up again to boiling and pour the ferrous sulphate solution into B. Turn on the tap cautiously, and allow nearly all the liquid to run into the flask. Now fill the measuring tube, K, with mercury, and invert it over the end of the evolution tube. Pour 40 c.c. of strong sulphuric acid into B, and turn on the tap so that the acid may drop slowly into the flask. Nitric oxide will at once come off. When *nearly all* the acid has been added (only so much being left as will prevent the access of air to the tap), turn off the tap and heat the flask cautiously. After all the gas has come off from the apparatus—*i.e.*, when it ceases to collect in K—boil briskly for half-a-minute, and allow to cool. Remove the measuring tube to the deepest part of the trough, and allow to stand for an hour to cool. When cold, sink the tube until the mercury stands at the same level inside and outside. Now read off the volume of the gas. Usually a little water collects over the mercury inside the tube. In adjusting the levels of the mercury this is neglected, but the volume of the water must be noted. Note also the height of the barometer and the temperature of the air in the room.

Nitric oxide is slightly soluble in water, and therefore an allowance must be made. Experiment has shown that under the conditions of this experiment the water which collects in

the tube dissolves one twentieth of its volume of gas. The total volume of gas evolved is therefore the volume read off on the collecting vessel + $\frac{1}{20}$ the volume of water standing above the mercury.

108. **Calculation.**—Having found the volume of gas, including the correction for solubility, at a certain known temperature and pressure, the first thing to do is to find what that volume would be at the normal temperature and pressure of 0° C. and 760 mm. This is done by the formula

$$V_2 = \frac{V_1 \times 273 \times p}{(273+t) \times 760}$$

where V_2 = volume at 0° C. and 760 mm. ;
V_1 = volume noted ;
p = pressure noted in millimetres ;
t = temperature noted in degrees Centigrade.

For the explanation of this formula the student is referred to any elementary book on physics.

Having reduced our volume to normal temperature and pressure, we make use of the following data : 1 c.c. of NO at 0° C. and 760 mm. represents 1·343 milligram of NO. This is equivalent to ·627 milligram of nitrogen or 3·805 of $NaNO_3$.[1] We have, therefore, only to multiply the reduced volume in c.c. by ·000627 to find the weight of N present in the KNO_3, and from this we may calculate the percentage. When a large number of estimations have to be made this calculation becomes somewhat tedious. The table on pages 74–77 will simplify this very much. This table contains a set of factors which are used as follows :

Having read off the temperature and the pressure, refer to

[1] Sodium nitrate is mentioned here, as it is the substance in which agricultural analysts most commonly have to carry out this estimation. *Potassium* nitrate is suggested for the student, as it is more easily prepared in the pure state.

TABLE FOR REDUCING VOLUMES OF GAS TO 0° C. AND 760 MM.

—	7°	8°	9°	10°	11°	12°	13°	14°
730	·9365	·9332	·9299	·9266	·9233	·9201	·9169	·9137
731	·9378	·9345	·9311	·9278	·9246	·9214	·9182	·9150
732	·9391	·9357	·9324	·9291	·9258	·9226	·9194	·9162
733	·9404	·9370	·9337	·9304	·9271	·9239	·9207	·9175
734	·9416	·9383	·9350	·9317	·9284	·9252	·9220	·9187
735	·9429	·9396	·9362	·9329	·9297	·9264	·9232	·9200
736	·9442	·9408	·9375	·9342	·9309	·9276	·9244	·9212
737	·9455	·9421	·9388	·9354	·9321	·9288	·9255	·9225
738	·9468	·9434	·9401	·9368	·9335	·9302	·9269	·9237
739	·9481	·9447	·9413	·9381	·9348	·9315	·9282	·9250
740	·9493	·9459	·9426	·9393	·9360	·9327	·9294	·9262
741	·9506	·9472	·9439	·9406	·9373	·9340	·9307	·9275
742	·9519	·9485	·9452	·9419	·9386	·9352	·9320	·9287
743	·9532	·9498	·9464	·9431	·9398	·9365	·9332	·9300
744	·9545	·9511	·9477	·9444	·9411	·9378	·9345	·9312
745	·9558	·9523	·9490	·9457	·9424	·9390	·9357	·9325
746	·9570	·9536	·9502	·9469	·9436	·9403	·9370	·9337
747	·9583	·9549	·9515	·9482	·9449	·9416	·9383	·9350
748	·9596	·9562	·9528	·9495	·9462	·9428	·9395	·9362
749	·9609	·9575	·9541	·9507	·9474	·9441	·9408	·9375
750	·9622	·9587	·9554	·9520	·9486	·9453	·9421	·9387
751	·9635	·9600	·9566	·9533	·9499	·9466	·9434	·9400
752	·9647	·9613	·9579	·9545	·9512	·9478	·9446	·9412
753	·9660	·9626	·9592	·9558	·9524	·9491	·9459	·9425
754	·9673	·9638	·9604	·9571	·9536	·9503	·9471	·9437

TABLE FOR REDUCING VOLUMES OF GAS TO 0° C. AND 760 MM. (*continued*).

—	15°	16°	17°	18°	19°	20°	21°	22°
730	·9105	·9074	·9042	·9011	·8980	·8950	·8919	·8887
731	·9118	·9086	·9055	·9023	·8993	·8962	·8932	·8899
732	·9130	·9099	·9067	·9035	·9005	·8974	·8944	·8911
733	·9143	·9111	·9079	·9048	·9017	·8986	·8956	·8923
734	·9155	·9123	·9092	·9060	·9030	·8999	·8968	·8935
735	·9168	·9136	·9104	·9072	·9042	·9011	·8980	·8948
736	·9180	·9148	·9116	·9085	·9054	·9023	·8993	·8960
737	·9193	·9161	·9129	·9098	·9067	·9035	·9005	·8972
738	·9205	·9172	·9141	·9110	·9079	·9047	·9017	·8984
739	·9218	·9186	·9153	·9122	·9091	·9059	·9029	·8996
740	·9230	·9198	·9166	·9135	·9103	·9071	·9041	·9009
741	·9243	·9211	·9178	·9147	·9116	·9084	·9054	·9021
742	·9255	·9223	·9191	·9159	·9128	·9096	·9066	·9033
743	·9268	·9236	·9203	·9172	·9140	·9108	·9078	·9045
744	·9280	·9248	·9215	·9184	·9153	·9120	·9090	·9057
745	·9293	·9261	·9228	·9197	·9165	·9133	·9102	·9070
746	·9305	·9273	·9240	·9209	·9177	·9145	·9115	·9082
747	·9318	·9285	·9252	·9221	·9190	·9157	·9127	·9094
748	·9330	·9297	·9265	·9234	·9202	·9169	·9139	·9106
749	·9343	·9310	·9277	·9246	·9214	·9182	·9151	·9118
750	·9354	·9322	·9290	·9258	·9226	·9194	·9164	·9130
751	·9367	·9335	·9302	·9270	·9239	·9206	·9176	·9143
752	·9379	·9347	·9314	·9283	·9251	·9218	·9188	·9155
753	·9392	·9360	·9327	·9295	·9263	·9231	·9200	·9167
754	·9404	·9372	·9339	·9307	·9276	·9243	·9212	·9179

TABLE FOR REDUCING VOLUMES OF GAS TO 0° C. AND 760 MM. (*continued*).

—	7°	8°	9°	10°	11°	12°	13°	14°
755	·9686	·9651	·9617	·9583	·9548	·9516	·9484	·9450
756	·9699	·9664	·9630	·9596	·9561	·9528	·9496	·9462
757	·9712	·9677	·9643	·9609	·9574	·9541	·9509	·9475
758	·9724	·9690	·9655	·9621	·9587	·9554	·9522	·9487
759	·9737	·9702	·9668	·9633	·9600	·9566	·9535	·9500
760	·9750	·9715	·9681	·9646	·9613	·9579	·9547	·9512
761	·9763	·9728	·9693	·9659	·9625	·9591	·9560	·9525
762	·9776	·9741	·9706	·9672	·9638	·9604	·9572	·9537
763	·9788	·9754	·9719	·9684	·9650	·9617	·9585	·9550
764	·9801	·9766	·9732	·9697	·9663	·9630	·9598	·9562
765	·9814	·9779	·9744	·9710	·9676	·9642	·9610	·9575
766	·9827	·9792	·9757	·9722	·9688	·9655	·9623	·9587
767	·9840	·9805	·9770	·9735	·9701	·9668	·9635	·9600
768	·9853	·9817	·9783	·9748	·9714	·9680	·9648	·9612
769	·9865	·9830	·9795	·9760	·9726	·9693	·9660	·9625
770	·9878	·9843	·9808	·9773	·9739	·9705	·9673	·9637
771	·9891	·9856	·9821	·9786	·9752	·9718	·9685	·9650
772	·9904	·9868	·9834	·9798	·9764	·9731	·9698	·9662
773	·9917	·9881	·9846	·9811	·9777	·9743	·9710	·9675
774	·9930	·9894	·9859	·9824	·9790	·9751	·9723	·9687
775	·9942	·9907	·9872	·9836	·9802	·9768	·9735	·9700
776	·9955	·9919	·9884	·9849	·9815	·9781	·9748	·9712
777	·9968	·9932	·9897	·9862	·9828	·9794	·9760	·9725
778	·9981	·9945	·9910	·9874	·9840	·9806	·9773	·9737
779	·9994	·9958	·9923	·9887	·9853	·9819	·9785	·9750
780	1·0007	·9971	·9935	·9899	·9866	·9831	·9798	·9762

TABLE FOR REDUCING VOLUMES OF GAS TO 0° C. AND 760 MM. (*continued*).

—	15°	16°	17°	18°	19°	20°	21°	22°
755	·9417	·9385	·9351	·9320	·9288	·9255	·9225	·9191
756	·9429	·9397	·9364	·9332	·9300	·9267	·9237	·9204
757	·9442	·9410	·9376	·9344	·9313	·9280	·9249	·9216
758	·9454	·9422	·9389	·9357	·9325	·9292	·9261	·9228
759	·9467	·9434	·9401	·9369	·9337	·9304	·9273	·9240
760	·9479	·9446	·9414	·9381	·9349	·9316	·9286	·9252
761	·9492	·9459	·9426	·9394	·9362	·9329	·9298	·9264
762	·9504	·9471	·9438	·9406	·9374	·9341	·9310	·9276
763	·9517	·9484	·9451	·9418	·9387	·9353	·9322	·9289
764	·9529	·9496	·9463	·9431	·9399	·9365	·9334	·9301
765	·9542	·9509	·9475	·9443	·9411	·9378	·9347	·9313
766	·9554	·9521	·9488	·9455	·9424	·9390	·9359	·9325
767	·9567	·9533	9500	·9468	·9436	·9402	·9371	·9337
768	·9579	·9545	·9512	·9480	·9448	·9414	·9383	·9349
769	·9592	·9558	·9525	·9492	·9460	·9427	·9395	·9362
770	·9604	·9571	·9538	·9505	·9472	·9439	·9408	·9374
771	·9617	·9583	·9550	·9517	·9485	·9451	.9420	·9386
772	·9629	·9595	·9562	·9529	·9497	·9463	·9432	·9398
773	·9642	·9608	·9575	·9542	·9509	·9476	·9444	·9410
774	·9654	·9620	·9587	·9554	·9522	·9488	·9456	·9422
775	·9667	·9632	·9600	·9566	·9534	·9500	·9469	·9435
776	·9679	·9644	·9613	·9579	·9546	·9512	·9481	·9447
777	·9692	·9657	·9625	·9591	·9559	·9525	·9493	·9459
778	·9704	·9670	·9638	·9603	·9571	·9537	·9505	·9471
779	·9717	·9682	·9650	·9615	·9582	·9549	·9517	·9483
780	·9729	·9695	·9662	·9628	·9595	·9562	·9530	.9496

the table ; find the figure denoting the number of millimetres of pressure in the first column, and glance along this line until you come to the column which is headed by the number of degrees Centigrade which you have read off on the thermometer. Multiply the number of c.c. of gas obtained by the factor here found. The product will be the volume at 0° C. and 760 mm.

For instance, supposing we found our volume to be 89.2 c.c. at 17° and 772 mm., we find the factor for this temperature and pressure in the table to be ·9562. We calculate the volume at 0° C. and 760 mm. thus :

$$89{\cdot}2 \times {\cdot}9562 = 85{\cdot}29$$

and multiplying this by ·000627 we get the weight of N in our substance—*i.e.*, ·05348 gram.

109. The second apparatus is shown in fig. 32. The operation is carried on in the flask A, which is of 6-oz. capacity

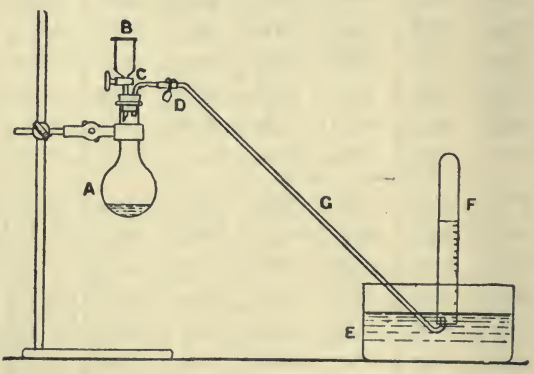

FIG. 32.

and is fitted with an india-rubber stopper in which two holes have been bored. Through one passes the tap funnel B, through the other an evolution tube, C O, which is cut at D and joined with a piece of india-rubber, which can be closed at will

by a pinchcock. The pneumatic trough, E, is filled with water.

This apparatus is arranged specially for estimating the amount of nitric nitrogen in commercial nitrate of soda, and has to be calibrated after each operation. The method may be briefly described as follows. Make up solutions of

1 gram pure $NaNO_3$ made up to 100 c.c.
1 gram commercial $NaNO_3$ made up to 100 c.c.
2 grams $FeSO_4$ dissolved in 50 c.c. of water and a drop of H_2SO_4.

When passing a slightly soluble gas like nitric oxide through large quantities of water, it is practically impossible to make any correct allowance for the quantity that may be lost. The only plan, therefore, is to make a comparison between the volume of gas obtained from a pure sample of the nitrate and that obtained from the sample under consideration.

110. **Calibration.**—Boil 20 c.c. of the pure $NaNO_3$ solution with 20 c.c. water as before to expel air. Close the india-rubber joint D and add 25 c.c. $FeSO_4$ solution. Place the collecting tube in position, and add 50 c.c. strong sulphuric acid cautiously to the liquid in the flask, opening D at the same time. Complete the reaction exactly as in the other apparatus. Read off the volume of gas.

111. **The Estimation.**—Wash out the apparatus immediately the calibration is finished, and do a second operation, using 20 c.c. of the commercial nitrate solution.

112. **Calculation.**—This is very simple, being a mere comparison of the two results. Thus, supposing the calibration gave x c.c. of gas and the estimation y c.c., then the percentage of pure $NaNO_3$ in the commercial sample would be $\frac{y}{x}$ 100. There is no need, with this apparatus, to correct

for temperature and pressure, as the two operations were conducted under as nearly as possible the same conditions.

113. **Lunge's Nitrometer Method.**—Lunge's nitrometer was originally invented to estimate the amount of nitrogen in 'nitrous vitriol.' Two modern forms of the apparatus are shown in figs. 33 and 34, the only difference between the two forms being their capacity. In fig. 33 *a* is a calibrated tube connected above with a three-way tap, *d*, and below with a piece of stout-walled india-rubber tubing *c*. The tube *b* is not calibrated. *f* is

FIG. 33.


FIG. 34.

a funnel by means of which liquids may be introduced into *a*, and *e* is a thick-walled tube of small bore by means of which gases may be introduced or drawn off. In fig. 34 the same parts are shown, but two large bulbs are blown in the tubes, so that the amount of gas which may be experimented with is greatly increased.

114. **The Estimation.**—Fill the apparatus with the bulbs (fig. 34) with mercury as shown in fig. 33, and turn the tap so that

communication is made between the calibrated tube and the air. Raise the tube *b* until the mercury entirely fills *a*. Close the tap. Return *b* to its position, clamping the tubes in a retort stand as shown in fig. 33. Weigh out about ·3 gram of sodium nitrate, and introduce the powder into the funnel. Add about 1 c.c. of water. As soon as the nitrate is dissolved, draw it into the measuring tube. Wash the cup with another c.c. of water, and draw that into the measuring tube. Finally, add 15 c.c. of pure strong sulphuric acid, and draw that in.

Now unclamp the tube containing the acid mixture, and incline it once or twice so as to place the mercury in contact with the liquid ; gas will commence to come off and collect at the top. When this ceases shake more violently, so that the mercury at the surface of contact gets broken up into a number of globules, thus coming into thorough contact with the nitric acid. By this means the whole of the nitrogen will be transformed into nitric oxide, and if the tubes be clamped so that the mercury stands at the same level in both tubes, the volume may be read off. It may be assumed, for measuring purposes, that mercury has 6·5 times the specific gravity of sulphuric acid. This must be allowed for in adjusting the heights of the columns in the two tubes. Allow the whole apparatus to cool down for half-an-hour. Readjust the height of the mercury column. Note volume of gas, temperature of air, and height of barometer in millimetres.

The calculation is exactly the same as that used for Schloesing's apparatus (see paragraph 108).

PART IV

SAMPLES AND SAMPLING

115. Large quantities of material are often valued by the analysis of a couple of grams, or even less, which has been taken from the bulk. Whether that analysis represents accurately the composition of the whole quantity or not depends, therefore, quite as much upon the care with which that two grams has been selected as upon the accuracy with which the analysis has been made. In fact, in every case where a sample has been drawn from a large bulk of material, there is a certain chance of error. The object of careful and scientific sampling is to reduce this chance to a minimum.

In practice all substances for analysis are sampled twice: first, when the sample is taken from the bulk, and, second, when the analyst selects from this first sample the portion upon which he intends to experiment.

As a rule this first operation is performed by the person who wishes to have the analysis made, whilst the second is done by the analyst. It would seem, therefore, at first sight that the second was the only one with which the analyst need be familiar; but the buyer or seller who wishes the sample to be analysed has often no one to guide him in the sampling except the analyst himself. Both operations are described in detail in this chapter.

116. **The Sampling of Minerals.**—The only cases in which the sampling of minerals concerns the agricultural analyst

are those of mineral phosphates and limestones. Much ingenuity has been expended in devising machinery and implements with which an accurate sample can be drawn. The simplest of these is the *sampling* spade, shown in fig. 35. When this is driven into a mass of ore a certain small quantity is collected in the central compartment, whilst a much larger portion finds its place on the sides. A dexterous throw with the shovel sends all the larger portion off on to another heap, leaving the small part still in its place. This is then thrown on to another spot. Thus, after digging away a large portion from different parts of the bulk we get a large and a small heap, the small one being a fair sample of all the rest. By repeating the operation on this sample a still smaller sample is obtained.

Fig. 35.

When, by repeated samplings of this kind, a sufficiently small heap has been formed, it is spread out on the ground, the larger lumps broken up, and half-a-dozen small spadefuls taken from different parts. This small quantity is broken up to pieces about the size of marbles, spread out, and five or six handfuls taken from different parts. This portion may be sent to the laboratory.

Should a sampling shovel not be available, the first heap may be made by selecting a spadeful at a time from different parts of the bulk, and reducing this to smaller heaps as before.

117. In a *sampling machine* the whole mass of the mineral is made to pass through a spout which is continually moving backwards and forwards so as to distribute the ore all over a large platform. At one part of the platform is a hole, so that whenever the spout passes that place a small portion of the mineral falls through into a receptacle beneath. This portion is again passed through the machine, until it becomes of

workable size. It is then broken up, and the laboratory sample taken as before.

118. **Sampling aided by Grinding.**—Fortunately, in agricultural work, such rough methods as those described in the last article are seldom necessary. The manure manufacturer materially aids the sampler when he grinds the mineral; for, whether it be for the preparation of superphosphate or for direct application to the land, the substance must pass through this process.

When a mineral is ground or crushed two ends are gained. In the first place, the particles of the substance are reduced in size; and, in the second, these particles are more or less thoroughly mixed, so that after grinding it is far more homogeneous in character than it was before.

119. **The Sampling of Manures.**—This subject has been so thoroughly dealt with by Dr. J. A. Voelcker in the 'Journal of the Royal Agricultural Society' that no better advice can be given than is contained in the following quotation:

'If a purchase consists of six or any lesser number of bags, each one should be opened and a portion drawn from each bag; if it consist of a much larger number, then a dozen bags, or certainly not less than six bags, should be taken out from different parts of the delivery and be set aside for the purpose of drawing a sample from them. Having set these aside, the very best way with any ordinary artificial manure—such as superphosphate, dissolved bones, bone-meal, compound manures, nitrate of soda, kainit, and other salts (anything, in fact, that is in a fairly powdery and uniform condition, and not bulky or matted together like shoddy or similar refuse materials)—is to provide oneself with a special instrument which we call a "sampler." This is an iron tool about 2 feet 6 inches long, very like a cheese sampler, and fitted with a wooden

handle. It is made of U-shaped iron, with the end sharpened and the edges rounded; the diameter of the groove being about 1 inch.'

This is represented in fig. 36.

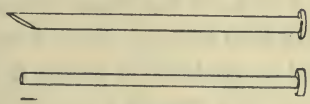

Fig. 36.

'An instrument like this can be driven down into each of the selected bags from top to bottom, and by tilting the bag, giving the sampler a twist round, and then withdrawing it, a section of the entire contents of the bag can be obtained. This may be repeated once or twice for each bag, and other similar sections taken from the other bags. The different lots withdrawn must be thoroughly mixed together. Any lump should be broken down with a shovel, and if the heap is too much to form a conveniently sized sample for sending for analysis, it should be reduced in amount by division and subdivision.

'This is best done by turning over the heap and mixing it up carefully though quickly, flattening down any lumps, and then dividing the heap into two halves; one half may be rejected altogether, and the remainder again quickly turned over and mixed thoroughly, divided as before, and so on as often as may be necessary, until a quantity weighing only three or four pounds is left.

'Two well-fitting tins, each capable of holding from $\frac{1}{2}$ lb. to 1 lb. of the material, should be then filled from the heap thus left. One of these should be wrapped up and sent by post to the analyst, and the other be kept by the farmer for reference. Instead of a tin a wide-mouthed bottle with a well-fitting cork may be used, and this be enclosed in a wooden

box, and so be sent by post or rail; or the sample may be wrapped in tinfoil or in oiled silk, and be enclosed in a box or in a stout linen lined envelope. This latter is a very convenient form for nitrate of soda, sulphate of ammonia, kainit, and similar salts. The tin is, on the whole, the most satisfactory, as it is easy to send from ½ lb. to 1 lb. of manure in it, whilst if a bottle or tinfoil or oiled silk be used it is not easy to send so large a quantity. If a smaller quantity be sent, the heap must be mixed still more carefully, and the sample be taken from different portions of it. In no case, however, should less than 4 oz. be sent as a sample, and when the material is at all uneven in character, or lumpy, or of a mixed nature, it is not satisfactory unless a 1-lb. sample, or in some cases as much as 2 lbs., be sent. The more uneven the manure, the larger the sample must be; the finer and more even it is, the smaller may be the quantity sent for analysis.

'One caution further is necessary. Whilst care must be taken to ensure a fair example being drawn, care must also be exercised not to let the portion that is being sampled lie about exposed too long. The sampling must be done carefully but also quickly, or the material may dry considerably during the process.

'In the absence of a special sampling tool, such as that described, the best way is, after selecting several bags as directed, either to turn them out one after the other upon a floor, and, taking a few shovelfuls from each, to mix these shovelfuls well together for one sample, or (which is not so good) to drive a spade into each of the selected bags and, after a little mixing, to draw out from as near the centre as possible a couple of spadefuls from each bag, subsequently mixing these lots together, flattening the lumps down, and dividing and subdividing the heap until only three or four pounds are left. From this the tins and bottles may be filled

as mentioned before, one sample being sent for analysis and the other retained for reference.'

120. The sampling of *feeding meal* and *grain* is conducted in exactly the same manner as that of manures.

121. **The Sampling of Oil Cakes.**—Very frequently a farmer will break a small piece off the corner of an oil cake and send it for analysis. This is pretty sure to lead to an erroneous result. It is well known that the percentage of oil varies considerably in different parts of a cake. Again, the cakes may vary considerably one from another. Dr. Voelcker, in the article already quoted, recommends the following procedure:

'A purchaser should first look over the cakes comprising the delivery, and note any difference of appearance that may strike him, or see whether all the cakes seem much alike. He should then select samples from each different variety he notices, the number of samples being in proportion to the number of cakes of each kind that make up the bulk. Three or four cakes of each sort should be selected, or, if uniform throughout, say six cakes from the whole lot; pieces should be broken out of the middle, and these pieces passed through a cake-breaker. The broken nuts or lumps must next be mixed up thoroughly and then divided successively, just as was advised in the case of manures, until only a couple of pounds weight are left. Two tins may now be filled with the cake, one for sending to the analyst, the other to be kept for reference.'

By the sentence 'Pieces should be broken out of the middle' is meant 'Break a whole cake across the middle; then off each of the halves take a strip about 4 inches wide, also right across the cake, and from what was before the middle piece of the whole cake.'

122. **The Sampling of Hay Silage, &c.**—When a stack

is to be valued by an expert, the usual method of examination is to cut out a groove about 2 feet wide by 2 feet deep, extending from the top to the bottom of the stack. This is to enable the valuer to see the hay in the interior. When this has been done, a sample for analysis may be obtained by pulling out portions of the freshly exposed hay from different levels.

Another and, where practicable, better method is to take the sample from different parts of the stack whilst it is being made. In either case, the hay should be cut up in a clean chaff-cutter, and placed in large wide-mouthed bottles immediately, so that it may not get damp or mouldy, or, on the other hand, lose moisture by being stored in a hot place.

123. **Water Samples.**—A sample of water should be taken in a clean glass-stoppered Winchester quart bottle. The bottle should be washed out with the water which is to be analysed before the sample is taken. If it be from a tap, the water should be allowed to run for several minutes before filling the bottle. If it be from a well, the mouth of the bottle should be sunk some inches beneath the surface when filling.

For an analysis such as is described in this book, one Winchester quart is sufficient ; but should a complete analysis according to the 'Frankland' method be required, twice as much will be necessary.

124. **The Sampling of Soils.**—Two methods are in vogue for the taking of soil samples. The Royal Agricultural Society recommend one, and the Highland and Agricultural Society another.

125. *Royal Agricultural Society.*—'Have a wooden box made 6 inches long and wide, and from 9 to 12 inches deep according to the depth of soil and subsoil of the field. Mark out in the field a space of about 12 inches square ; dig round, in a slanting direction, a trench, so as to leave undisturbed a

block of soil with its subsoil from 9 to 12 inches deep ; trim this block or plan of the field so as to make it fit into the wooden box ; invert the box over it, press down firmly, then pass a spade under the box and lift it up. Gently turn over the box and nail on the lid. The soil will then be received in the exact position in which it is found in the field.

'In the case of very light, sandy, and porous soils, the wooden box may be at once inverted over the soil, forced down by pressure, and then dug out.'

126. *Highland and Agricultural Society.*—'Dig a little trench about 2 feet deep, exposing the soil and subsoil. Cut from the side of this trench horizontal scrapings of the soil down to the top of the subsoil. Catch these on a clean board, and collect in this manner about one pound weight of soil taken from the whole surface of the section. Similar scrapings of subsoil immediately below should be taken and preserved separately.

'Five or six similarly drawn samples should be taken from different parts of the field, and kept separate while being sent to the chemist, that he may examine them individually before mixing in the laboratory.'

127. **Transit.**—Where samples are to be sent by post, the following precautions should be taken :

Bottles should be enclosed in boxes or hampers.

Acid manures or ensilage should not be sent in tins, but in pots or bottles.

Substances which are liable to gain or lose moisture should not be sent in bags, but in closed tins or well-stoppered jars or bottles.

PREPARATION IN THE LABORATORY

128. For preparing the samples for analysis, the following equipment is necessary :

A large iron mortar and pestle. The mortar should be about 12 inches in diameter.

A steel spatula, having a blade 10 inches long by $1\frac{1}{2}$ inch broad. An ordinary butcher's broad-bladed knife will do excellently.

A set of sieves having meshes varying from 4 to 16 per linear inch. Sieves made with wire gauze are often very difficult to clean, which leads to much waste of time. Perforated zinc is much preferable, and may be obtained with different sized holes.

Some form of mill. A coffee-mill will do very well, if arranged so that it may be taken to pieces ; otherwise it will be found impossible to clean it thoroughly.

A number of sheets of brown paper.

129. The preparation in the laboratory sampling room varies according to the *texture of the sample.* The substances ordinarily occurring may be classed under the following heads :

130. **Liquids.**—Water, milk, sewage, phosphoric acid, &c. These need no preparation, as they may be shaken up and analysed at once.

131. **Hard Minerals.**—Limestone and mineral phosphates. Break up in an iron mortar until the whole of the sample may be passed through a sieve with $\frac{1}{4}$-inch meshes. Spread it out on a piece of brown paper, and select from different parts of the heap sufficient to fill a sample bottle (10-oz. wide-mouthed bottles of common glass are best). A finer sample must be prepared by selecting in the same way about 20 grams, and grinding up in an agate mortar until the whole will pass through a sieve having 90 meshes to the linear inch.

132. **Soils.**—Soils must be first dried at 60° to 70° C., then sifted through a $\frac{1}{4}$-inch sieve. The stones which will not pass the sieve are rejected, and the rest treated exactly like a mineral.

133. **Moist Substances.**—Superphosphates, dissolved bones, and acid manures. These are the most difficult of all to obtain in a fine state. They should be sifted, and the larger pieces broken up by gently rolling round in an iron mortar. Just before weighing out in the laboratory they should be pounded into a homogeneous paste in a small iron mortar.

134. **Soft Substances.**—Wool waste, shoddy, &c. Must be cut up small with scissors.

135. **Cakes.**—May be broken into pieces, a fair sample of the pieces selected, and ground fine in the mill.

PART V

ANALYSIS OF FEEDING MATERIALS

THE ANALYSIS OF OIL CAKES

136. The examination of an oil cake may be divided into two distinct parts : the *quantitative* and the *qualitative.* These will be treated separately, as the first refers entirely to its feeding qualities and the second to the purity and wholesomeness of the seeds which it contains.

Quantitative Analysis

The substances usually estimated in a cake are *moisture*, *oil*, *albuminoids*, *woody fibre*, *ash*, and *sand.* To these may be added the *carbohydrates*, which are as a rule determined by difference.

137. **Moisture.**—Two grams of the ground sample of cake are weighed out in a porcelain capsule, and heated in a steam oven until of constant weight. Five hours is generally sufficient time for this.

138. **Ash.**—The portion used for the estimation of moisture is removed to a weighed platinum dish—sweeping in the last traces with a camel's-hair brush—and ignited, until the weight is again constant. It must be remembered in performing this operation that some seeds, of which these cakes often contain large quantities, have a high percentage of alkalis, and

the ash is therefore liable to fuse. Should this take place before all the carbonaceous matter has been burned off, the liquid alkali will completely shut off the oxygen of the air by coating the particles of charred substance. As a rule, an Argand burner with the flame turned down low will be found to burn the cake without any difficulty; but the operation must be watched carefully, especially if the cake in question contain cotton seed. Decorticated cotton cakes give a very fusible ash. Linseed cakes need no such precaution, and may be ignited at a dull red heat. The residue is cooled and weighed. It should be quite white.

139. **Sand.**—Wash the ash out of the platinum dish with a jet of dilute HCl into a 4-oz. beaker. Add 10 c.c. of strong HCl, digest on the water bath for ten minutes, filter, and wash well with hot water. Transfer the filter without drying to a platinum dish. Heat up very slowly over an Argand. When perfectly dry, turn the light up strongly and ignite until the paper is thoroughly burned. Cool and weigh.

140. **Oil.**—The oil is dissolved out from a weighed quantity of the cake by means of ether and weighed after drying. This is done by means of some form of Soxhlet's fat extractor. Fig. 37 shows three of these, the first of the three being the most convenient. The substance to be extracted is wrapped in filter paper and placed in the wide tube, E. Ether is poured upon this until it rises to the level of the top of the bent syphon tube, *s*. It then runs along

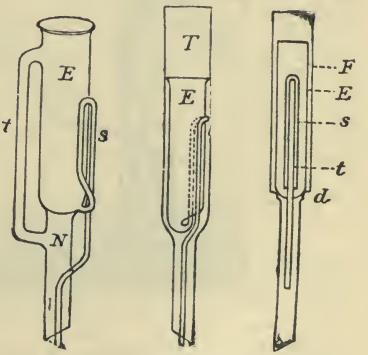

FIG. 37.

this tube, and E is thus completely emptied of liquid. A convenient receptacle is affixed to N, in which the liquid may be heated and the ether vaporised. The vapour passes up the tube *t*, and after being condensed in a condenser above, falls back upon the substance until the level of the syphon top is again reached, when the operation will repeat automatically. The other extractors figured are exactly the same in principle, but slightly different in construction.

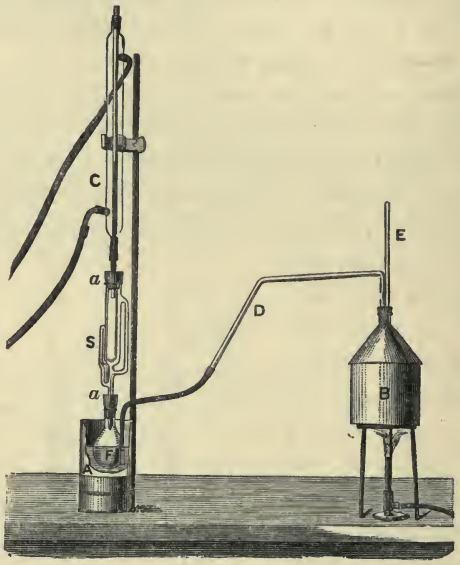

FIG. 38.

The apparatus, fully fitted up, is shown in fig. 38.

The Soxhlet extractor, S, is fitted at the top to a condenser, C, and below to a small round flask, F. The corks *a*, *a* are carefully selected for their soundness, and extracted with ether. The flask F just dips beneath the surface of the water in the bath A. For this bath any tin of convenient size may be

used. The water in the bath is warmed to about 60° C., and kept at that temperature by bubbling steam into it. A very convenient and substantial steam generator is shown in fig. 38. It is made by fitting a half-gallon oil can with a cork, through which pass two tubes—one, D, to conduct steam to the bath, and the other, E, to act as a sort of safety tube and prevent the water rushing back up D when the boiler is cooled. E should pass right down to within an inch of the bottom of the oil can, and stand out at least six inches above the cork. D should terminate at one end just inside the cork, whilst to the other end a metal T piece should be attached to make the distribution of steam more even.

141. **The Operation.**—Cut up a sheet of white English filter paper into pieces 5 by 8 inches in size, roll them into a loose roll, and wash them two or three times with ether to extract any traces of fat which they may contain. When dry, fold one of these round a piece of glass tubing of such size that the roll will easily slide into the extractor (see fig. 37). Partially withdraw the glass tube until about an inch of the paper roll projects beyond its end. Fold this projecting part of paper so as completely to block the end of the roll; then withdraw the tube altogether. A sort of cartridge case will thus be formed into which the powdered cake may be introduced.

Weigh out about 3 grams of *finely* ground cake on a watch glass, and sweep it with a camel's-hair brush into the cartridge case.

Place the case in the broad tube of the extractor, and affix the flask F. Pour ether (S.G. ·720) on to the cake until it begins to syphon over. Allow it all to run into the flask, then half-fill again. Fix the apparatus on to the condenser. Place the water bath as in the figure, and half-fill it with water at 60° C. Light the lamp under B, and allow the extraction to

proceed until the ether has passed over ten times. This should take one and a-half hour.

The extracted fat has now to be weighed. This is sometimes done in the extraction flask, but such a proceeding is not advisable, as the oil takes a much longer time to dry in a flask than in a more open vessel.

Whilst the extraction is going on, a small beaker, $1\frac{1}{2}$ inch high by 1 inch diameter, is cleaned, dried, and weighed. When the extraction is finished the extractor is removed from the condenser and the cartridge case withdrawn. This is placed on a clock glass in the steam oven to dry. The extractor is replaced on the condenser, and the ether in the flask allowed to distil over until the large tube (E, fig. 37) is filled to within half-an-inch of the top of the syphon ; it is then removed from the condenser. The flask is taken off from below, and the ether poured out of the extractor into the ether bottle. The whole apparatus is replaced, and the rest of the ether distilled off from the flask to the extractor. The flask may now be finally removed.

A small quantity of oil may have got on to the cork of the flask by the too rapid boiling of the ethereal solution. The cork and tip of the extractor should be washed with a fine spray of ether, allowing the washings to flow into the flask.

142. The next operation is to remove the oil into the weighed beaker. The sides of the flask are washed down with a fine spray of ether delivered from the jet of a wash bottle until about 1 c.c. of liquid has collected in the flask. The liquid is poured into the beaker. This operation is repeated four or five times, when all the oil will have been washed away. Some, however, will have crept over the lip of the flask, therefore the outside of the neck should be sprayed, allowing the ether to drip into the beaker.

The ether is allowed to evaporate by placing the beaker on

top of the steam oven, overheating being prevented by placing two or three filter papers between the beaker and the metallic surface of the oven.

When the ether has all gone, the beaker is heated inside the steam oven until it ceases to lose weight. The difference between this final weight and the weight of the beaker gives the weight of the oil.

143. **Estimation of Woody Fibre.**—The portion of cake which has been extracted with ether and dried in the cartridge case is used for this estimation. It is transferred to a 16-oz. beaker. If a portion adhere to the filter paper it may be removed by opening the case and rubbing the adhering substance off with another part of the paper. When it is all in the beaker 50 c.c. of a 5 per cent. solution of sulphuric acid are added, together with 75 c.c. of distilled water. The beaker is placed over a Bunsen burner, and the liquid raised to a boil. As it approaches the boiling-point it must be watched carefully, as it has a tendency to froth up and boil over. As soon as the frothing starts it should be stirred rapidly with a glass rod, and, if the frothing become too violent, removed for a moment from the burner. When all frothing has ceased any particles of cake which adhere to the side are washed down into the liquid with a small quantity of hot water, and the solution is allowed to boil gently for half-an-hour. As the liquid becomes more concentrated on boiling, it is necessary to add a little hot water from time to time. The level of the surface of the liquid may be marked by sticking a piece of gummed paper on the outside of the beaker. It will then be easy to see when more water ought to be added. At the end of the half-hour the beaker is filled up with cold water and allowed to stand for an hour.

A clean piece of linen is placed over the top of a beaker, or, better, a strong jam pot of about 20 oz. capacity. The liquid

in the beaker is decanted through this linen. The solid matter on the linen is washed back into the beaker with hot water. Fifty c.c. of 5 per cent. KHO solution are added, and then water up to the 126-c.c. mark. The beaker is returned to the burner and the liquor boiled for half-an-hour, filled with cold water, and allowed to stand as before.

The remaining solid matter, which contains only woody fibre and sand, is filtered off by means of the linen and well washed : firstly, three times with hot water; secondly, once with dilute HCl; thirdly, three times with hot water; and, lastly, twice with alcohol.

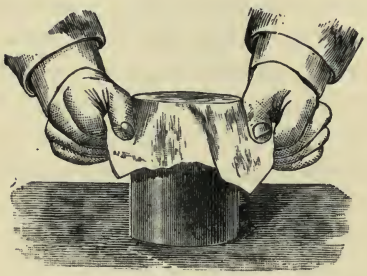

FIG. 39.

Filtration may be very much hastened by drawing the linen tightly over the edges of the pot, as shown in fig. 39. This causes a partial vacuum below, and the pressure of the air above forces the liquid through the cloth.

The next operation is to transfer the fibre to a weighed porcelain capsule, which requires some little dexterity.

FIG. 40.

As much of the alcohol as possible is squeezed out, and the cloth is stretched on a tile, holding it as in fig. 40. The fibre is removed with the tip of a steel spatula and placed in the weighed capsule, care being taken to scrape all the substance

off the stretched linen. The capsule is dried in the steam oven until it ceases to lose weight.

The fibre thus estimated will contain whatever sand there is in the 3 grams of cake used. It is therefore transferred to a weighed platinum dish, burned, and the weight of the ash taken. This is subtracted from the total weight of the fibre.

144. **Albuminoids.**—If the percentage of nitrogen be multiplied by 6·25, the percentage of albuminoid matter is obtained.[1]

It is, therefore, only necessary to estimate the nitrogen in the cake. This is done by either the soda lime (paragraphs 86–89) or the sulphuric acid process (paragraphs 90–95), using about 1 gram of the cake.

145. **Remarks on Cake Analysis.**—Should the operations described in paragraphs 137–144 be performed one after the other in the order given, it would take a very long time to complete the whole analysis. The following method of procedure will enable the student to complete the analysis in the minimum time:

1. Weigh out three portions of the ground-up sample as follows:

(*a*) About 2 grams in a porcelain capsule.
(*b*) About 3 grams on a watch glass.
(*c*) About 1 gram on a watch glass.

2. Place (*a*) in the steam oven.

3. Put (*c*) in a flask with strong sulphuric acid to estimate the nitrogen.

4. Prepare the Soxhlet's apparatus, and start the oil estimation with (*b*).

[1] This factor 6·25 is based on the fact that the average percentage of nitrogen in the albuminoids of vegetable foods is 16%.

$$100 \div 16 = 6{\cdot}25.$$

The order in which the rest of the operations should be taken depends very much on the operator.

146. **Method of Entry.**—The student should describe in his note book the operations performed, and in entering data should use one page for weights and reserve the page facing it for calculation of percentages.

After calculating, the results of analysis are entered as follows:

—	Good linseed cake	Bad linseed cake	Cotton cake undecorticated	Cotton cake decorticated
Moisture	9·45	14·05	8·69	8·10
Oil	13·20	8·80	5·30	11·67
*Albuminoid compounds . .	26·31	23·72	26·00	41·94
Mucilage, starch, &c. . .	36·02	32·87	29·50	25·41
Woody fibre	8·61	10·71	25·67	4·63
†Ash	6·41	9.85	4·84	8·25
	100·00	100·00	100·00	100·00
*Containing nitrogen . .	4·21	3·79	4·16	6·71
†Containing sand . . .	1·40	5·20	—	—

These analyses are typical.

Qualitative Examination

147. Although the feeding value of an oil cake depends very largely on the percentage of oil and albuminoid compounds which it contains, still two cakes which give identical analyses may vary in value on account of their *condition*, *purity*, and *taste*.

The *condition* may be judged by breaking up the cake and noting its hardness and structure.

The *purity* cannot be determined without careful microscopic examination, though there are one or two tests by means

of which injurious substances may be detected. These are given below.

The *taste* is the most difficult property of all to give an opinion upon, unless the cake have a distinctly nasty taste, in which case the analyst should make some remark thereon.

148. **Testing Linseed Cakes.**—Linseed cake should be rich in mucilage and free from starch. Both of these properties are readily tested. Five grams of the ground sample are weighed out on a rough balance and placed in an 8-oz. beaker. A hundred c.c. of *boiling* water are poured over the cake, and the pasty mass is stirred for a few moments, then allowed to stand for about ten minutes. A rich linseed cake will, when treated in this manner, settle down into a jelly-like mass, whilst a poor cake will settle down in a more granular state. By experimenting with a few samples the student will readily see the value of this test in judging the mucilaginous properties of the cake. To test for starch, a little of the hot liquor with the cake in suspension is poured into a test tube and boiled smartly for a few moments. It is then cooled down, and when *quite cold* a few drops of a solution of iodine in alcohol are added. The emulsion should only become slightly blue. If it become dark blue some starchy material is present.

149. **Microscopic Examination.**—The student should prepare and mount for himself specimens of the husks of the various seeds occurring in feeding materials, and make himself familiar with the appearance of each. The following method will be found useful in preparing the husk of the seed for examination :

Digest a portion (about 5 grams) of the material with dilute sulphuric acid (2 per cent.) on the water bath for half-an-hour. Remove the acid liquid by decantation, and wash several times

in the same manner. Next digest with equally dilute caustic alkali, and repeat the washing. This renders the texture of all those seeds commonly met with in cattle foods, and the impurities occurring with them, sufficiently transparent to be readily recognised under the microscope. After washing the alkaline liquid away, it is sometimes an advantage to wash the material with dilute hydrochloric acid, which reduces the strong colour produced by the alkali.

Another method which produces the same effect is to place the substance on a slip of glass, add a drop of glycerin, and heat until the glycerin begins to boil. The glycerin is withdrawn by means of filter paper, and the operation repeated until sufficient transparency is attained.

ANALYSIS OF FEEDING MEALS

150. Feeding meals are usually analysed in exactly the same way as oil cakes, excepting that the carbohydrates, and in the case of flour the gluten, are occasionally estimated.

151. **Starch.**—This may be estimated roughly by kneading 5 grams of the meal with a little water on a piece of linen, such as is used in the estimation of woody fibre, and washing thoroughly with water. The starch will pass through the cloth with the filtrate. This must be allowed to settle, then the starch filtered off on a weighed filter, washed, dried at a low temperature, and weighed.

152. A more scientific method of procedure is to convert the starch, inuline, and dextrin into sugar, and estimate that as described in paragraphs 82–84. The starch is converted into sugar by means of diastase.

153. **Preparation of Diastase.**—Place about 5 lbs. of malt, finely ground, in a large beaker, and just cover it with

water. Allow to stand four hours. Squeeze the liquid from this pulp through a bag of fine linen. (The press shown in fig. 43 would be admirable for this purpose.) Filter if necessary. Add strong alcohol until a white precipitate (diastase) forms. Filter, wash with alcohol. Press the precipitate between folds of cloth until as dry as possible, transfer to a dish, and place in an exhausted receiver until quite dry. Bottle the powder, and keep in a cool dry place.

154. **The Analysis.**—Weigh out 1·5 gram of the meal. Mix with a little water in a 6-oz. beaker, add 50 c.c. of boiling water, stirring well meanwhile. Place the beaker on the water bath until all clots have been thoroughly broken down, then cool down to 62° C. and add about 30 milligrams of diastase powder dissolved in a few c.c. of water. Keep at 62° to 65° C. for about an hour by standing on the water oven. This will convert the whole of the starch into dextrin and maltose. Filter off the liquid, and dilute to 250 c.c. Measure off 50 c.c. of this solution into a beaker, add 2 c.c. of sulphuric acid (1 to 8), and heat in the water bath for four hours, adding water from time to time as the liquid evaporates. Then neutralise with KHO, make up to 100 c.c., and estimate the glucose as described in paragraphs 82–84.

155. **Gluten in Flour.**—Weigh out about 30 grams of flour, knead to a paste with water, and transfer to a linen fibre cloth—or, better, fine silk. Tie it up like a pudding, and knead with the fingers under clear water until no further starch comes out. This may be recognised by its no longer turning the water milky. Remove gluten as described in the case of woody fibre (fig. 40), keeping the spatula wet all the time. Roll the gluten into a ball with wet fingers, wash thoroughly in water, wipe off any moisture, and weigh.

156. A few typical analyses of *feeding meals* are appended.

—	Rice meal	Malt dust	Barley meal	Palm nut meal	Maize meal	Wheat sharps
Moisture . .	10·30	9·30	10·81	9·24	12·93	11·68
Oil . . .	9·31	1·40	2·90	8·27	4·30	4·73
*Albuminoid compounds .	13·06	22·88	12·76	15·75	9·94	15·50
Carbohydrates, &c. .	53·97	47·54	63·59	47·76	68·73	59·88
Woody fibre . .	6·12	11·83	6·30	14·13	2·60	4·47
†Ash . . .	7·24	7·05	3·64	4·85	1·50	3·74
	100·00	100·00	100·00	100·00	100·00	100·00
*Containing nitrogen	2·09	3·66	2·04	2·52	1·59	2·48
†Containing sand .	—	2·35	—	—	—	·78

ANALYSIS OF GRASS AND HAY

157. These substances are not often analysed for commercial purposes, but it is sometimes necessary for experimental work to find the relative values of different samples of grass and hay. A certain amount of information may be gained by treating the samples as though they were oil cakes. It must be remembered, however, that in the case of substances containing green colouring matter this will be to a great extent extracted by ether along with the fat.

The method of analysis about to be described gives all the information concerning a sample which is likely to be required.

If the student reads through this description, and the following one—analysis of roots—he will see that both of them are very long and very tedious. He is therefore advised to miss these two analyses for the present and return to them after he has completed the section on manures.

When performing the analyses many long intervals will occur during which the operator has to wait. There is no need to be idle, as soil analysis may be started during these waits.

158. **Moisture.**—It is of great importance that the water

in grass be estimated as soon as possible after the sample has been taken, otherwise much will be lost by evaporation. It is best to weigh out all the portions required for different parts of the analysis immediately after the grass or hay has been cut up. The following portions should be weighed out:

20 grams of hay, or
50 „ grass } for moisture;

5 grams of hay, or
10 „ grass } for woody fibre;

10 grams of hay, or
40 „ grass } for crude fibre.

These substances are somewhat too bulky to weigh out on a delicate balance; therefore a large balance, such as is repre-

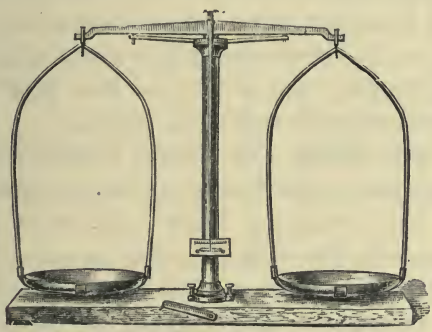

FIG. 41.

sented in fig. 41, is used. It must be capable of discerning ·005 gram.

The moisture portion is weighed out in a sheet of filter paper which has been folded to form a sort of bag for holding the grass. Instead of weighing the filter paper to begin with, it should be counterpoised by placing a similar piece in the other scale pan, and cutting off bits of the heavier one until both pieces are of the same weight. Both pieces of paper

are dried in exactly the same way. They are heated together in the steam oven until the hay ceases to lose weight.

When the moisture has been determined, the dry matter left in the filter paper is ground up finely in a laboratory mill, bottled, and labelled 'Dry matter.' This operation is greatly facilitated by placing the hay in the water bath for a few minutes after it has been finally weighed, and then grinding whilst hot, as it is then much more brittle than when cold.

159. **Woody Fibre.**—The portion which has been weighed out for this estimation is placed in a 20-oz. beaker and treated exactly as described in the case of oil cakes, paragraph 143, except that in each digestion double the quantity of liquid is used. After the fibre has been transferred to the cloth it will often contain green colouring matter. This should be removed by soaking for an hour in alcohol, then for another hour in ether. It is then transferred to a small weighed beaker, dried, and weighed. The ash in the fibre should be determined and subtracted from the total weight.

160. **Crude Fibre.**—The portion weighed out is placed in a 20-oz. beaker. The beaker is filled up with water and allowed to stand twenty-four hours. The liquid is decanted off and rejected. The beaker is filled up again, allowed to stand three hours, and decanted. A third soaking is made for one hour. It next has to be treated with hot water. The total washing is as follows:

24 hours in cold water;
3 „ „ „ „
1 „ „ „ „
½ „ „ hot „ (four times)

After these soakings have been performed, boil for a minute with water twice. When decanting it is difficult to remove most of the water. This, however, may be accomplished by

placing a disc of glass just inside the beaker, and squeezing as shown in fig. 42.

After this treatment all matter which is soluble in water will have been removed. It remains now to extract the colouring matter. This often takes some time. It is done by soaking in alcohol for an hour at a time, straining off the spirit after each soaking until it runs off colourless. Ether is then used until the fibre is quite white. It is then dried and weighed in the same manner as the woody fibre.

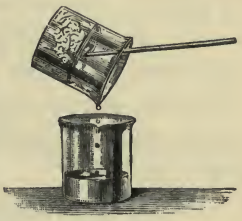

Fig. 42.

Considerable annoyance is frequently caused in this operation by the evaporation of the ether, especially when the fibre is allowed to soak over night. This may, to a very great extent, be prevented by placing over the mouth of the beaker half-a-dozen thicknesses of filter paper, covering these with a glass disc, and placing a small weight on the top of the disc. In this way the beaker is made fairly air-tight, and much less loss occurs than when the beaker is merely covered with a clock glass.

The crude fibre must be ground up, bottled, and labelled.

So far the only constituents which have been estimated are moisture, woody fibre, and crude fibre. The two bottled portions may now be proceeded with.

Analysis of the 'Dry Matter'

161. Before any portion is weighed out, the 'dry matter' must be heated in the steam oven for an hour and cooled in the desiccator. This is necessary, as the powdered substance is very hygroscopic.

162. **Total Nitrogen.**—Weigh out about 2 grams of the

freshly dried substance, and estimate the nitrogen by the acid process (paragraphs 90–95). The flask must be carefully watched whilst heating, as the acid is apt to froth. Should the solution take a long time to clear, it may be hastened by adding a drop of mercury. If this be done, the mercury must be precipitated by adding sufficient potassium sulphide along with the caustic soda before distilling off the ammonia. Otherwise mercury ammonium compounds are often formed which are not completely decomposed by NaHO (see paragraph 93).

163. **Total Albuminoids.**—Weigh out 2 grams of freshly dried 'dry matter,' place it in a 4-oz. beaker, and fill the beaker with 4 per cent. carbolic acid solution in water. Add a drop of meta-phosphoric acid and allow to soak for twenty-four hours. Decant the liquid through a filter paper, and boil up the residue with a fresh portion of the carbolic acid solution. Filter, wash three or four times with carbolic acid, and dry. This treatment, whilst coagulating all the albuminoids and rendering them insoluble, dissolves all the amides.

When the substance is dry introduce it, together with the filter paper, into an 8-oz. flask, and estimate the nitrogen by the acid process (paragraphs 90–95).

164. **Total Ash.**—Weigh out 2 grams of freshly dried substance into a platinum dish, and determine the ash as in a sample of oil cake.

Analysis of the Crude Fibre

165. **Insoluble Albuminoids.**—All the amides being soluble in water, the insoluble albuminoids may be calculated from the nitrogen in the crude fibre. Weigh out 2 grams of freshly dried crude fibre, and determine the nitrogen in the same way as has been done in the dry matter.

166. **Insoluble Ash.**—Weigh out 2 grams of dry crude fibre in a platinum dish, and determine the ash as before.

167. **Calculation.**—First calculate from the weights of different substances the following percentages:

Percentage of	moisture	in the sample;
,,	woody fibre	
,,	crude fibre	
,,	total nitrogen	in the dry matter;
,,	albuminoid nitrogen	
,,	ash	
,,	nitrogen	in the crude fibre.
,,	ash	

Work out the percentages of albuminoids contained in the dry matter and crude fibre respectively by multiplying the percentages of albuminoid nitrogen by 6·25.

Reduce all the percentages to parts per hundred of the total sample, thus:

$$\frac{\text{percentage of ash in dry matter} \times \text{percentage of dry matter}}{100} = \text{percentage of ash in sample.}$$

Likewise

$$\frac{\text{percentage of ash in crude fibre} \times \text{percentage of crude fibre}}{100} = \text{percentage of insoluble ash in sample.}$$

Make the following additions and subtractions:

Total nitrogen − albuminoid nitrogen = amide N;
Total albuminoids − insoluble albuminoids = soluble albuminoids;
Total ash − insoluble ash = soluble ash;
Crude fibre − (insoluble albuminoids + woody fibre + insoluble ash) = digestible fibre.

168. The following figures, taken from actual analyses of grass and hay, show the method of entering results.

—	Grass	Hay
Moisture	69·34	14·00
Soluble albuminoids	0·11	·98
Insoluble albuminoids	2·30	7·89
Digestible fibre	10·39	28·68
Woody fibre	8·53	22·92
Soluble ash	1·34	2·20
Insoluble ash	·87	4·66
*Chlorophyll amides, &c. (by difference)	7·12	18·67
	100·00	100·00
*Containing nitrogen	·12	·12
Total nitrogen	·50	1·54

SILAGE

169. The analysis of this substance is conducted in much the same way as that of hay and grass, using the same quantities of substance as for grass. The only difference is that the acidity is estimated in addition to the constituents given above.

This is done in the 40 grams weighed out for the estimation of crude fibre.

170. **Acidity.**—The liquids from the first three soakings (see paragraph 160) are collected and made up to a litre with distilled water. Five hundred c.c. are taken, and the total acidity determined with $\frac{N}{10}$ KHO. It is a matter of some difficulty to detect the exact point of neutrality owing to the greenish colour of the solution. A dozen drops of phenol-phthalein are placed with a stirring rod on different parts of a glass plate. The alkali is run into the liquid, a few drops at a time. After each addition it is stirred vigorously, and tested by touching one of the drops on the plate with a drop of the liquid on the end of the rod. When the indicator gives a faint pink reaction the quantity of potash added must be read off.

The remaining 500 c.c. are boiled down in a beaker over a

Bunsen until only 50 c.c. are left; this volatilises all the acetic acid. About 200 c.c. of water are added, and the liquid titrated as before.

171. **Calculation.**—The number of c.c. used in the second titration are subtracted from the number used in the first. The difference gives the potash required to neutralise the volatile acids. These are calculated by taking the amount of acetic acid, CH_3CO_2H, equivalent to the potash.

From the second equation the non-volatile acids are calculated as lactic acid, $C_2H_4(OH)CO_2H$.

172. The following are typical analyses of silage:

—	Sour	Sweet
Water	64·31	67·33
Acetic acid	·49	·07
Lactic acid	·96	·60
Soluble ash	1·51	1·02
Insoluble ash	1·37	1·35
Soluble albuminoids	·96	·60
Insoluble albuminoids	1·86	1·88
Digestible fibre	7·77	8·66
Woody fibre	11·46	8·91
*Chlorophyll, &c.	9·31	9·58
	100·00	100·00
*Containing nitrogen	·23	·17
Total nitrogen	·67	·57

ROOTS, SWEDES, MANGELS, TURNIPS, &c.

173. This analysis is conducted in a somewhat peculiar manner, and requires a slight preliminary explanation.

The constituent parts of roots may be divided into the insoluble and the soluble portions; but seeing that the water in these plants amounts to between 80 and 90 per cent., it is to be expected that the whole of the soluble matter will be in solution. The analysis, therefore, divides itself into two parts—

namely, the analysis of the juice or soluble portion, and the analysis of the crude fibre or insoluble portion.

From the sample it is therefore necessary to procure two sub-samples, one of the juice and one of the insoluble matter. These two must be analysed separately, in the same way as the different parts of hay or grass are worked upon. And just as happens in the case of hay, &c., the first thing to be estimated in roots is the moisture, which leads to the following

Preliminary Treatment

174. Take three or four average-sized roots, and split each with a clean knife into eight pieces. Take one of these pieces from each root. Cut the portions into thin slices, and weigh out about 100 grams of the slices in the rough balance as described in paragraph 158. When weighed spread the slices out on the filter paper, and dry them in the air oven at 60° C. until they become shrivelled up. The slices will now be hard and fairly brittle. Break them up as finely as can conveniently be done by hand, and then dry in the steam oven until no further loss in weight takes place.

This operation takes up three or four days. It will take considerably longer if the oven be allowed to cool during the night, as the partially dried material is very hygroscopic, and absorbs a considerable amount of water whilst the oven is cold. In laboratories where the ovens do not keep hot day and night matters may be considerably hastened by removing the substance from the oven to a desiccator every evening, and returning to the oven as soon as it is warm in the morning.

175. The moisture, however, is not the only constituent which must be estimated in the fresh root. The two principal portions, as mentioned above, are the crude fibre and the juice. If one of these be estimated, the other may be calcu-

lated by difference. Therefore we estimate the crude fibre directly and the juice by difference, analysing samples of both.

176. **Estimation of Crude Fibre.**—When the roots are split up into eighths, a section of each is taken for this estimation. The portions, however, are not weighed, but are rubbed down on a bread-grater as rapidly as possible, so as to obtain a pulp before any evaporation has taken place. When a sufficient amount has been pulped, about 1,000 grams are weighed out on a large clock glass, transferred to a linen bag, and placed in a press. The object of this press is to get a fair sample of the juice. It has been found by experiment that the first portions of the juice to be squeezed out are very slightly different from the last; hence although for very accurate analyses it is necessary to squeeze out most of the juice, still, should a powerful press be unobtainable, a very good result may be got by pressing out a small amount of the liquid.

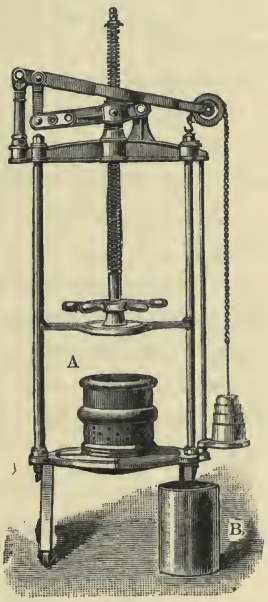

FIG. 43.

177. An ordinary cheese press may be utilised for separating the juice, if a little extra apparatus be added to it. Fig. 43 shows a press, on the table of which is placed a cylinder, A, to hold the pulp. Into this is fitted a plunger, B. Around the bottom part of the cylinder holes are drilled to allow the juice to escape.

The linen bag containing the weighed quantity of pulp is squeezed in the press until as much juice as possible has been obtained. The juice is collected in wide-mouthed bottles, and

corked up for analysis. Not that this analysis may be deferred for any length of time; in fact, the portions of juice for different operations must be measured out as soon as the quantities for crude and woody fibre have been weighed from the pulp.

178. When no further juice can be pressed out, loosen the press, remove the bag, place it on a counterpoise clock glass, and weigh on the 'rough' balance. The next three weighings must be performed as rapidly as possible, to prevent loss by evaporation. They are as follows:

Weigh out 50 grams of the pressed pulp for crude fibre.

Weigh out 10 grams of the pressed pulp for woody fibre.

Remove the rest of the pulp completely from the linen bag, and weigh the bag whilst still moist.

All these weighings may be performed on the rough balance.

Treat the two portions of pulp thus weighed out for crude and woody fibre exactly as though they were samples of hay, except that the washings with ether and alcohol are unnecessary, as the pulp contains little or no colouring matter. When these have been started, proceed at once to the analysis of the juice.

Analysis of the Juice

179. The substances to be estimated in the juice are *total solids* in the juice, *soluble albuminoids*, *glucose*, *cane sugar*, and *soluble ash*.

To save the trouble of weighing out separate portions, it is usual to take the specific gravity of the juice and measure out the amounts required, calculating the weights afterwards.

180. Since the juice is apt to change in composition if kept for any length of time, the immediate treatment of each portion is first described, and the determination entered into more fully

afterwards. First get together the apparatus and solutions required, so that no time may be lost after the work has once begun.

Apparatus. A 50-c.c. pipette;
A 20-c.c. pipette;
A 10-c.c. pipette;
Two measuring flasks, 100 c.c.;
A shallow evaporating basin (weighed);
A 4-oz. beaker;
A thermometer;
A sp. gr. bottle.

Solutions. Saturated solution of lead acetate;
Strong lactic acid.

181. **Immediate Treatment.**—Note the temperature.

Glucose. Measure out 10 c.c. and run it into one of the 100-c.c. flasks. Add about 5 c.c. of distilled water, then 10 c.c. of the lead acetate solution. Make up to 100 c.c. with water, shake well, and allow to settle.

Total Sugar. Measure out 20 c.c. of the juice into the other 100-c.c. flask, and treat in exactly the same way.

Total Solids and Ash. Measure out 50 c.c. of the juice, and run into the evaporating dish. Place this on the water bath to evaporate.

Soluble Albuminoids. Measure out 50 c.c. of the juice into a 4-oz. beaker; add six drops of strong lactic acid; stir well, cover with a clock glass, and allow to stand for twenty-four hours.

Take the temperature of the juice again.

182. If these operations have been performed with a fair amount of rapidity, the temperature of the juice will not have appreciably changed. This is of importance, as any heating or cooling of the juice will alter its specific gravity, and the results obtained will not be strictly comparable.

Should the temperature have altered, the specific gravity is taken at the mean temperature between the two readings.

The specific gravity is determined by means of a hydrometer or a specific gravity bottle.

Details of Juice Analysis

183. **Glucose.**—The lead acetate which has been added to the diluted juice will form a heavy precipitate with the substances which caused turbidity, so that in the course of a few hours a perfectly clear solution will be obtained, all the precipitate having settled at the bottom of the flask.

In a normal swede this clear solution will be of just about the correct strength for treatment with Fehling's solution. Remove 50 c.c. from the flask with a pipette, taking care not to disturb the precipitate, and transfer to a clean, dry burette. Determine the glucose with Fehling's solution exactly as described in paragraphs 82–84.

184. This method gives results sufficiently accurate for most purposes. If, however, results are required of the highest possible accuracy, the excess of lead should be removed from the solution before titration. In this case the sugar solution should not be made up to 100 c.c. immediately after adding the lead acetate solution, but should be allowed to stand for two hours to settle. At the end of that time 20 c.c. of a saturated solution of alum should be added. This will precipitate the excess of lead. The solution should then be made up to 100 c.c., shaken up, and allowed to settle. When quite clear it must be treated as described in the last paragraph.

185. **Total Sugar.**—Measure out 50 c.c. of the solution, clarified for this determination, into a 4-oz. beaker, taking care as before not to remove any of the sediment. Add 10 c.c. of dilute sulphuric acid (1 to 4), and digest on the water bath for

twenty minutes. Filter into a 100-c.c. flask, and wash the precipitate well with successive small quantities of hot water until the filtrate measures rather less than 100 c.c. ; neutralise with KHO. Cool the flask, and make up to 100 c.c. Transfer to a burette, and determine the glucose with Fehling's solution (paragraphs 82–84).

186. **Total Solids.**—Evaporate the 50 c.c. measured into the dish until a scum forms on the surface. Weigh a piece of platinum wire about 4 inches long ; bend one end into a hook and place in the dish so that the hooked end remains out of the liquid, and by hanging on to the edge of the basin prevents the wire from slipping in altogether. This platinum wire is used from time to time to break up the scum and thus assist evaporation. When the whole of the juice is reduced to a stiff paste, place the dish in the steam oven until it ceases to lose weight. This will occupy two or three days, and the dish should be removed to a desiccator at night time, or whenever the oven is allowed to cool.

187. **Soluble Ash.**—When the solids in the juice no longer lose weight, the dish is heated very cautiously on an Argand burner, and the ash determined as in a sample of oil cake. Special care must be taken to prevent the charred mass from fusing.

188. **Soluble Albuminoids.**—The lactic acid which has been added to the portion measured off for this estimation will precipitate all the albuminoids in a coagulated state. After the liquid has stood twenty-four hours or more, decant off the liquor through a filter paper, arranged with a filter pump as shown in fig. 15. Remove the solid matter with hot water to the paper, and wash well. Dry the precipitate in the steam oven. Place the filter paper with its contents in an 8-oz. flask, and determine the nitrogen by the acid process.

Analysis of the Crude Fibre

189. The crude fibre is treated in exactly the same manner as the crude fibre of hay, estimations being made of *nitrogen* and *ash.*

Analysis of the Dry Matter

190. Estimate the ash and nitrogen exactly as in a sample of hay.

191. **Calculation.**—This is much the same as the calculation of grass analysis, only more complicated. First calculate from the weight of different substances the following percentages:

Percentage of	moisture . . .	in the sample;
,,	pressed pulp . .	
,,	crude fibre . .	in the pressed pulp;
,,	woody fibre . .	
,,	nitrogen . . .	in the dry matter;
,,	ash . . .	
,,	nitrogen . . .	in the crude fibre;
,,	ash . . .	
,,	albuminoid nitrogen	in the juice.
,,	ash . . .	
,,	glucose . . .	
,,	cane sugar . .	

Multiply the percentages of nitrogen in crude fibre and juice by 6·25 to obtain insoluble and soluble albuminoids.

Reduce the percentages of crude and woody fibre to parts per hundred of the original sample, thus:

$$\frac{\text{Percentage of crude fibre} \times \text{percentage of pulp}}{100}$$

= percentage of crude fibre in the sample.

Similarly for the woody fibre.

Having obtained the percentage of crude fibre, or insoluble matter, we have only to subtract that number from 100 to obtain the percentage of juice, which contains all the water and soluble matter.

Next reduce all the numbers calculated as percentages of the juice, crude fibre, and dry matter to percentages of the root, exactly as in the case of grass (paragraph 167).

Make the following additions and subtractions:

Crude fibre − (woody fibre + insoluble ash + insoluble albuminoids) = digestible fibre.

192. The following analysis of a swede sample shows the method of entering results:

Juice, 97·466 per cent.	
Water, Amides, &c.	90·020
*Soluble albuminoids	·167
Cane sugar	·817
Glucose	6·030
Soluble ash	·432
Fibre, 2·534.	
Insoluble ash	·205
†Insoluble albuminoids	·216
Digestible fibre, Woody fibre	2·113
	100·000
*Containing nitrogen	·0268
† ,, ,,	·0345
Non-albuminoid nitrogen	·1173
Total nitrogen	·1786
S.G. of juice	1·0356

In this analysis neither the water nor the woody fibre was estimated separately.

PART VI

ANALYSIS AND VALUATION OF MANURES

193. In commerce certain constituents of the substances dealt with are valuable; others are of no value. Hence a commercial analysis—*i.e.*, one which shall indicate the value of a substance—will only estimate the valuable parts. Take, for instance, the analysis of a superphosphate. Supposing that we wished to make a complete investigation of the substances contained therein, we should estimate the amounts of lime, alumina, oxide of iron, sulphuric acid, phosphoric acid, and the different alkalis, both in the soluble and insoluble state; also the amounts of moisture, organic matter, and siliceous matter which it contains. In scientific investigations this is, of course, often necessary. The agriculturist, however, who simply wishes to know whether he has got value for his money or not, or the manufacturer who wishes to value his manure, does not want any such complex knowledge. In many cases nothing is required but the percentage of soluble phosphoric acid,[1] and even when a so-called 'full' analysis is asked for the only constituents needed are those which are tabulated on page 143.

The methods described in this chapter are strictly commercial ones, and will enable a student who has not time to go

[1] See notes on valuation, paragraphs 259–262.

through a full course of analytical chemistry to do all the work which is ordinarily necessary in an agricultural laboratory.

ANALYSIS OF MINERAL PHOSPHATES

194. **Moisture.**—The moisture given off at 100° C. is very small and of no importance, and it is usual to estimate it together with the combined water and organic matter. If, however, it should be required, it may be found by weighing out about 2 grams of the sample in a porcelain capsule, and heating in the steam oven until it ceases to lose weight. The loss is the moisture.

195. **Combined Water and Organic Matter.**—The portion used for the estimation of moisture is emptied into a weighed platinum dish, heated over an Argand at the highest temperature procurable without allowing the flame to touch the platinum. After about an hour the dish is placed in a Fletcher muffle furnace (see fig. 17), and kept at a bright yellow heat for twenty minutes. At the end of this time the gas is turned off, and the open muffle allowed to cool to a dull red. The dish is then removed to a desiccator and, when cool, weighed. The loss of weight gives the sum of the combined water, the organic matter, and the carbonic anhydride.

If in the subsequent analysis it should be noticed that the mineral effervesces on the addition of hydrochloric acid, the CO_2 may be estimated by one of the methods described in paragraphs 48–56. The amount of CO_2 is, however, not of much consequence to the manure manufacturer (see page 155), and very often a fairly accurate idea of it may be obtained from the quantities of lime and phosphoric acid present, the excess of lime over the phosphoric acid being considered as $CaCO_3$. This method of calculation is of course impossible in the case of apatites.

<table>
<tr><td colspan="4">Dissolve the mineral in HCl.</td></tr>
<tr><td rowspan="4">Precipitate consists of silica and silicates. Weigh.</td><td colspan="3">Filtrate. Add citric acid, make alkaline with ammonia, then acid with acetic acid. Boil, and add ammonium oxalate. Filter.</td></tr>
<tr><td rowspan="3">Precipitate consists of calcium oxalate. Heat to convert to calcium carbonate, and weigh.</td><td colspan="2">Filtrate. Add excess of strong ammonia and magnesia mixture. Allow to filter.</td></tr>
<tr><td rowspan="2">Precipitate consists of magnesium ammonium phosphate. Burn to convert to $Mg_2P_2O_7$ and weigh.</td><td colspan="2">Filtrate. Add excess of ammonium sulphide. Boil and filter.</td></tr>
<tr><td>Precipitate consists of ferrous sulphide. Burn to Fe_2O_3 and weigh.</td><td>Filtrate. Boil down to dryness, ignite to burn off organic matter, dissolve residue in HCl. Add slight excess of ammonia, boil, and filter. Reject filtrate. Ignite precipitate, and weigh as Al_2O_3.</td></tr>
</table>

The portion in italics is a description of the old-fashioned method for estimating iron oxide and alumina in phosphates. The modern method will be found described in paragraph 202.

METHOD OF ANALYSIS

196. The method followed in the complete analysis of a mineral phosphate may be seen at a glance from the table on page 122. A word or two, however, should be said concerning the principles involved. The determination of phosphoric acid in manures is always rendered difficult by the presence of lime, alumina, and oxide of iron. At one time analysts were content to dissolve the phosphate in hydrochloric acid and make alkaline with ammonia. This gave a precipitate of mixed phosphates of iron, aluminium, and calcium which was weighed as 'total phosphates.' In the method described below, advantage is taken of the fact that the *phosphates of iron and aluminium are not precipitated by ammonia in the presence of ammonium citrate.* The mixed phosphates may thus be kept in solution by a mixture of ammonium citrate and acetic acid. Ammonium oxalate will completely precipitate the lime from this solution in the form of calcium oxalate. After this precipitation the filtrate may be rendered alkaline without causing any further precipitate, and the phosphoric acid may be determined by magnesia mixture as described on page 27. Each process is described in detail in the sequel.

197. **Estimation of Sand and Siliceous Matter.**— Weigh out about 2 grams of the powdered mineral, transfer to a 4-oz. wide-mouthed beaker, removing the last traces of powder from the watch glass with the smallest possible quantity of hot water. Add 10 c.c. of dilute hydrochloric acid, and cover with a watch glass. If any carbonates be present, as is nearly always the case, the beaker must be placed on top of the steam oven until all effervescence ceases. Add 20 c.c. of strong HCl and evaporate down to dryness on the water bath, driving off the last traces of moisture on the sand bath. Allow the beaker to cool, then add 5 c.c. of strong HCl, which must be shaken

gently round the beaker until all the substance has been moistened with it. Warm for a few minutes on the water bath, then add about 20 c.c. of dilute HCl and allow to digest for ten minutes. Filter off, and wash with hot water until the washings are no longer acid to litmus paper. Transfer the filter paper, without drying, to a weighed platinum dish. Heat over an Argand turned down very low, keeping the dish covered with a square of platinum foil. When the paper is dry, turn up the flame so as just to char the paper. As soon as fumes cease to come off, turn up the Argand to its full power until the paper is completely burned. Cool in a desiccator, and weigh. Subtract the weight of the dish and filter ash. Calculate the percentage of the residue, and enter it as sand and insoluble silicates.

198. **Lime.**—To the filtrate from the sand add ammonia until a precipitate is formed. Dissolve this by adding 2 grams of citric acid.[1] If the precipitate all dissolves, add ammonia until it reappears, and strong acetic acid until it goes again. If it does not dissolve, the ammonia may be omitted. By going through these operations it will be ensured that sufficient ammonia is present to convert the whole of the citric and a portion of the acetic acid into ammonium salts. Raise to a boil, add 2 grams of solid ammonium oxalate, and estimate the lime exactly as described in paragraphs 42–45. The reason for adding citric acid is that ammonium citrate prevents the precipitation of phosphates of iron and aluminium.

199. **Phosphoric Acid.**—Allow the filtrate from the lime, which should not exceed 200 c.c., to cool, or cool it by placing the beaker in a vessel through which passes a stream of cold water. Then add 50 c.c. of strong ammonia and 40 c.c. of

[1] Citric acid sometimes contains insoluble matter. It is, therefore, better to dissolve the 2 grams of acid in water, and filter, if necessary, before adding to the liquid.

magnesium chloride mixture (see page 26), stirring vigorously all the while. Allow the beaker to stand two hours, stirring occasionally. At the end of this time decant the liquid off through a filter paper. When as much of the liquid has been removed as possible without getting the precipitate on to the filter, remove the filtrate beaker, and place the one containing the precipitate under the funnel. Wash the filter paper with dilute hydrochloric acid until the washings are sufficient to dissolve the precipitate in the beaker below. Then give the paper one wash with dilute ammonia. Where the ammonia touches the liquid in the beaker it will give a white precipitate. Complete the precipitation by adding strong ammonia until strongly ammoniacal. (The strong ammonia should form a quarter of the whole bulk.) Allow to stand, with frequent stirrings, for half-an-hour, then filter through the same paper as before. Wash, ignite, and weigh exactly as in paragraphs 39 and 40.

200. **Corrections for Solubility.**—It is unfortunate that phosphoric acid, which is so important a constituent of manures, should be one of the most difficult to estimate accurately. If the above instructions be followed out carefully, the ammonium oxalate and the citric acid being weighed out before adding to the solution, then a result will be obtained which is considerably below the truth. Several circumstances combine to bring this about. In the first place, $Mg_2(NH_4)_2(PO_4)_2$ is slightly soluble in water even when it contains a large quantity of ammonia. Ammonium chloride and ammonium oxalate increase the solvent power of the liquid, as also do citrates of iron and aluminium. Ammonium citrate does not seem to have very much influence, except that it makes the precipitation much slower. On the other hand, $MgCl_2$ decreases the solubility of the precipitate, but should large excess be used various impurities, including magnesia and magnesium oxalate, occur in

the precipitate. The second precipitation is used on this account.

Under these circumstances it is necessary to make an allowance for solubility. The matter was very thoroughly investigated by the late Dr. Augustus Voelcker, who considered that when two grams of substance are taken and the citrate process is used as described above, the percentage of P_2O_5 found is ·33 below the truth. This is probably the best addition to make, and it is used in all analyses throughout this book where any addition is made. Any exceptions are notified in the text.

In methods where neither citrates nor oxalates are present in the solution (see paragraphs 207, 208, 237), Fresenius' allowance of 1 milligram of $Mg_2P_2O_7$ for every 54 c.c. of liquid in the filtrate may be used.

201. **Iron and Aluminium.**—This estimation is not always performed, as a very shrewd idea of the quantity of these substances present may be obtained by adding up the results of other determinations and subtracting their sum from 100. It is, however, of considerable importance in manure works where the 'mineral phosphate' is to be converted into 'superphosphate.' The amount of H_2SO_4 which will be needed for this work varies considerably with the amount of Fe_2O_3 and Al_2O_3 present, as will be readily seen by comparing the two equations:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2 + 3H_2O;$$
$$Ca_3(PO_4)_2 + Al_2O_3 + 5H_2SO_4 = 2CaSO_4 + Al_2(SO_4)_3 + CaH_4(PO_4)_2.$$

Should insufficient acid be used, some of the soluble phosphate will be rendered insoluble, thus:

$$CaH_4(PO_4)_2 + Al_2O_3 + H_2SO_4 = CaSO_4 + Al_2(PO_4)_2 + 3H_2O.$$

The best method at present in use was originally invented by Glaser, but has gone through many modifications as to details. It is known as the Glaser, or alcohol, method. Like

many other of the special methods used in agricultural analysis, or indeed in any other branch of technical analysis, it is very necessary that the instructions as to quantities, &c., should be exactly followed out.

202. Weigh out 2·5 grams of the finely powdered mineral on a watch glass. Transfer to a beaker, washing the glass with a little hot water. Add a little dilute HCl, and digest on top of the water oven until all effervescence ceases. Now add 20 to 30 c.c. of pure strong HCl, and evaporate *thoroughly* to dryness on the water bath. This will get rid of any fluorine which may be present. When dry dissolve in about 10 c.c. of dilute HCl (one part of strong acid to four of water), allowing it to digest until nothing is left undissolved excepting the siliceous matter. This operation may be materially assisted by breaking up any lumps with a stirring rod. Pour the liquid into a 250-c.c. flask, washing the residue into the flask with the smallest possible quantity of water—25 c.c. should be sufficient. Measure out 10 c.c. of pure strong H_2SO_4 with a pipette, and run it into the flask. A thick precipitate of $CaSO_4$ will be formed. Shake the flask gently in a rotatory manner until the liquids are thoroughly mixed, and allow to cool. Fill up to the 250-c.c. mark with 95 per cent. alcohol. On allowing this to stand, the liquid will be found to contract. Shake it up well; allow it to cool, and make up to the mark again with alcohol and shake. Place a funnel with a dry filter paper in the mouth of a 200-c.c. flask, and filter off the liquid until 200 c.c. have been collected. Evaporate these 200 c.c. (which contain the Fe and Al in 2 grams of the mineral) in a large platinum dish. This may be started over a water bath, but as soon as most of the alcohol has evaporated it must be placed on a pipeclay triangle over a rose burner. Heat until the sulphuric acid begins to fume strongly. This will thoroughly char any organic matter which might otherwise interfere with subsequent operations. Allow the dish to cool, then wash it out

into a tall beaker, diluting to about 50 c.c. Add good excess of bromine and boil to oxidise the carbonaceous matter. When the bromine has all gone, make just alkaline with ammonia. Add about 5 grams of pure ammonium acetate, then make just acid with acetic acid. Bring the liquid up to a boil, then cool quickly, and filter. Wash with hot water containing a little ammonium nitrate. This precipitate contains the normal phosphates of iron and aluminium. (Some analysts weigh this precipitate, and consider the Fe_2O_3 and Al_2O_3 to constitute half its weight. This, however, leads to faulty results.) Dissolve the precipitate in dilute nitric acid, collecting the liquid in a 4-oz. conical flask fitted with an india-rubber stopper. Add about 5 c.c. of strong NH_4NO_3 solution; heat nearly to boiling (85° C. is the correct temperature). Add 25 c.c. of *ammonium molybdate* solution. Cork up the flask, and shake vigorously for about three minutes. Filter off the yellow precipitate, which will contain all the phosphoric acid. Make the filtrate alkaline with ammonia, boil, and filter. The precipitate will consist of the hydrates of iron and alumina, slightly contaminated with molybdic acid. To remove this, dissolve in HCl and reprecipitate with ammonia. Wash well, dry, ignite, and weigh as $Fe_2O_3 + Al_2O_3$. To separate these two, dissolve in strong HCl.[1] Make up to 250 c.c. with water. Mix the solution thoroughly, and determine the iron as described in paragraphs 75–77.

203. **Calculation of Results.**—*Phosphoric acid.* This is calculated as P_2O_5 from the $Mg_2P_2O_7$. It is always best in calculating results to begin by finding the percentage which the precipitate is of the substance taken. Thus we should begin by multiplying the weight of $Mg_2P_2O_7$ by 100, and dividing it by the weight of mineral phosphate which has been used.

[1] It will often be found that this precipitate, after ignition, is very insoluble in HCl. Some analysts always use H_2SO_4, which acts more rapidly.

This will be found to simplify further calculations considerably. The percentage so found may be calculated into P_2O_5 by the proportion

Mol. wt. of $Mg_2P_2O_7$: Mol. wt. of P_2O_5 : : % of $Mg_2P_2O_7$: % of P_2O_5.

From the percentage of P_2O_5 so found that of the $Ca_3P_2O_8$ is calculated.

These calculations, and most others, are very much simplified by using factors, of which a list is given in the appendix. Thus, the percentage of $Mg_2P_2O_7 \times \cdot 64 =$ the percentage of P_2O_5. To this the addition of ·33 must be made, and the result multiplied by 155 and divided by 71, or simply multiplied by 2·1831, which gives the percentage of $Ca_3P_2O_8$. In future the simplest means of calculation is always given, and should be verified by using the ordinary method.

Lime. The substance weighed is $CaCO_3$. Find the percentage and multiply by ·56; this gives the percentage of CaO. Subtract the P_2O_5 from the $Ca_3P_2O_8$. This gives the CaO combined with the P_2O_5. To find the amount of CaO as carbonate, subtract the amount combined with P_2O_5 from the total, and divide by ·56. Should the CO_2 be determined separately, the excess of CaO is entered as such.

204. **Mode of Entry:**

—	Cambridge coprolites	Spanish phosphorite	Canadian apatite	West Indian phosphate	German phosphate
Moisture				5·91	
Combined water	4·04	·16	·11		·25
Organic matter				5·46	
Calcic phosphate	58·09	85·33	82·25	68·07	83·21
Calcic carbonate	21·12	6·89		1·60	6·25
Oxide of iron	2·18				
Alumina	2·05	1·66	13·35	17·94	10·20
Magnesia, alkalis, &c.	4·33				
Silicates	8·19	5·96	4·29	1·02	·09
	100·00	100·00	100·00	100·00	100·00

ANALYSIS OF BASIC SLAG

205. A. The *moisture* is estimated as usual in 2 grams of substance. It contains neither organic matter nor combined water, as is to be expected from a substance which is produced at the high temperature of the Bessemer converter.

205. B. **Lime and Phosphoric Acid.**—The phosphate of lime which is contained in this substance has the formula $Ca_4P_2O_9$, and its constitution may be understood by considering it to be a compound of $Ca_3(PO_4)_2$ and CaO. Thus the four phosphates of lime met with in manures are

$CaO.P_2O_5.2H_2O$ or $CaH_4P_2O_8$, soluble phosphate;
$2CaO.P_2O_5.H_2O$ or $Ca_2H_2P_2O_8$, reverted phosphate;
$3CaO.P_2O_5$ or $Ca_3P_2O_8$, tricalcic phosphate;
$4CaO.P_2O_5$ or $Ca_4P_2O_9$, basic phosphate.

Four methods are given here for the analysis of basic slag.

206. The *first* method of analysis is similar to that of mineral phosphates with the following differences: A mixture of nitric and hydrochloric acids, equal parts, is used to dissolve the substance. This is in order to oxidise the large amount of ferrous oxide present.

Eight grams of citric acid, and a consequent increase in the amount of ammonia, are used to keep the oxide of iron in solution. Even then the magnesium ammonium phosphate precipitate will contain a trace of iron, and this must be removed by adding ·5 gram of citric acid before reprecipitating. For the precipitation of this lime 3 to 4 grams of ammonium oxalate must be used, and the precipitate redissolved and reprecipitated.

The extra amount of citric acid makes the precipitation of the $Mg_2(NH_4)_2(PO_4)_2$ somewhat slower. The solution must therefore be allowed to stand, with frequent stirring, for two and

a-half hours. The reprecipitation in the same way will occupy an hour.

207. *Second* method, used for estimation of phosphoric acid only. Should the percentage of lime not be required, the weighed portion of slag (1 gram) may be dissolved in 25 c.c. of strong H_2SO_4. This is done in a flask on a sand bath, and the liquid heated until it fumes strongly. It is then allowed to cool and is poured into a beaker containing 75 c.c. of water. The flask is rinsed out two or three times with water. The muddy liquid is allowed to settle, and filtered. The precipitate is well washed, 8 grams of citric acid and excess of ammonia are added, and the liquid cooled. The phosphoric acid is precipitated as before by 25 c.c. of $MgCl_2$ mixture and excess of strong ammonia. This method is not so reliable as the last, as the calcium citrate has a solvent action on the precipitate, whilst, on the other hand, the sulphuric acid present tends to throw down a basic magnesium sulphate along with the phosphate precipitate.

208. *Rapid* method for the estimation of phosphoric acid. For this estimation it is necessary to prepare two solutions, one of ammonium nitrate, the other of ammonium molybdate.

Ammonium Nitrate. Dissolve 100 grams in 90 c.c. of hot water; when cold, make up to 165 c.c. with distilled water.

Ammonium Molybdate. Measure 100 c.c. of water into a large flask. Add 50 grams of molybdic acid, then 100 c.c. of ·880 ammonia. Stir until dissolved. Pour the solution quickly into a large stoneware jug containing 720 c.c. of cold nitric acid (S.G. 1·20), stirring well whilst adding. Allow to stand over night, and filter.

Weigh out exactly ·5 gram of the sample. Transfer to a 4-oz. wide-mouthed beaker, and add 8 c.c. of strong pure HCl. Evaporate to dryness on the water bath, finishing on the sand bath. Allow to cool; then moisten with 8 c.c. of pure HCl,

and add 12 c.c. of water. Evaporate on the water bath until the liquid has diminished to about half its original bulk. Filter into a 250-c.c. flask. Wash with water slightly acidulated with HCl. Make up to 250 c.c. with distilled H_2O. After mixing take 25 c.c. and transfer to a 5-oz. conical flask fitted with a caoutchouc stopper. Add 18 c.c. of the ammonium nitrate solution. Heat to 85° C. Add 20 c.c. of ammonium molybdate solution, cork the flask, and shake vigorously for one minute. Filter through a very smooth filter paper. Wash three times with dilute HNO_3 (1–20). Then remove the paper, and wash all the yellow precipitate from the paper into a weighed platinum dish. Evaporate to dryness on the water bath. Finally, dry in the steam oven, cool, and weigh. The weight of the precipitate × 74·66 = percentage of P_2O_5.

209. *Molybdate* and *magnesia* method. This is perhaps the most reliable method for the estimation of phosphoric acid, and certainly the one most generally applicable.

Weigh out 1 gram of the sample. Dissolve in a mixture of 15 c.c. hydrochloric acid (S.G. 1·16) and 15 c.c. nitric acid (S.G. 1·42), evaporating to dryness to separate the silica. Add 20 c.c. hydrochloric acid (S.G. 1·16), and evaporate until it only occupies about half the original bulk. Add 20 c.c. boiling water, and filter. Collect the filtrate in a 250-c.c. flask. Make up to the 250-c.c. mark with water. Take 50 c.c. of this liquid with a pipette, and introduce it into an 8-oz. conical flask fitted with an india-rubber cork. Add ammonia until a permanent precipitate is formed. Dissolve this in the smallest possible quantity of nitric acid. Heat to 85° C. Add 200 c.c. ammonium molybdate solution (see paragraph 208). Cork the flask, and shake vigorously for five minutes. Allow the precipitate to settle, then filter. Wash once by decantation, then two or three times on the filter paper, using 1 in 20 nitric acid. This precipitate will contain all the phosphoric acid.

Dissolve it in dilute ammonia, and wash the filter well with hot water, collecting the solution and washings in an 8-oz. beaker. Neutralise the liquid with HCl, then add 20 c.c. of magnesia mixture and 20 c.c. of strong ammonia. Stir well, and allow to stand for an hour and a-half. Filter, wash with ammonia, dry, ignite, and weigh as $Mg_2P_2O_7$.

210. **Calculation.**—In the case of basic slag the calculation is simple, as nothing is required beyond the percentages of lime, phosphoric acid (P_2O_5), and silica. The difference between the sum of these percentages and 100 is put down as oxide of iron, &c. It consists of MgO, Al_2O_3, FeO, V_2O_3, and SO_3.

The following are a few typical results:

—	I	II	III	IV
Moisture . . .	—	—	0·13	—
Lime, CaO . .	46·00	43·48	32·42	46·33
*Phosphoric acid .	15·82	11·46	18·44	17·95
Ferrous oxide, &c. .	29·87	29·44	39·46	25·59
Silica . . .	8·31	15·62	9·55	10·13
	100·00	100·00	100·00	100·00
*Equal to $Ca_3(PO_4)_2$.	34·53	25·02	40·26	39·19

211. **Estimation of Fineness.**—The value of basic slag is greatly increased by being well ground; therefore it is often necessary to test its fineness. This is readily done by weighing out 10 grams into a small wire sieve having 100 meshes to the linear inch. It is ordinarily said that the *whole* of the 10 grams should pass through this, but in practice it is generally found that from 70 to 95 per cent. passes through. The sieve is shaken until as much has been passed through as will go, and this is collected and weighed.

ANALYSIS OF BONE MEAL

212. **Moisture and Organic Matter.**—Estimated as in mineral phosphates (see paragraphs 194 and 195).

213. **Sand.**—About 2 grams of the substance are weighed out and dissolved in hydrochloric acid, with all the precautions described in paragraph 10. Then, instead of boiling down to dryness, the liquid containing the sand and organic matter is treated with ammonia, citric acid, and acetic acid, raised to boiling-point, and the lime thrown down with ammonium oxalate, every detail as to quantities being carried out as described in paragraphs 198 and 199. The precipitate is collected on a filter, washed, and finally burned, as though it were calcium oxalate. The organic matter will be oxidised, and the precipitate may be weighed as $CaCO_3$ + sand. After weighing, the dish is emptied into a beaker, and the $CaCO_3$ dissolved in dilute HCl. The sand may then be filtered off, washed, and weighed, as in paragraph 197.

214. The reason for this mode of procedure is twofold:

Firstly. If the acid liquid containing the phosphate of lime, &c., in solution and the sand in suspension be filtered at once, the gelatinous nature of the organic matter in the liquid will often render filtration very slow. The precipitate of calcium oxalate carries down the gelatinous matter with it, and thus, after precipitation with ammonium oxalate, the liquid passes through the paper quite easily.

Secondly. Since the precipitation of phosphoric acid with magnesia mixture takes some considerable time, it is advisable to get it thrown down as soon as possible. By precipitating lime and sand together we get the liquid for precipitation with magnesia mixture at once, and thus we are enabled to go on with the lime and sand estimation whilst the phosphoric precipitate is forming, using 40 c.c. $MgCl_2$ mixture.

215. **Phosphoric Acid.**—This is estimated in the filtrate from the lime and sand, exactly as described in paragraph 199 for mineral phosphates.

216. **Nitrogen.**—Two grams are used for this estimation, which may be done by either of the two methods described in paragraphs 86–95.

217. **Calculation of Results.**—From the $Mg_2P_2O_7$ calculate the percentages of P_2O_5 and $Ca_3P_2O_8$. From the $CaCO_3$ calculate the percentage of CaO. Find the excess of CaO as in mineral phosphate analysis.

The excess of CaO is used as a check on the accuracy of the rest of the analysis, which is put out in this form :

—	Raw bones	Boiled bones	Bone ash	Bone flour
Moisture . . .	8·29	9·65	11·99	8·45
*Organic matter .	27·18	16·95	2·77	17·29
Phosphate of lime .	48·92	62·15	74·55	63·99
†Carbonate of lime, &c.	7·71	8·56	9·48	8·97
Sand	7·90	2·69	1·21	1·30
	100·00	100·00	100·00	100·00
*Containing nitrogen .	4·10	1·18	—	1·35
Equal to ammonia .	4·98	1·43	—	1·64
†Containing lime .	3·31	4·02	1·61	4·57

It is not usual to state the excess of lime, but it is always well to calculate it out. It should amount (in bones) to a little less than half the '$CaCO_3$, &c.,' which is the difference between the sum of the other percentages and 100.

The percentage of nitrogen, multiplied by 17 and divided by 14, gives the percentage of ammonia.

The analysis of *bone ash* is exactly similar to that of bone meal, except that the nitrogen is not estimated.

ANALYSIS OF GUANO

218. The name 'guano' is applied to such a large assortment of manures that no one method can be described applicable to all. Any manure, therefore, bearing the simple name 'guano' should be tested with blue litmus paper. If it give a decidedly acid reaction, it must be analysed by the method given for superphosphates. If not, it should be proceeded with in much the same manner as bones, except that *the organic matter must be burned off before the lime and phosphoric acid are estimated.*

219. **Moisture.**—When a Peruvian guano is heated to 100° C., it gives off not only moisture, but also a certain amount of ammonia. For ordinary commercial purposes this makes very little difference, and the estimation may be performed in the usual way. A more exact method is as follows: About 5 grams are weighed out in a U tube. One end of this tube is connected with a small wash bottle, containing 20 c.c. of seminormal acid, in such a manner that when a current of air is aspirated through the apparatus it passes first through the U tube and then bubbles through the acid. The lower part of the U tube which contains the guano is immersed in boiling water, and the free tube of the wash bottle connected with an air-pump or aspirator. In this manner all the ammonia which is liberated is absorbed by the acid. When the U tube no longer loses weight the acid is titrated with quinquinormal potash, and from this the NH_3 which has been absorbed may be calculated. The loss of weight sustained by the guano is moisture plus ammonia. The moisture may thus be calculated by difference.

220. **Sand, Lime, and Phosphoric Acid.**—Weigh out about 2 grams of guano in a platinum dish and burn over

an Argand, being careful not to exceed a dull-red heat, or some of the alkaline salt will fuse and render the mass difficult to remove from the dish.

The ash of a pure guano should be perfectly white.

Weigh the dish and guano after burning, and enter the loss as organic matter plus moisture.

Transfer the residue to a beaker, washing the last traces off the dish with a little dilute HCl; dissolve up in strong HCl, and proceed as in the case of mineral phosphates (see paragraphs 198 and 199), adding, however, only 1½ gram of ammonium oxalate.

221. **Nitrogen.**—The guano should be tested for nitrates thus: About 5 grams of guano are extracted with water; to the filtered solution are added a small quantity of indigo solution and strong sulphuric acid equal in bulk to the water used. Bleaching of the liquid indicates the presence of nitrates.

Should nitrates be absent, the acid method may be used (see paragraphs 90–95).

Should nitrates be present, the modified method described in paragraph 99 must be used.

The ammonia in a true guano should be about a quarter of the organic matter.

Ordinary guanoes do not contain nitrates, with the exception of Bats' guano, which probably contains nitric acid in combination with lime. The name 'guano,' however, is so popular with farmers that many compound artificial manures are sold as guano. Hence the necessity for testing with indigo.

222. **Calculation.**—On calculating out the quantities of CaO and P_2O_5 a true guano will show an excess of P_2O_5 over the CaO. Should the CaO be in excess, the result is entered exactly like that of bones. Should the P_2O_5 be in excess, there are two methods in use. The most scientific is to put down in

order the percentages of moisture, organic matter, P_2O_5, CaO, difference (alkalis, &c.), and sand, stating as footnotes the percentage of N and its equivalent of ammonia, and also the equivalent of P_2O_5 in $Ca_3P_2O_8$. The more common method, however, is to calculate out the $Ca_3P_2O_8$ equivalent to the CaO present, and set out the analysis thus :

——	Peruvian	Peruvian	Patagonian	Meat guano
Moisture	15·00	9·71	29·20	9·60
*Organic matter . . .	23·65	40·19	26·40	50·85
$Ca_3(PO_4)_2$	31·68	19·00	20·44	26·92
†Alkalis, &c. . . .	23·02	13·05	7·36	11·38
Sand	6·65	18·05	16·60	1·25
	100·00	100·00	100·00	100·00
*Containing nitrogen . .	4·83	8·45	6·81	5·94
Equal to ammonia . .	5·87	10·26	8·27	7·22
†Containing P_2O_5 . . .	4·92	·40	·56	4·87
Equal to $Ca_3(PO_4)_2$ . .	10·74	·87	1·22	7·04
Total P_2O_5	19·43	9·10	9·92	16·20
Equal to $Ca_3(PO_4)_2$ . .	42·42	19·87	21·66	33·96

A Bats' guano contains about 12 per cent. phosphate of lime, with 5 per cent. of organic nitrogen and 4 per cent. of nitric nitrogen.

223. **Fish Manure,** or fish guano, is analysed exactly like guano, with the exception that the oil is estimated. This is done in the same manner as the oil in oil cakes (see paragraphs 140, 141, and 142). The oil should not be above 3 per cent., as it forms a protective covering and prevents the manure from rotting in the ground.

ANALYSIS OF SUPERPHOSPHATE OF LIME

224. The general outline of the method may be seen from the following table:

<table>
<tr><td colspan="4">Treat with water. Filter.</td></tr>
<tr><td colspan="2">Precipitate. Transfer to a platinum capsule, and burn off paper and organic matter. Treat with dilute HCl. Filter.</td><td colspan="2" rowspan="2">Filtrate. Treat with citric acid, ammonia, and acetic acid. Boil. Add ammonium oxalate. Filter.</td></tr>
<tr><td>Precipitate. Weigh as Sand.</td><td>Filtrate. Add ammonia in excess, filter, and weigh precipitates as insoluble phosphates.</td><td>Precipitate consists of calcium oxalate. Reject.</td><td>Filtrate. Add strong ammonia and magnesia mixture. Weigh the precipitate as $Mg_2P_2O_7$ and calculate from this the soluble phosphoric acid.</td></tr>
</table>

225. **Moisture.**—Weigh out 2 grams in a porcelain capsule, heat in the steam oven for about five hours, cool in desiccator, and weigh; return to oven for about half-an-hour. Cool and weigh again. Repeat until weight is constant.

226. **Organic Matter.**—The organic matter in a mineral superphosphate is very small, but in one made from bones it is considerable. Should the analyst require to know the amount exactly, the following process must be carried out: Two grams are weighed out into a platinum crucible, and milk of lime is added until the mass is alkaline. It is then dried in the air bath at 150° C. until its weight is constant. It is next ignited on the Fletcher muffle furnace for twenty minutes, cooled, and weighed. The difference between this weight and the weight after drying at 150° C. is the weight of organic matter and combined water. Should the amount only be

required approximately, the superphosphate, after drying, may be transferred to a weighed platinum dish, ignited over an Argand in a draught cupboard until it has lost its dark colour, then heated over the blow-pipe until it ceases to fume. It is then cooled in a desiccator and weighed. The loss is due to organic matter, sulphuric acid, and changes in the composition of the phosphates. In almost all cases the loss due to sulphuric acid and the changes in the phosphates amounts to half the weight of soluble phosphate calculated as CaP_2O_6. If this amount, therefore, be subtracted from the total loss, a very close approximation to the amount of organic matter will be obtained.[1]

227. **Soluble Phosphoric Acid.**—A portion of the powdery sample is selected as described in the chapter on sampling, Part IV., paragraph 119, and placed in an iron mortar. It is banged with the pestle until a smooth, pasty mass is obtained. This takes two or three minutes. Of course it may happen that a very dry sample has been obtained, in which case it will not become pasty. In such a case it must be remembered that the object of triturating in an iron mortar is to break down all hard lumps and to render the mass as homogeneous as possible. When the mass is thoroughly mixed, a portion is taken out with a spatula. It takes some little practice to enable the operator to take off about the right quantity, but

[1] When soluble phosphate of lime is strongly heated with calcium sulphate the following reaction takes place :

$$CaH_4(PO_4)_2 + CaSO_4 = Ca_2H_2(PO_4)_2 + H_2SO_4,$$

of which the H_2SO_4 is volatilised—*i.e.*, one molecule of $CaH_4(PO_4)_2$ which is calculated in the analytical result as CaP_2O_6 [$CaH_4(PO_4)_2 - 2H_2O$] will liberate one molecule of H_2SO_4. Or, in figures, 198 parts by weight of CaP_2O_6 will liberate 98 parts of H_2SO_4. Hence the change in the phosphates and loss of H_2SO_4 on heating a superphosphate amounts to $\frac{98}{198}$, or about half the weight of the soluble phosphate calculated as CaP_2O_6.

if more than 3 grams or less than 1 gram has been taken, then another portion should be taken from the mortar. Two grams should be the quantity used. This is weighed out on a watch glass. The next operation is to mix this thoroughly with water. The method which is most effective is somewhat difficult to describe, though in reality very simple. A beaker about $2\frac{1}{2}$ inches high by $1\frac{1}{2}$ inch broad is taken, and the weighed mass of 'super' is placed in it by means of a stout glass rod $3\frac{1}{2}$ inches long. The portion sticking to the watch glass is washed in with not more than 10 c.c. of water. The substance has now to be rubbed round the beaker with the rod very rapidly until it forms with the water a thin paste containing no clots. In doing this the sides of the beaker will become smeared all over with the paste. This is washed to the bottom of the beaker with a jet of cold water, and the liquid made up to about 50 c.c. It is then allowed to stand ten minutes, when it will have settled to a considerable extent. The liquid is decanted through a filter into an 8-oz. beaker. The beaker is filled up again to the same level and decanted off. This is repeated with cold and hot water until all the soluble portion is extracted. The following series of washings should be followed exactly :

(*a*) Stir up with cold water 50 c.c. ;
(*b*) Fill up twice with cold water 50 c.c. ;
(*c*) Twice with hot water 30 c.c. ;
(*d*) Boil smartly with 30 c.c. water.

After the boiling the whole must be transferred to the filter paper and the filtrate tested as it drops from the funnel with blue litmus paper. If an acid reaction is shown, another washing with the hot wash bottle must be given, but as a rule the filtrate is found to be neutral.

228. **Treatment of the Soluble Portion.**—This

contains the soluble phosphoric acid, together with a certain amount of H_2SO_4 and $CaSO_4$.

The only thing to be estimated is the P_2O_5. The liquid is treated exactly as the solution of mineral phosphate (paragraphs 198 and 199), rejecting the lime precipitate and weighing the $Mg_2P_2O_7$. Only 1 gram of ammonium oxalate and 25 c.c. of $MgCl_2$ mixture must be used.

229. **Treatment of the Insoluble Portion.**—The filter paper containing the insoluble part of the manure is transferred without drying to a platinum dish, and heated over an Argand, very slightly at first, but as soon as the substance is dry at the highest temperature obtainable. When the paper is quite burned, the dish is allowed to cool and the substance washed out with dilute HCl into a beaker of the same size as that which was used for washing out the soluble portion. Twenty c.c. of strong HCl are added, and allowed to digest for five minutes on the water bath. Fifty c.c. of water are added to complete the solution of any $CaSO_4$ which may be left. This will take about a quarter of an hour. Finally, the sand is filtered off, washed, and treated as described in the case of mineral phosphates (paragraph 197). The filtrate is raised to a boil, and ammonia added in excess. This precipitates all the P_2O_5 left by the water, in combination with iron, aluminium, and lime. It is filtered off, dried, ignited, and weighed.

230. **Calculation.**—From the amount of $Mg_2P_2O_7$ the P_2O_5 is calculated, and the correction of ·33 per cent. made (see paragraph 200). The percentage thus found is multiplied by 99 and divided by 71 to give the percentage of soluble phosphate, CaP_2O_6 (the anhydrous form of $CaH_4P_2O_8$).

For purposes of valuation, the P_2O_5 is also calculated into

its equivalent of $Ca_3(PO_4)_2$ (multiply percentage of P_2O_5 by 155 and divide by 71), and the result entered thus :

—	I	II
Moisture	13·90	14·55
Organic matter and combined water .	10·11	9·54
Soluble phosphate of lime . . .	19·69	16·66
(Equal to $Ca_3(PO_4)_2$	(30·82)	(26·09)
Insoluble phosphates	4·20	5·25
Sulphate of lime, &c.	45·85	46·51
Sand	6·25	7·49
	100·00	100·00

231. A second method, which is rather more scientific, is as follows: *Moisture*, *organic matter*, and *soluble phosphoric acid* are estimated as before.

Total *phosphate* and *lime*. Two grams are weighed out and treated exactly as though a sample of bones, $CaCO_3$, sand, and $Mg_2P_2O_7$ were being weighed.

232. **Calculation.**—The soluble phosphate is calculated as before, together with its equivalent in tribasic phosphate of lime. The total P_2O_5 is calculated into $Ca_3P_2O_8$. From this is subtracted the $Ca_3P_2O_8$ which has been calculated as equivalent to the soluble phosphoric acid. The remainder is the insoluble phosphate of lime.

From the weight of $CaCO_3$ the percentage of CaO is calculated (multiply by ·56). From this is subtracted the amount of CaO contained in the soluble CaP_2O_6 and the insoluble $Ca_3P_2O_8$, and the remainder is calculated out as $CaSO_4$.

These calculations from the $CaCO_3$ precipitate may be simply and rapidly done as follows :

Subtract the soluble from the total P_2O_5 ; result = insoluble P_2O_5.

Subtract soluble P_2O_5 from CaP_2O_6; result = lime in soluble phosphate.

Subtract insoluble P_2O_5 from insoluble $Ca_2P_2O_8$; result = lime in insoluble phosphate.

Add CaO in CaP_2O_6 to CaO in $Ca_3P_2O_8$; result = CaO combined with P_2O_5.

Subtract this last amount from total CaO; result = CaO combined with SO_3. Multiply this amount by 17 and divide by 7; result = percentage of $CaSO_4$. Enter results as

Moisture	15·00
Organic matter	12·00
Soluble phosphate	18·00
Equal to $Ca_3(PO_4)_2$	(28·28)
Insoluble phosphate	6·00
Sulphate of lime	41·95
Alkalis, &c.	·55
Sand	6·50
	100·00

233. **Dissolved Bones and Guanoes with an Acid Reaction** are analysed by one of the above methods with the additional *determination of* N. This is best done by the acid method, but should the soda lime be preferred, a difficulty will be met with in the mixing of the pasty material with soda lime. This is overcome as follows: From 1 to 2 grams are weighed out on a watch glass and covered over with about 4 grams of gypsum. The watch glass with its contents is then left in a desiccator. In about half-an-hour the substance is removed to a mortar, rinsing out the watch glass with fine sand which has been well ignited. The mass will be now fairly dry, and by adding sand in small quantities at a time, grinding with the pestle after every addition, it will soon become perfectly powdered. It may then be mixed with soda lime, and proceeded with as described in paragraph 88.

The following are typical analyses of dissolved bones:

—	I	II
Moisture	14·43	19·40
*Organic matter	22·01	21·67
Soluble phosphate	12·62	8·46
(Equal to $Ca_3(PO_4)_2$	(19·75)	(13·25)
Insoluble phosphate	11·09	20·70
Calcic sulphate, &c.	33·64	27·08
Sand	6·21	2·69
	100·00	100·00
*Containing nitrogen	1·38	2·59
Equal to ammonia	1·66	3·14

ANALYSIS OF REFUSE MANURES

234. This name is used simply for want of a better; but it does not exactly express what is meant. Thus, fish is, in the strict meaning of the term, a refuse material, but in practice it would be analysed as already described under the heading of guano. The manures analysed according to the method put forward in this article all contain small amounts of P_2O_5, and relatively very large percentages of oxide of iron and alumina, together with large quantities of organic matter. The more common of these are *farmyard manure*, *nightsoil* (*corporation manure*), *shoddy*, *hair*, *blood*, *horn*, and *soot*. The most important constituent is generally nitrogen.

235. **Method of Analysis.**

Burn off organic matter. Treat with HCl, and filter.

Precipitate consists of sand and insoluble matter. Weigh.

Filtrate. Add ammonia in excess, and filter.

Precipitate. Weigh as Fe_2O_3, Al_2O_3, and P_2O_5. Re-dissolve in HCl and HNO_3. Boil nearly to dryness. Add NH_3, then HNO_3. Heat to 85° C. and add ammonium molybdate. Filter. Reject filtrate. Dissolve precipitate in NH_3. Add magnesia mixture and weigh ppt. as $Mg_2P_2O_7$.

Filtrate. Boil and add ammonium oxalate. Filter. Burn ppt. and weigh as $CaCO_3$.

236. **Moisture.**—Two grams are dried at 100° C. as usual.

237. **Organic Matter.**—Two grams are weighed out in a platinum dish, and ignited until of constant weight. The loss gives moisture and organic matter.

238. **Sand.**—The ash left after burning is dissolved in strong HCl, diluted, and filtered. The sand on the filter is washed, ignited, and weighed.

239. **Phosphoric Acid.**—The filtrate from the sand is raised to a boil and excess of ammonia added. The precipitate is allowed to settle and washed twice by decantation. It is then dissolved in HCl, boiled, re-precipitated with ammonia, allowed to settle again, and washed well by decantation. When fairly clean it is transferred to the filter, washed with hot water, dried, ignited, and weighed, the amount being entered as ammonia precipitate. The ignited mass is then re-dissolved by digestion on the water bath with strong HCl. The solution is boiled down nearly to dryness. Ten c.c. of dilute HNO_3 (3–1) are added with 50 c.c. of water, then ammonia until nearly neutral. Excess of HNO_3 is next added, and the solution heated to 85° C. This heating and the next operation are most conveniently carried out in an 8-oz. conical flask fitted with an india-rubber stopper. Forty c.c. of ammonium molybdate solution are added to the liquid and the whole shaken up well for three minutes, then placed on the water bath for twenty minutes to settle. The yellow precipitate is filtered off and washed with dilute HNO_3. To the filtrate another 10 c.c. of molybdate solution are added, and if further precipitation occurs it is heated to 85° C., shaken up again, and the operation repeated. The washed precipitate is dissolved in dilute ammonia, which must be poured into the filter so that only the soluble portion may come through. To the ammoniacal solution 10 c.c. of magnesia mixture are added, drop by drop, stirring all the while; 10 c.c. of

strong NH_3 solution are then added, and the liquid is allowed to stand two hours. The magnesium ammonium phosphate is filtered off, washed with ammonia, dried, ignited, and weighed as usual.

The correction necessary in this case is very small, and must be obtained by measuring the filtrate and washings. For every 60 c.c. 1 milligram is added to the weight of the ignited precipitate.

240. **Lime.**—The lime is contained in the filtrate from the ammonia precipitate and the washings after re-precipitation. It is precipitated by ammonium oxalate and weighed as usual, Should the precipitate be very small—*i.e.*, less than ·05 gram—it is ignited for twenty minutes in the Fletcher muffle and weighed as CaO.

241. **Nitrogen.**—Best determined by the acid method (paragraphs 90–95).

242. **Calculation.**—From the $Mg_2P_2O_7$ are calculated first the P_2O_5, then the $Ca_3P_2O_8$ to which this is equivalent. From the $CaCO_3$ the CaO is calculated, and from this the CaO as $Ca_3P_2O_8$ is subtracted. The remainder is calculated back into $CaCO_3$, and the analysis entered as follows :

—	Soot	Shoddy	Rabbits' dung	Dried sewage	Sugar scum
Moisture . . .	10·42	9·77	67·30	14·55	46·65
*Organic matter .	45·28	68·85	28·71	41·80	17·77
Phosphate of lime .	—	—	1·49	16·37	9·69
Carbonate of lime .	20·06	5·20	—	—	6·09
Oxide of iron and alumina, &c.	8·99	5·04	1·16	9·58	14·98
Sand . . .	15·25	11·14	1·34	17·70	4·82
	100·00	100·00	100·00	100·00	100·00
*Containing nitrogen	3·59	5·65	·87	2·64	·44
Equal to ammonia	4·36	6·86	1·05	3·21	·53

ANALYSIS OF MANURE CAKES

243. Such substances as *rape cake*, *castor-bean cake*, and *damaged cotton and linseed cakes* are often used as manures. The principal manurial constituent is, of course, nitrogen, but in addition to this there is always a certain quantity of phosphoric acid in the ash usually combined with an alkali metal.

244. **Method of Analysis.**

Burn. Treat ash with HCl. Filter.	
Precipitate. Weigh as sand.	*Filtrate.* Add ammonia and calcium chloride. Filter, and weigh precipitate as $Ca_3P_2O_8$.

245. *Moisture*, *nitrogen*, and *organic matter* are estimated as in guano.

246. **Sand and Calcic Phosphate.**—Two grams of the substance are weighed out in a platinum dish and burned, with the precautions described in the analysis of feeding cakes. The ash is transferred to a small beaker, and dissolved in about 20 c.c. of strong hydrochloric acid. The insoluble portion is filtered off, washed with hot water, burned as described under the estimation of sand in mineral phosphates, and weighed.

The filtrate from the sand contains the phosphoric acid, together with lime and alkalis. Of course this phosphoric acid may be determined either by the citric acid or the molybdate method, but it is customary to determine it by the simple method indicated in the last table. The liquid must be raised to the boiling-point, about 10 c.c. of the ordinary laboratory solution of calcium chloride added, then excess of ammonia. The precipitate of calcium phosphate so formed must be filtered rapidly, washed, and weighed as $Ca_3P_2O_8$.

From this weight the amount of phosphoric acid may be calculated, or the result may be set out in this form :

—	Rape cake	Castor cake	Cotton cake
Moisture	9·54	10·72	10·81
*Organic matter . .	80·02	82·88	82·49
Calcic phosphate . .	5·95	5·29	5·55
Alkalis, &c. . . .	·84	·42	·50
Sand	3·65	·69	·65
	100·00	100·00	100·00
*Containing N . . .	4·78	4·94	7·56
NH_2	5·81	5·99	9·18

ANALYSIS OF POTASSIC MANURES: KAINIT, MURIATE OF POTASH, SULPHATE OF POTASH, &c.

247. As a rule, nothing but the *potash* is estimated in these substances. Occasionally, however, a somewhat fuller analysis is required.

248. *Moisture* is estimated as usual.

249. *Sand* is estimated by dissolving in water slightly acidulated with HCl, filtering, washing, and igniting and weighing.

The other two substances are *potash* and *magnesia.*

250. **Potash.**—The simplest method is as follows: Weigh out ·5 gram, dissolve in water with a small amount of dilute HCl, filter off the sand and wash well. To the filtrate add about ·5 gram pure NaCl and 15 c.c. $PtCl_4$ solution (10 grams $PtCl_4$ in 100 c.c. H_2O). Evaporate exactly as described in paragraph 33 to a pasty state. Add 2 c.c. $PtCl_4$ solution. Shake round the beaker, allow to stand for five minutes, and filter through two counterpoised papers. Allow *the whole* of the liquid to run through, then with the least possible quantity of $PtCl_4$ solution (not more than 3 c.c.) rinse the beaker and wash the precipitate. When the liquid has again entirely passed through, the rest of the precipitate must be removed to the

paper with strong alcohol, well washed, dried, and weighed as described in paragraph 32. The NaCl is added to turn all K_2SO_4 into KCl. The preliminary washing with $PtCl_4$ is to remove any double compounds of platinum with magnesium and sodium, which would be insoluble in alcohol.

251. *Another Method.*—Weigh out about ·5 gram of the substance. Dissolve in water. To the solution, which contains the sand in suspension, add $Ba(OH)_2$ solution until alkaline. Allow the precipitate to settle, keeping the beaker on the water bath. Filter rapidly, and wash well with boiling water. The precipitate consists of barium sulphate and magnesia, which may be rejected. Make the solution acid with HCl. Raise it to boiling-point, then add hot $BaCl_2$ drop by drop, until no further precipitate occurs. This is best done by keeping the beaker on a water bath, and allowing the precipitate to subside after each few drops. When no further precipitate forms there will be a small amount of $BaCl_2$ in solution, together with all the potassium in the state of chloride. The barium must be removed by a drop or two of dilute H_2SO_4 and the $BaSO_4$ filtered off and washed. The filtrate is evaporated down and estimated as in paragraphs 33–35. As small quantities of Mg and Na may be present, it is best to moisten the pasty substance with a little $PtCl_4$ solution and decant through the filter paper before using alcohol.

ANALYSIS OF AMMONIUM SALTS

252. As these salts are generally prepared as by products in coal gas manufacture, it is always possible that they may contain traces of ammonium sulphocyanate, which is a strong plant poison. They should therefore be tested qualitatively for NH_4CNS with Fe_2Cl_6, which should give no red colouration.

253. **Estimation of Ammonia.**—This may be done by the soda lime method. As the substance is often damp, and would give off ammonia as soon as it touched the alkaline substance, it should be well mixed with gypsum before adding to the soda lime. About ·5 gram should be used, and the tube should be about 12 inches long.

It is very seldom that anything else is estimated in ammonium salts, but it is sometimes necessary to estimate the moisture and 'ash'—*i.e.*, the non-volatile matter.

254. Moisture is estimated as usual.

255. Non-volatile matter is estimated by weighing out 2 grams in a platinum capsule and heating on an Argand until it ceases to fume, then weighing the residue. The burner should be very low to begin with, but the temperature may be increased as the operation proceeds, using a red heat to drive off the last traces of volatile matter.

ANALYSIS OF NITRATE OF SODA

256. This substance is generally guaranteed to contain 95 per cent. pure $NaNO_3$, the impurities being sand, together with sulphate and chloride of sodium. The *chlorine* and *sulphuric acid* should be determined as in paragraphs 28–31, and 69–70.

257. **Nitric Acid.**—Any of the methods described in the chapter on nitrogen determination may be used, Ulsch's being the most easily managed.

ANALYSIS OF COMPOUND MANURES

258. This is a somewhat comprehensive term, including all kinds of special manure. Ordinarily a compound manure will be found to consist of mineral or bone superphosphate mixed with some nitrogenous substance. It will often contain

salts of potassium, and sometimes nitrates. The first thing to do is, of course, to find out what the manure consists of. The following tests may be used:

Experiment I.—Make into a paste with water and add a piece of blue litmus paper. If it be strongly acid, the soluble P_2O_5 must be estimated.

Experiment II.—Boil a small quantity (about 4 grams) with 100 c.c. distilled water; filter, and divide the filtrate into two parts, *A* and *B*.

(*A*) Add 1 c.c. indigo solution and 50 c.c. strong H_2SO_4. Should the indigo bleach, the manure contains nitrates.

(*B*) Add 5 c.c. strong H_2SO_4. Boil to dryness in a platinum dish; ignite the residue until it no longer fumes. Dissolve in alcohol; filter. To the filtrate add 1 c.c. of $PtCl_4$ solution. A yellow precipitate indicates potash.

If the substance contain soluble phosphoric acid, it must be analysed exactly like a superphosphate.

If the substance be not acid, it must be analysed exactly like a sample of bones.

If the substance contain N_2O_5 the nitrogen must be estimated by the modified acid method.

If the substance contain potash, 2 grams of the substance are ignited at a dull red heat until all the organic matter and salts of ammonia have been driven off. The residue is boiled with water, filtered, and washed. The K_2O in the washings is estimated by one of the two methods given under *potash manures*, paragraphs 250 and 251.

VALUATION OF MANURES BY ANALYSIS

259. The word *value* has two very distinct meanings. It may either indicate the price which must be paid when purchasing a manure, or it may mean the profit which is to be obtained

by using it. Thus, it is by no means proved—in fact, it is highly improbable—that the soluble phosphate in dissolved bones is any more efficient as a manure than that contained in a mineral superphosphate. Therefore, so far as the *produce* of this manurial constituent is concerned, it is of the same value in each case; whereas *commercially* the price of the soluble phosphate in bones is very much higher than that in mineral superphosphate.

260. **Definition of a Unit.**—The commercial unit of any manurial constituent is the hundredth part of a ton. Thus, if a mineral superphosphate be found to contain 27·85 per cent. of soluble phosphate, it is said to contain 27·85 units of soluble phosphate per ton.

N.B.—The commercial unit of soluble phosphate is really the unit of $Ca_3P_2O_8$ equivalent to the soluble phosphate; thus it is sometimes quoted as 'phosphate made soluble.'

261. **Valuation by Units.**—Of course the prices of various manures fluctuate considerably, and it is therefore necessary, when an exact valuation is required, to know the present prices per unit. These are published every month by some of the principal manure merchants, and also by several of the leading agricultural societies. The following table shows the form in which these prices are published, and gives an idea of what those prices are per unit:

	s.	*d.*		*s.*	*d.*
Phosphate made soluble ($Ca_3P_2O_8$):					
From raw bones	2	8	to	2	10
From bone ash	2	8	,,	2	11
From mineral	2	2	,,	2	5
Insoluble phosphate ($Ca_3P_2O_8$):					
In natural guano	2	0	,,	2	4
In bones or fish manures	1	3	,,	1	8
In ground minerals	1	0	,,	1	3
In basic slag	0	10½	,,	1	1
In mineral superphosphate	0	6	,,	0	8

	s.	d.		s.	d.
Phosphoric acid (P_2O_5):					
Varies according to source	4	9	to	6	2
Ammonia (NH):					
Peruvian guano (6–9 per cent. NH_3)	18	6	,,	22	6
Peruvian guano (3–5 per cent. NH_3)	15	0	,,	18	0
Ammoniated Peruvian guano (10–11 per cent. NH_3)	13	6	,,	14	6
Ichaboe guano (10–11 per cent. NH_3)	17	0	,,	18	0
Rape meal	13	6	,,	17	0
Ground bones	10	0	,,	11	0
Sulphate of ammonia	8	9	,,	9	6
Fish manures	10	0	,,	11	0
Shoddy, high quality (over 8 per cent. NH_3)	5	0	,,	7	0
Shoddy, low quality (ground leather, hoof, and horn).	3	0	,,	5	0
Equivalent to nitrogen in $NaNO_3$	10	0	,,	11	0
Which is equal to $NaNO_3$	2	1	,,	2	3
Potash (K_2O):					
In kainit	2	9	,,	3	5
In sulphate of potash	3	8	,,	4	1
Equivalent in muriate of potash	3	4	,,	3	8

262. To calculate the price per ton of a manure. Multiply the percentage of each manurial constituent by its price per unit, and add up the amounts so obtained.

Take, for instance, a compound manure of the following composition :

Moisture	13·30
*Organic matter	15·24
Soluble phosphate	7·42
(Equal to $Ca_3P_2O_8$)	(11·61)
Insoluble phosphate	22·30
†Calcic sulphate, &c.	39·04
Sand	2·70
	100·00
*Containing N	·88
Equal to NH_3	1·07
†Containing K_2O	5·22
And N_2O_5	4·70
Equal to $NaNO_3$	7·37

The price may be added up in this manner:

		s.	*d.*		£	*s.*	*d.*
$Ca_3P_2O_8$ made soluble (bone)	11·61 ×	2	9	=	1	11	11
Insoluble $Ca_3P_2O_8$ (bone) .	22·30 ×	1	5	=	1	11	7
NH_3 (bone) . . .	1·07 ×	10	0	=	0	10	8
K_2O (say kainit) . . .	5·22 ×	3	0	=	0	15	8
$NaNO_3$	7·37 ×	2	2	=	0	15	10½
					5	5	8½

The market price of such a manure would therefore be £5 5*s.* 8½*d.* plus the cost of mixing the ingredients.

263. **Valuation of Mineral Phosphates.**—In this country, now that the coprolite beds are almost used up, the use of mineral phosphates in the raw state as manures is quite exceptional. Therefore the valuation is based on the readiness with which they are converted into superphosphate and on the quality of that product when made. The principal impurities which influence superphosphate manufacture are the oxides of iron and aluminium, carbonate of lime, and fluorides. The extent to which these impurities are detrimental is partly shown in the following table, which gives the amount of pure H_2SO_4, oil of vitriol S.G. 1·6, and oil of vitriol S.G. 1·55 absorbed by 100 parts of each substance:

Substances	Pure H_2SO_4	Oil of vitriol S.G. 1·6	Oil of vitriol S.G. 1·55	Substances formed
$Ca_3P_2O_8$	63·2	94	100	$CaH_4P_2O_8$ and $CaSO_4$
$CaCO_3$	97·5	146	155	CO_2 and $CaSO_4$
CaF_2	79·6	118	126	HF and $CaSO_4$
Fe_2O_3	61·2	91	97	$Fe_2(SO_4)_3$
Al_2O_3	95·1	141	151	$Al_2(SO_4)_3$

Against this waste of sulphuric acid must be placed the fact that a certain amount of $CaCO_3$ is somewhat beneficial. The carbonic acid gas escaping within the mass promotes sponginess and lightness in the manure, and facilitates drying.

In the case of CaF_2, the whole of the HF does not escape,

but attacks any silica which may be present, forming SiF_4, and this in its turn may be acted upon by water, forming SiO_2 and H_2SiF_6.

Thus it will be seen that the exact valuation of a mineral phosphate by analysis would entail a very complex calculation. A rough method is very often employed based upon the percentages of $Ca_3P_2O_8$, Fe_2O_3, and Al_2O_3, the other impurities being neglected. When less than 3 per cent. of the mixed oxides of iron and aluminium is present, the valuation is calculated entirely from the percentage of $Ca_3P_2O_8$. When more than 3 per cent. is present, the excess is multiplied by 2 and subtracted from the percentage of phosphate. Thus, supposing that analysis showed a mineral to contain 80 per cent. of $Ca_3P_2O_8$ and 5 per cent. of oxides of iron and aluminium, the excess of 2 per cent. over the 3 allowed would be doubled and subtracted from the 80. The mineral would be then valued as containing 76 per cent. $Ca_3P_2O_8$. In fact, many vendors would sell it as guaranteed to contain 76 per cent. phosphate of lime.

PART VII

SOIL ANALYSIS

Soil analysis leads to no such accurate valuation of a soil as manure analysis does of a manure. Hence it is not a true commercial analysis. An analyst is frequently asked to investigate a soil with a view to advising the farmer as to its treatment. This is an exceedingly difficult problem, involving as it does many conditions which cannot be determined in the laboratory. Even in the laboratory the problem to be faced by the chemist presents many difficulties. Perhaps this will be best understood by reading the following excerpt from a paper read before the Chemical Society by Dr. Bernard Dyer in 1894 :

'The chemical analysis of soils, which in the early days of agricultural chemistry was looked upon as likely to be of great practical use in agriculture, was soon found to be, as ordinarily practised, of very limited value. Determinations in the soil of the total quantities of the more important mineral elements of plant food have been long recognised as affording useful information only in exceptional cases ; and even in these exceptional cases the results obtained have rather afforded "probable indications" than absolute information. The reason, as has often been pointed out, is that an analysis of soil, as ordinarily made, shows the total percentage of its constituents, or at any rate, the percentage dissolved by strong

mineral acids, without reference to the fact that only *a very small proportion of this total may be available for plant use.*'

We know that plants can only take up food from the soil in a state of solution, the chief solvents being water saturated with CO_2 or the acid excretions of the plants' own roots.

Dr. Dyer has estimated the acid contents of the root sap of over a hundred varieties of plants, and finds that, on the average, a 1 per cent. solution of citric acid is very similar in its action to this acid secretion.

A long series of experiments on Rothamsted soils, of which the history was known, confirmed his opinion that a citric acid solution of this strength would give an accurate idea of the available potash and phosphoric acid in the soils.

As this method occupies some time, it is described first. The student should start this analysis, and whilst it is standing he should proceed with the fuller analyses described in paragraph 270.

264. **Solubility in Citric Acid Solution.**—Take a Winchester quart bottle which has been used for the storage of strong acids, and which, therefore, will be unlikely to yield up potash, &c., to the citric acid solution, and rinse it thoroughly. Weigh out 200 grams of air-dried soil and place it in the Winchester. Dissolve 20 grams of citric acid in 2 litres of distilled water and pour it over the soil. Stopper the bottle and shake up thoroughly. This shaking must be repeated several times each day for seven days. At the end of seven days the solution is decanted through a large filter, two portions, each of 500 c.c., are collected, and treated as described in the next two paragraphs.

At the same time weigh out 50 grams of the same air-dried soil in a tared evaporating basin. Place this in a steam oven and leave for about five hours; after this weigh every twenty minutes until the weight is constant. The loss represents

moisture. From this estimation calculate the quantity of *dry* soil in the 200 grams.

265. **Available Phosphoric Acid.**—Evaporate 500 c.c. of the clear liquid on a water bath until it measures about 100 c.c. Allow it to cool thoroughly and add 40 c.c. clear ammonium molybdate dissolved in nitric acid (paragraph 208). Allow to stand for forty-eight hours with occasional stirring. Decant the liquid through a filter and wash several times, first with dilute nitric acid (1–4), then with pure water in very small doses, and finally transfer to the filter and wash free from excess of acid. The ammonium phospho-molybdate is dissolved in dilute ammonia, allowing the solution to run into a weighed platinum dish. When the filter has been washed two or three times, the dish is placed on the water bath and the ammoniacal liquor evaporated to dryness. It is finally dried in a steam oven and weighed. The residue contains 3·5 per cent. of its weight of phosphoric acid (P_2O_5).

266. **Available Potash.**—Five hundred c.c. of the clear liquid is evaporated on the water bath with a little strong hydrochloric acid ; when quite dry it is gently heated over an Argand until all the organic matter is burned off and the residue is nearly white. This residue is dissolved in HCl, and evaporated slowly with 5 c.c. platinum chloride solution (10 per cent.). If the evaporation be conducted slowly, the platinum potassium chloride settles out well, in spite of the various salts present. When nearly dry, decant through a filter paper, wash twice with small quantities of platinum chloride solution, and finally with strong alcohol. When the alcohol comes through clear, dry the filter at 100°, then wash through with hot water into a tared dish. Evaporate to dryness, dry in a water oven and weigh. Calculate the percentage of potash as described in paragraph 36.

267. **Calculation.**—The 200 grams originally dissolved in the citric acid contained a certain amount of moisture, which

has been estimated. Hence we know how much dry soil the 200 grams contained. One quarter of this—*i.e.*, something less than 50 grams—is used for each estimation.

268. **Conclusion.**—Dr. Dyer's conclusion from many analyses was that

(*a*) 'When a soil is found to contain so little as about 0·01 per cent. of phosphoric acid (P_2O_5) soluble in a 1 per cent. solution of citric acid, it would be justifiable to assume that it stands in immediate need of phosphatic manure.'

(*b*) It is difficult—'more difficult than in the case of phosphoric acid—to give any plausible suggestion as to what percentage of citric-acid-soluble potash may be regarded as marking the non-necessity of special potash applications. Probably this limit lies below 0·005 per cent.'

269. **Full Analysis of Soil.**—In many cases a much fuller analysis is required than the one just described. It is not only necessary to discover what plant food is immediately available, but also what stores of food are locked up in such a manner that good tillage and weathering may at some future time bend them to the use of the crop. This is generally done by two separate sets of operations. The first is to analyse that portion soluble in hydrochloric acid, and the second to analyse the insoluble residue.

FULL ANALYSIS OF PORTION SOLUBLE IN HCl

270. **Preliminary Operations.**—Dry, finely powdered soil, prepared as directed in paragraph 132, is such a very hygroscopic substance that it is rather difficult to weigh out accurately. The following method is therefore recommended as avoiding the difficulty:

Place about 30 grams of the powdered soil in a porcelain

basin, and allow it to stand for half-an-hour in the balance case. Then weigh out portions as follows:

(*a*) 5 grams in a platinum dish;
(*b*) 5 grams in a pair of watch glasses with clip;
(*c*) 5 grams in a wide-mouthed 4-oz. beaker.

Treat the different portions as follows.

N.B.—Each of the following operations occupies a considerable length of time; it is, therefore, best to get them all started as nearly together as possible, so that no time may be wasted.

(*a*) Determination of moisture plus organic matter and salts of ammonia. Place the dish containing the weighed portion of soil on an Argand which has its flame turned down very low. Turn up the flame very gradually, about once every five minutes, until in an hour it is about as hot as when used for turning calcium oxalate to calcium carbonate. The soil will turn darker in colour, and then slowly lighter, as the carbonised organic matter is burned off. In order that all the hot soil may be exposed to the air it is necessary to stir it occasionally. To do this use a piece of No. 10 B.W.G. copper wire about 4 inches long, having one end flattened out for about $\frac{3}{4}$ inch. See that the wire is polished, and free from any roughness which may cause the soil to adhere. With this instrument a little care will enable the operator to stir the powder without causing any loss whatever. At least five hours will be required for the complete oxidation of the organic matter. When that time has elapsed, cool the dish in a desiccator and weigh, then return to the Argand for half-an-hour. Repeat the process until no further loss is sustained. After the burning has been completed, this portion is treated with HCl and used for the general analysis (see paragraph 271).

The reason for keeping the temperature below a red heat is to prevent the decomposition of the $CaCO_3$.

(*b*) Determination of *moisture.* This determination is of no value to the farmer, since the moisture in any soil exposed to the weather is, perforce, a very variable quantity. It is therefore only made to enable the operator to calculate out his results as parts per hundred of the perfectly dry sample.

Remove the clip, and place the watch glasses containing the soil in the steam oven. In two hours replace the clip, allow to cool in a desiccator, and weigh. Repeat the drying operation for half-an-hour at a time until the weight is constant.

(*c*) Determination of *sulphuric* and *phosphoric* acids. Add to the soil in the beaker 5 c.c. dilute HCl, cover with a clock glass, and allow it to stand on the top of the steam oven until effervescence ceases. Remove the clock glass, washing any liquid condensed on it back into the beaker, and add 25 c.c. strong HCl. Evaporate to dryness on the water bath. Heat for a minute or two on the sand bath until completely dry, cool, moisten with strong HCl, add 25 c.c. dilute HCl (1–2), mix thoroughly with a short glass rod, heat on the water bath until the sediment settles, and decant through a filter into a 12-oz beaker. Wash by decantation until the washings are no longer acid, reject the precipitate, and treat the liquid as directed in the following table :

Raise nearly to boiling, add ammonia in slight excess, boil, allow to settle, filter, washing by decantation.	
Precipitate. Make a hole through the paper ; wash the ppt. into a 16-oz. beaker with dilute HNO_3, removing the last traces by dropping strong HNO_3 into the filter, then washing with hot water. Heat to 85° C. Add 25 c.c. ammonium molybdate solution, allow to stand one hour in a warm place, and determine P_2O_5 as described in paragraph 209.	*Filtrate.* Add HCl until acid, boil, add hot $BaCl_2$. Allow to stand on water bath for an hour, filter, and weigh $BaSO_4$ as in paragraphs 29 and 30.

General Analysis of the Burned Portion

271. Remove the substance left in the platinum dish, after burning, to a 4-oz. wide-mouthed beaker, and treat with HCl exactly in the same manner as the portion used for the determination of sulphuric and phosphoric acids. Evaporate to dryness, and moisten with strong HCl. Add 25 c.c. dilute HCl, filter and wash by decantation. Dry, burn, and weigh.

This weighing operation may cause some little trouble, as the dry silicates are very hygroscopic. The weighing should be performed as rapidly as possible. Directly after weighing, the dish with its contents should be returned to the Argand, and allowed to cool again in the desiccator. Before weighing again, the weights, as found in the first weighing, should be placed on the pan, so that no time may be lost after the dish has been taken from the desiccator.

272. The filtrate from the insoluble portion is analysed according to the following scheme:

<table>
<tr><td colspan="3">Add ammonia and filter.</td></tr>
<tr><td rowspan="4">*Precipitate* contains Fe_2O_3, Al_2O_3, and P_2O_5. Weigh, then re-dissolve in HCl, and estimate Fe by $K_2Cr_2O_7$ solution (see paragraph 77).</td><td colspan="2">*Filtrate.* Add ammonium oxalate. Filter.</td></tr>
<tr><td>*Precipitate.* Calcium oxalate. Ignite, and weigh as $CaCO_3$.</td><td>*Filtrate.* Add HCl. Boil to dryness. Ignite to drive off ammonium salts. Weigh as MgO, NaCl, and KCl. Dissolve in hot water. Filter.</td></tr>
<tr><td></td><td><table><tr><td>*Precipitate.* Ignite, and weigh as MgO.</td><td>*Filtrate.* Estimate potassium by $PtCl_4$ as in paragraphs 33–36.</td></tr></table></td></tr>
<tr><td></td><td>The sodium is estimated here as the difference between total residue (MgO, KCl, and NaCl) and the sum of MgO and KCl.</td></tr>
</table>

Details of the Analysis

273. **Oxide of Iron and Alumina.**—Boil the filtrate from the insoluble portion over a Bunsen, then add dilute ammonia in slight excess. Boil for a few seconds, then allow the precipitate to settle. Filter rapidly, wash once by decantation, then re-dissolve in HCl and re-precipitate with ammonia. Boil again and filter, collecting the filtrates from both precipitations in the same beaker. Wash well with hot water, dry, ignite, and weigh.

The object of this double precipitation is to prevent the precipitate from being contaminated with $CaCO_3$. Should there be any considerable quantity of lime in the soil, the precipitate first formed by ammonia is sure to contain some.

After weighing the mixed oxides, dissolve them by digesting with a few c.c. of strong HCl. When the digestion has gone on for about half-an-hour, decant the liquid into a 250-c.c. flask and add a further quantity of acid. When it is all dissolved, make up to 250 c.c. with water. Reduce the iron in 50 c.c. of this, and titrate exactly as described in paragraph 77.

The percentage of Al_2O_3 is obtained by subtracting the sum of the percentages of Fe_2O_3 and P_2O_5 from the percentage of ammonia precipitate.

274. **Lime.**—Boil the filtrate and washings from the ammonia precipitate, and add ½ gram of solid ammonium oxalate. Allow to settle, and test the supernatant liquid for lime with a drop of ammonium oxalate solution. Should lime be present in the liquid, another ½ gram of solid oxalate must be added. Filter. Wash well with hot water. Dry the precipitate, ignite in a Fletcher furnace (see paragraph 46), and weigh as CaO.

275. **Magnesia and Alkalis.**—Transfer the filtrate

from the lime, which will be of considerable bulk, to a weighed platinum dish 3 inches in diameter, and evaporate over a rose burner turned down so low that ebullition does not quite take place. When all the liquid has been boiled down to a very small bulk, add 5 c.c. of strong HCl, and finish by evaporating to dryness on the water bath. Next place on an Argand, and ignite at a low temperature so as to drive off the ammonium salts. This ignition will take two or three hours. When all fuming ceases, heat to dull redness in the Bunsen flame for about half-a-minute, cool in a desiccator, and weigh. The contents of the dish are MgO, KCl, and NaCl.

276. **Magnesia.**—Dissolve the weighed residue in *hot* water and filter rapidly, washing with hot water. Dry the precipitate, ignite, and weigh as MgO.

277. **Potash.**—Add 5 c.c. of platinum chloride solution, evaporate on the water bath, and estimate the potash exactly as in paragraphs 33–36.

278. **Soda.**—This, as stated in the table, is calculated by difference. This is done as follows: Calculate the K_2PtCl_6 obtained in the last operation as percentage of the total weight of soil taken. This multiplied by ·193 gives percentage of K_2O in the soil.

Percentage of $K_2O \times 1{\cdot}585$ gives percentage of KCl. Add the percentage of KCl to that of magnesia, and subtract from the percentage of alkaline chlorides and magnesia. The result is the percentage of NaCl. Multiply the percentage of NaCl by ·53, and the result will be the percentage of Na_2O in the soil.

DETERMINATIONS MADE IN SEPARATE PORTIONS OF THE SOIL

In addition to the general mineral analysis given above, it is usual to determine *nitrogen*, *nitrates*, *chlorides*, *carbonates*, and *organic carbon*.

279. **Nitrogen.**—Weigh out 20 grams of the finely ground sample of soil, and estimate the nitrogen by the acid method (paragraphs 92–95).

280. **Nitrates and Chlorides.**—These two constituents are estimated in the *water extract* of soil. The apparatus used for the extraction is shown in fig. 44. A is the top of a Winchester quart bottle which has been cut off from the bottom. This is connected, by means of a piece of glass tubing and two well-fitting corks, with the stout tabulated flask B.

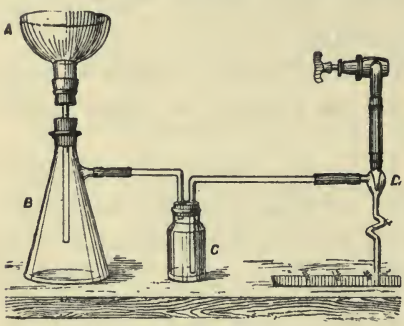

FIG. 44.

This apparatus is connected first with the safety bottle C, then with the pump D. Inside A is placed a disc of copper gauze 2 inches in diameter; this covers the aperture of the neck, and serves as support for a piece of filter paper. By means of this apparatus the whole of the nitrates and chlorides in 500 grams of soil may be extracted with 100 c.c. of water.

Weigh out 500 grams of the original sample (undried) of the soil, and place it over the filter paper in A (fig. 44). If it be of a loose texture, press it down well; then pour 50 c.c. of distilled water over it. After it has stood five minutes, set the

pump going and allow the water to run through. Now add another 50 c.c., and allow the pump to continue working until water ceases to drop into B. The liquid is then ready for further treatment.

281. **Nitrates.**—Pour the extract obtained as described in the last paragraph into a platinum dish. Wash the flask twice, and add the washings to the rest of the liquid. Evaporate over the water bath until only about 5 c.c. is left. Wash this liquid with a little hot water into Schloesing's nitrate apparatus (fig. 31), and determine the nitrogen exactly as described in paragraph 107.

282. **Chlorine.**—Extract another portion of the soil in exactly the same manner, and estimate the chlorine with standard $AgNO_3$ solution as described in paragraph 69.

283. **Carbonates.**—Estimate the CO_2 by one of the methods described in paragraphs 48–53. The quantity of soil to be used in this operation varies according to the nature of the soil. About 5 grams will generally be found convenient, but should large quantities of lime or magnesia be found in the earlier part of the analysis, a smaller quantity of the soil will be required. On the other hand, soils very poor in lime and magnesia are correspondingly poor in carbonic acid.

284. **Organic Carbon.**—The organic portion of a soil generally goes by the name of 'humus,' and this humus is usually found to contain 58 per cent. of carbon. If, therefore, we estimate the carbon, we are able to calculate the quantity of humus ; and seeing that we have in a previous part of the analysis estimated the loss on burning, we can calculate, by difference, the percentage of combined water in the soil. The determination of carbon is conducted as follows: Fit up an apparatus similar to the one described in paragraph 55 and shown in fig. 22, the only difference to be made being the omission of the pipette *b*, for which is substituted an ordinary

straight glass tube with a piece of india-rubber tubing and a soda lime tube attached in the same manner as shown in fig. 22.

Weigh out from 2 to 8 grams of the soil, according to its nature, into the flask, and add first 20 c.c. of water, then 30 c.c. of strong sulphuric acid. Now connect the flask *directly* with the aspirator, so that the CO_2 formed in the flask by decomposition of the carbonates may be drawn off. Whilst this is proceeding, weigh the U tube (*f*, fig. 22), and place all the tubes together. Next connect up the apparatus as shown in the figure. Take the cork out of the flask, and introduce 8 grams of coarsely powdered pure potassic dichromate. Close the flask again, and heat gently as long as gas is evolved; then heat nearly to boiling for some time. Finally, aspirate air through the apparatus for about ten minutes. Detach the weighed U tube, allow it to cool, and weigh again. The increase of weight is due to the CO_2 formed from the oxidation of the humus. If this amount of CO_2 be multiplied by ·471, the weight of humus is obtained.

ANALYSIS OF THE PORTION INSOLUBLE IN HYDROCHLORIC ACID

The actual analysis of this portion of the soil is exactly similar to the analysis of the soluble portion, the only difficulty being to get it into solution. This is accomplished by one of three methods.

285. **The Sulphuric Acid Method.**—Weigh out roughly 2 grams of the insoluble portion of the soil in a weighed platinum dish. Ignite over an Argand, allow to cool in a desiccator, and weigh accurately. Add 10 c.c. of strong sulphuric acid, and heat on an Argand very cautiously. This operation must be carried on in a draught cupboard, as the heating has

to be continued until nearly all the acid has been volatilised. When the capsule is nearly dry, allow it to cool, dilute with water acidulated with hydrochloric acid, filter, wash thoroughly, dry, ignite, and weigh. The residue consists of sand and amorphous silica. The silica which results from the decomposition of the clay may be dissolved out with strong sodium carbonate solution, and the residue weighed again as sand. The filtrate is analysed as described in paragraph 272.

286. **Hydrofluoric Acid Method.**—This method depends upon the fact that when hydrofluoric acid acts upon silica a gaseous product is formed according to the equation

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

Thus all the silica will pass off in the course of evaporation.

Weigh out about 2 grams of the soil in a platinum dish, ignite, and weigh accurately as described in paragraph 285. Now add concentrated HF until the substance is just covered. Digest on the water bath for an hour, then add another portion of the acid, and digest again for half-an-hour. Now add 2 c.c. of sulphuric acid (equal parts acid and water), and heat up gradually over an Argand. The heating must be continued until the acid fumes cease to come off. Allow the residue to cool, and treat with 20 c c. of strong HCl. Allow to stand on the water bath for half-an-hour, then dilute. A clear solution should be obtained. Should any insoluble matter be present, decant the liquor into a beaker, and treat with HF again.

The liquid eventually obtained may be analysed according to the table shown in paragraph 272, the silica being estimated by difference.

287. **The Fusion Method.**—For this method two portions must be used, one of which is fused with a mixture of potassic and sodic carbonates, which form alkaline silicates and so render the substance soluble; whilst the other is heated

with calcic carbonate and ammonium chloride, which break down the insoluble silicates and set free the alkalis in the form of alkaline chlorides.

Fusion with Alkaline Carbonates

288. *Preparation of Fusion Mixture.*—This mixture of Na_2CO_3 and K_2CO_3 in molecular proportions may be prepared either by mixing in a mortar 10 grams of sodium carbonate and 13 grams of potassium carbonate, both of which have been recently fused, or by igniting Rochelle salt in a platinum dish, extracting the charred mass with water, and evaporating the liquid to dryness.

In any case the mixture must be dried perfectly before using.

289. **The Operation.**—Weigh out about a gram of the substance in a platinum dish, ignite, and weigh again (paragraph 285). Weigh out roughly 5 grams of *dry* fusion mixture into a deep platinum crucible. Pour the weighed quantity of 'insoluble matter' on top of the fusion mixture, sweeping in the last portions with a small camel's-hair brush. Now stir up all the contents of the crucible with a stout piece of copper wire until they are fairly mixed. Brush back into the crucible any traces which may adhere to the wire. Place the cover loosely on top of the crucible, and heat it on a pipe-clay triangle over a Bunsen burner until the whole mass is fused. Continue this heating until effervescence becomes subdued, then transfer the crucible to a Fletcher muffle furnace (fig. 17), and keep at a bright-red heat for forty minutes. Allow it to cool just below redness, then cool rapidly by placing on a cold iron plate. This will induce the vitrified mass to become very brittle. When quite cool, place the crucible at the bottom of a 12-oz. beaker, covered by a clock glass, and from a wash bottle fill the

crucible with hydrochloric acid (equal parts acid and water). When effervescence has ceased, turn the beaker so as to lay the crucible on its side, and add more acid until the crucible is quite free from solid matter. Next remove the crucible with a glass rod and wash it thoroughly with hot water, adding the washings to the acid solution.

All the silica in the portion of soil taken will be in the gelatinous hydrated state. The liquid must be evaporated to dryness on the water bath, then heated on the sand bath to render all silica insoluble. A few c.c. of strong HCl must be added, to moisten the whole mass, and then 50 c.c. of weak acid. After evaporating to about half bulk on the water bath, the silica must be filtered off, dried, ignited, and weighed, and the filtrate must be analysed according to the table in paragraph 272.

DETERMINATION OF 'INSOLUBLE' ALKALIS

290. *Preparation of Pure Calcic Carbonate.*—Dissolve Iceland spar or good marble in the least possible quantity of HCl, add lime water until just alkaline, boil, and filter. Raise the clear filtrate to the boiling-point, and add pure ammonium carbonate in excess. Allow to settle, wash thoroughly by decantation, transfer to a platinum dish, and dry first in the steam oven, then at a low temperature over an Argand burner.

291. *Preparation of Pure Ammonium Chloride.*—The great difficulty in performing the operation to be described with commercial ammonium chloride is that the crystals are so tough and wiry as to render powdering well nigh impossible. This difficulty may be overcome by dissolving pure NH_4Cl of commerce in the smallest quantity of hot water, filtering, and evaporating until the salt begins to crystallise. If it be now cooled down rapidly by circulating cold water around the

vessel in which it is contained, and vigorously stirred, the ammonium chloride will crystallise out in minute crystals. These may be filtered off and dried. The result will be a fine powder just suitable for our purpose.

292. **The Operation.**—Weigh out about a gram of the dry substance, as described in paragraph 285, and introduce it into a deep platinum crucible, together with a gram of dry NH_4Cl and 6 grams of pure dry $CaCO_3$. Mix thoroughly with a stout wire, brushing back all adherent matter from the wire to the crucible. Cover the crucible, and raise it to a red heat over a Bunsen for an hour. The heating is best started by placing the crucible in an inclined position (see fig. 45) and heating the top of the crucible first, moving the burner from time to time until the whole is at a red heat. At the end of an hour place the crucible in a Fletcher muffle furnace (fig. 17), and keep at a bright red heat for forty minutes.

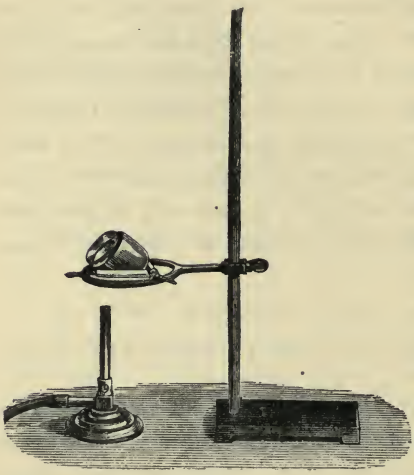

FIG. 45.

Allow the crucible to cool. Place in a 12-oz. beaker and slake the contents with hot water. They will rapidly break up, and may be detached from the crucible with a wash bottle. Remove the crucible with a glass rod and wash well, adding the washings to the liquid in the beaker. Boil the liquid for a few minutes. Decant through a filter. Wash three times

by decantation, using 50 c.c. of water for each washing ; then wash once with hot water on the filter.

The filtrate will contain all the alkalis in the form of chlorides, together with some calcic chloride and calcic hydrate. Precipitate the lime by adding ammonium carbonate solution in excess, together with a little ammonia and ammonium oxalate. Boil well and filter, washing by decantation. Evaporate the filtrate to dryness in a large platinum dish, and ignite gently to drive off all ammoniacal compounds. Weigh as NaCl + KCl, and proceed as described in paragraphs 277 and 278.

ANALYSIS OF LIMESTONES

There is very little difference in the general method adopted between the analysis of limestones and the analysis of the 'soluble' portion of soils, though it is not often necessary to determine any other constituents in a limestone than the silicates, the lime, and the magnesia.

293. General Table.

<table>
<tr><td colspan="3">Dissolve in HCl, and evaporate to dryness; dissolve in water, and filter.</td></tr>
<tr><td>Precipitate. Dry and weigh as insoluble silicates and sand.</td><td colspan="2">Filtrate. Treat with ammonia, filter, dissolve precipitate in HCl, and re-precipitate ; add both filtrates together.</td></tr>
<tr><td></td><td>Precipitate. Weigh as Fe_2O_3, Al_2O_3, and P_2O_5. Dissolve up and estimate P_2O_5, as in refuse manure.</td><td>Filtrate. Add HA, then $(NH_4)_2$ Ox ; filter.</td></tr>
<tr><td></td><td></td><td>Precipitate. Burn and weigh as $CaCO_2$.</td><td>Filtrate. Evaporate with HNO_3. Add microcosmic salt to boiling solution; cool, and render ammoniacal. Weigh precipitate as $Mg_2P_2O_7$.</td></tr>
</table>

Details of the Analysis

294. **Silicates.**—Weigh out about 1 gram of the air-dried substance; dissolve in HCl, as described in paragraph 10, and evaporate to dryness on the water bath. When quite dry, heat on the sand bath for a few minutes. Allow to cool, and moisten with 2 c.c. of strong HCl. Stir to break up clots. Add 25 c.c. of dilute HCl (1–3), evaporate for five minutes, then filter. Wash thoroughly with hot water, transfer the precipitate to a weighed platinum dish, ignite, and weigh.

295. **Iron Oxide and Alumina.**—The estimation of oxide of iron and alumina is complicated by the presence of the large excess of lime salts in the liquid. When ammonia is added a considerable quantity of $CaCO_3$ will be precipitated, together with the hydrated oxides.

Raise the filtrate from the silicates to boiling-point, remove from the flame, and add dilute ammonia until just alkaline. Boil again, and allow the precipitate to settle. Decant off the liquid through a filter. Wash once by decantation; then re-dissolve in dilute HCl, as described in paragraph 273. Boil, and re-precipitate with ammonia. Should the precipitate now be small (only a few milligrams) it may be weighed, but usually it should be dissolved and re-precipitated a third time.

After igniting and weighing, the precipitate should be dissolved and tested for P_2O_5, according to the method described in paragraph 239. Should it be present, it must be estimated.

296. **Lime.**—In a good agricultural limestone there is little difficulty about this estimation, which is carried out as described in paragraph 274. In dolomitic limestones, however, it is more difficult. When magnesic salts are present and a large excess of ammonium oxalate is used, the calcic oxalate precipitate is largely contaminated with magnesic

oxalate. On the other hand, should only just sufficient of the ammonium salt be added, the $MgCl_2$ present has a distinct solvent action on the calcium oxalate. The most simple way of overcoming this difficulty is by dissolving and re-precipitating, though it may be remarked that less magnesia is precipitated in the presence of acetic acid than in the presence of free ammonia.

To the total filtrates add acetic acid until slightly acid; boil, and add 1½ gram of pure ammonium oxalate. Allow to settle, and decant through a filter. Wash once by decantation, and dissolve in the smallest possible quantity of dilute HCl. Add ammonia until only slightly acid; boil, and add ammonium acetate solution in excess. Allow to settle, and filter, washing four times by decantation. Weigh as $CaCO_3$.

297. **Magnesia.**—The filtrates from the two lime filtrations will not only consist of a large bulk of liquid, but will contain great quantities of ammonium salts. It is therefore well to evaporate the liquid to smaller bulk. This is readily done by placing in a large wide-mouthed beaker over a Bunsen burner, keeping the liquid at such a temperature that it only just boils, and adding sufficient liquid from time to time to keep it about a quarter full. To the first lot of liquid add 5 c.c. of strong nitric acid, and as more liquid is added to replace what is evaporated, add more acid, 5 c.c. at a time, until 20 c.c. has been used. This will decompose the ammonium salts, which will first form ammonium nitrate, then nitrous oxide and water. When all the liquid has been concentrated to about 200 c.c., add to the hot solution 2 grams of pure microcosmic salt, stirring until quite dissolved. Allow to cool, and render strongly ammoniacal. Stir, and allow to stand for one and a-half hour. Filter, dry, ignite, and weigh as $Mg_2P_2O_7$ (using the precautions described in paragraph 40).

298. **Calculation.** — It is not usual to estimate the

CO_2 in limestones, as this may be calculated from the percentages of lime and magnesia, and the analysis is stated as follows:

—	Nottinghamshire dolomite	Derbyshire mountain limestone
Combined water, alkalis, &c. .	5·34	·22
$CaCO_3$	54·54	97·35
$MgCO_3$	38·35	·71
Fe_2O_3 and Al_2O_3 . . .	·48	·09
P_2O_5	·08	—
Silicates	1·21	1·63
	100·00	100·00

ANALYSIS OF LIME

299. This analysis is carried out in exactly the same way as the analysis of limestone, except that it is usual to estimate the CO_2 and the *combined water* present. The CO_2 may be estimated by one of the methods described in paragraphs 50–56.

Combined Water. Weigh out about 2 grams of the lime into a platinum dish, and place in a Fletcher muffle furnace (fig. 17), heated to a bright red for twenty minutes. Allow to cool to a dull red; remove to a desiccator, allow to cool thoroughly, and weigh. The loss of weight represents the quantity of CO_2 and combined water present. By subtracting CO_2 we obtain the amount of water combined with the CaO in the form of $Ca(HO)_2$.

ANALYSIS OF GAS LIME

The only difference between this and the analysis of lime is that in gas lime the *sulphur* must be estimated. Now, this sulphur exists in three forms—viz., sulphate of calcium, sulphite of calcium, and sulphide of calcium. It is usual to

estimate the *total sulphur* and the sulphur in the form of *calcic sulphate*. The 'sulphite' sulphur is less frequently estimated.

300. **Total Sulphur.**—Weigh out 2 grams of the gas lime; transfer to a 12-oz. conical flask; add 5 grams $KClO_3$; place a funnel in the neck to prevent loss by spirting, and pour in 50 c.c. pure HNO_3. When the reaction moderates in violence transfer to a water bath, and heat until Cl ceases to be evolved; this will take about an hour. Transfer to a wide-mouthed beaker, washing the flask thoroughly with hot water; add 20 c.c strong HCl, and evaporate to dryness. Heat for a minute on the sand bath. Cool, and moisten with 2 c.c. strong HCl. Add 100 c.c. H_2O. Stir well, and allow to stand for twenty minutes. This operation will oxidise all the sulphur to sulphuric acid, so that it will all be in the form of $CaSO_4$. Filter, and wash the precipitate with warm dilute HCl (1–20) to dissolve any traces of $CaSO_4$ left behind.

The next process is to remove the excess of lime, which would interfere with the subsequent precipitation. Render the solution just ammoniacal, and add ammonium carbonate solution in excess. Allow to settle, and decant through a filter. Wash by decantation with hot water. To the filtrate add HCl cautiously until effervescence ceases; then expel the dissolved CO_2 by heating for a short time on the water bath. Raise to a boil, add boiling $BaCl_2$ solution, and proceed to the estimation of $BaSO_4$ as described in paragraphs 28–31. The percentage of sulphur must be calculated from the percentage of $BaSO_4$.

301. **Sulphur as Calcic Sulphate.**—Weigh out 2 grams, dissolve in HCl, and separate the silicates as described in paragraph 271. Next separate the lime, and determine the SO_3 present exactly as described in the last paragraph. The HCl will expel all sulphites and sulphides as SO_2 and H_2S respectively, and only the sulphur originally in the state of calcic sulphate will be precipitated as barium sulphate.

PART VIII

ANALYSIS OF DAIRY PRODUCE

MILK ANALYSIS

MILK is an exceedingly complex substance. To separate and estimate its various component parts entails a long and difficult series of operations. In practice, however, it is found sufficient to make the following determinations:

Specific gravity;
Fat;
Total solids;
Ash.

Sometimes this analysis is carried out with the object of discovering whether the milk has been diluted with water or reduced in quality by the removal of cream; but the true commercial analysis is directed towards discovering the value of the milk for dairy purposes. Thus the chemist of the Aylesbury Dairy Company analyses over ten thousand samples yearly, not to detect fraud, but to see that the milk supplied to the public reaches a certain standard of richness.

302. **Specific Gravity.**—This is very readily determined by means of a hydrometer such as is used for taking the S.G. of turnip juice. The *lactometer* is a modified form of hydrometer, marked off in degrees. A difference of one degree represents a difference in specific gravity of ·001. The gradu-

ation generally begins at 15° (S.G.=1·015), and ends at 45° (S.G.=1·045).

To use this instrument, pour just as much milk as will conveniently fill the lactometer cylinder into a flask and insert a thermometer. Should the temperature be 60° F., or 15° C., the S.G. may at once be taken. Should the temperature, however, be different, it must be brought to 60° F. by immersing the flask in warm or cold water until the thermometer registers the right temperature.

Pour the milk into the cylinder, and lower the lactometer carefully into the liquid. Note the graduation at the top of the meniscus.

The specific gravity of pure milk is from 30° to 34° of the lactometer (S.G.= 1·030 to 1·034); the addition of 10 per cent. of water lowers the reading to 27° to 30°, or about three degrees.

A difficulty here arises, seeing that the removal of cream *increases* the density of milk to about 33° to 37°; hence the lactometer cannot be relied upon without some method of finding out whether we are dealing with skim milk or whole milk. This is provided in the creamometer, which usually consists of an ordinary stoppered graduated cylinder of 100 c.c. capacity.

Fill the cylinder up to the 100-c.c. mark with milk, and allow to stand twenty-four hours. The cream will then have risen to the top, and its volume may be read off.

Pure whole milk should give at least 10 c.c cream.

A rough estimate of the amount of water added may be obtained from using the creamometer and lactometer conjointly.

Very many conditions, however, affect the specific gravity of milk. When it is freshly drawn from the cow not only is it warm, but as a rule it contains a considerable quantity of air in

solution, so that its specific gravity is lower at the instant of drawing than four or five hours later.

Allowing for this source of error, there is a very definite relationship between the specific gravity and the chemical contents of the milk. Qualitatively, an increase in the fat or cream lessens the specific gravity, whilst an increase in the solids not fat renders the specific gravity higher.

Quantitatively this variation of the specific gravity has been used to check the accuracy or analysis, and also to give a rapid and fairly accurate estimate of the percentage of fat.

It will be seen from the later paragraphs in this chapter that the estimation of fat is the most difficult operation in the commercial analysis of milk; if, therefore, the exceedingly simple operations of estimating the total solids (paragraph 303) and the specific gravity will give a correct idea of the percentage of fat, much work may be saved.

Richmond's formula is as follows:

$$F = 0{\cdot}859T - 0{\cdot}2186G,$$

where F represents the percentage of fat, T the percentage of total solids, and G is the lactometer degree (*i.e.*, the number by which the specific gravity of the milk exceeds that of water (water = 1·000).

This formula is based on the fact, first worked out by Clausnizer and Mayer, that every addition of 1 per cent. of fat decreases the specific gravity of milk by ·001, whilst every addition of 1 per cent. of solids not fat increases the specific gravity by ·00375.

303. **Total Solids.**—Measure out accurately into a weighed platinum dish 25 c.c. of milk which has been well shaken up; add two drops of strong acetic acid, and evaporate to dryness on the water bath. Transfer to the steam oven, and

heat until the weight is constant. The final weight, minus the weight of the dish, gives the weight of total solids.

The acetic acid added curdles the milk, and prevents the formation of a scum which would retard the evaporation.

Fat.—This is the most important determination, and several methods are in use. The first of these is the most reliable.

304. **Adams Process.**—A known weight of milk is absorbed by a roll of filter paper. The paper is then dried and extracted with ether.

This method is the standard one in use by most analysts.

The roll of filter paper is prepared as follows : Cut a strip of white filter paper 22½ inches long and 2½ inches wide. Place it on a table, and lay along its surface a piece of string with one end just reaching to the end of the strip and the other end projecting about 6 inches beyond the paper. Now roll paper and string into a coil. The string will prevent the successive coils from touching one another. Tie the free end round the coil, so as to keep the paper permanently in position.

305. **Purification of the Paper.**—Fat-free paper may be purchased, but ordinary paper may be rendered practically free by extraction for 1½ hour in the Soxhlet apparatus. If many determinations be required, it is best to soak a number of the strips in several changes of rectified spirit containing 10 per cent. glacial acetic acid. The paper should stand at least two hours in this solution.

306. **The Determination.**—Suspend the roll of paper from a glass rod by means of the free end of the string. Shake up the sample of milk, and draw off 5 c.c. with a pipette. Allow it to run from the end of the pipette on to the roll, which will completely absorb it. Suspend the roll in the steam oven for about an hour to dry; then place it in the Soxhlet

apparatus (fig. 38), and extract with ether for 1½ hour. Transfer the fat to a beaker, and weigh exactly as described in paragraph 142.

307. **Rapid Methods.**—Of late years several forms of apparatus have been introduced which estimate the amount of fat in milk both rapidly and accurately. These may be divided into three classes, 'the gravimetric,' the 'areometric,' and the 'centrifugal.' In the areometric and gravimetric methods a certain quantity of ether is mixed with a certain quantity of milk, and then allowed to separate. The percentage of fat is deduced either from the specific gravity of the ether, or by evaporating an aliquot portion of the ether and weighing. In the centrifugal methods the milk is first acted upon by some reagent which will dissolve the casein, then the fat is separated by centrifugal force. One form of each of these three methods is given below.

The Werner Schmidt Method

In this method the casein, &c., are dissolved by boiling with hydrochloric acid. This leaves a brown solution from which the fat may be easily extracted by shaking with ether. The percentage of fat in the ether is estimated by evaporating a portion and weighing the dry residue.

308. **The Process.**—A Werner Schmidt tube is a stoppered test tube of 70 or 80 c.c. capacity; it has a mark to indicate when it contains 10 c.c. of liquid and another to indicate 20 c.c. Above the 20-c.c. mark are accurate graduations for every 0·1 c.c. up to 50 c.c.

Ten c.c. of the well mixed milk is poured into this tube, then 10 c.c. of strong hydrochloric acid is added. The mixture is well shaken, then boiled for a few minutes over a Bunsen. The liquid will then be clear but deep brown.

Some analysts prefer to heat the tube in a water bath, but this is a slow process, and as the only object of this method is to obtain a rapid result with fair accuracy, it is best to proceed as quickly as possible.

When the liquid is quite free from clots it is cooled down, and the tube filled up to the 50-c.c. mark with ether. The tube is corked up, well shaken, and allowed to stand until the ethereal layer has completely separated.

Ten c.c. of this ethereal extract is measured off into a weighed dish, evaporated to dryness, and weighed. The result, after subtracting the weight of the dish, will be one-fifth of the weight of fat in 10 c.c. of milk. Knowing the specific gravity of the milk, it is easy to calculate the percentage of fat.

Soxhlet's Areometric Method

309. **Apparatus.**—The apparatus, which is shown in fig. 46, consists of a bottle in which the solution of the fat takes place, and a tube surrounded by a water jacket and enclosing a delicate hydrometer giving specific gravities from ·743 to ·766. Attached to the hydrometer is a thermometer. The bottle may be connected with the water-jacketed tube by inserting an india-rubber stopper through which pass two tubes arranged as for a wash bottle, the delivery tube being attached to the apparatus whilst the blowing tube has an india-rubber blower fixed to it. This apparatus is complete for one determination. Should a large number be required in rapid succession, a large number of bottles will be required.

310. **The Operation.**—Measure out 200 c.c. of milk into one of the bottles; add 10 c.c. of caustic potash solution (the solution used for expelling ammonia after heating with H_2SO_4 in the acid process of nitrogen estimation, paragraph 91, may be used) and 60 c.c. of ether. The ether must be

TABLE FOR SOXHLET'S AREOMETRIC METHOD OF MILK FAT ESTIMATION.

Specific gravity	Fat per cent.	Specific gravity	Fat per cent.	Specific gravity	Fat per cent.	Specific gravity	Fat per cent.
43	2·07	45·9	2·39	48·8	2·74	51·7	3·09
43·1	2·08	46	2·40	48·9	2·75	51·8	3·10
43·2	2·09	46·1	2·42	49	2·76	51·9	3·11
43·3	2·10	46·2	2·43	49·1	2·77	52	3·12
43·4	2·11	46·3	2·44	49·2	2·78	52·1	3·14
43·5	2·12	46·4	2·45	49·3	2·79	52·2	3·15
43·6	2·13	46·5	2·46	49·4	2·80	52·3	3·16
43·7	2·14	46·6	2·47	49·5	2·81	52·4	3·17
43·8	2·16	46·7	2·49	49·6	2·83	52·5	3·18
43·9	2·17	46·8	2·50	49·7	2·84	52·6	3·20
44	2·18	46·9	2·51	49·8	2·86	52·7	3·21
44·1	2·19	47	2·52	49·9	2·87	52·8	3·22
44·2	2·20	47·1	2·54	50	2·88	52·9	3·23
44·3	2·22	47·2	2·55	50·1	2·90	53	3·25
44·4	2·23	47·3	2·56	50·2	2·91	53·1	3·26
44·5	2·24	47·4	2·57	50·3	2·92	53·2	3·27
44·6	2·25	47·5	2·58	50·4	2·93	53·3	3·28
44·7	2·26	47·6	2·60	50·5	2·94	53·4	3·29
44·8	2·27	47·7	2·61	50·6	2·96	53·5	3·30
44·9	2·28	47·8	2·62	50·7	2·97	53·6	3·31
45	2·30	47·9	2·63	50·8	2·98	53·7	3·33
45·1	2·31	48	2·64	50·9	2·99	53·8	3·34
45·2	2·32	48·1	2·66	51	3·00	53·9	3·35
45·3	2·33	48·2	2·67	51·1	3·01	54	3·37
45·4	2·34	48·3	2·68	51·2	3·03	54·1	3·38
45·5	2·35	48·4	2·70	51·3	3·04	54·2	3·39
45·6	2·36	48·5	2·71	51·4	3·05	54·3	3·40
45·7	2·37	48·6	2·72	51·5	3·06	54·4	3·41
45·8	2·38	48·7	2·73	51·6	3·08	54·5	3·43

TABLE FOR SOXHLET'S AREOMETRIC METHOD OF MILK FAT ESTIMATION—*continued.*

Specific gravity	Fat per cent.	Specific gravity	Fat per cent.	Specific gravity	Fat per cent.	Specific gravity	Fat per cent.
54·6	3·45	57·5	3·82	60·4	4·23	63·3	4·67
54·7	3·46	57·6	3·84	60·5	4·24	63·4	4·69
54·8	3·47	57·7	3·85	60·6	4·26	63·5	4·70
54·9	3·48	57·8	3·87	60·7	4·27	63·6	4·71
55	3·49	57·9	3·88	60·8	4·29	63·7	4·73
55·1	3·51	58	3·90	60·9	4·30	63·8	4·75
55·2	3·52	58·1	3·91	61	4·32	63·9	4·77
55·3	3·53	58·2	3·92	61·1	4·33	64	4·79
55·4	3·55	58·3	3·93	61·2	4·35	64·1	4·80
55·5	3·56	58·4	3·95	61·3	4·36	64·2	4·82
55·6	3·57	58·5	3·96	61·4	4·37	64·3	4·84
55·7	3·59	58·6	3·98	61·5	4·39	64·4	4·85
55·8	3·60	58·7	3·99	61·6	4·40	64·5	4·87
55·9	3·61	58·8	4·01	61·7	4·42	64·6	4·88
56	3·63	58·9	4·02	61·8	4·44	64·7	4·90
56·1	3·64	59	4·03	61·9	4·46	64·8	4·92
56·2	3·65	59·1	4·04	62	4·47	64·9	4·93
56·3	3·67	59·2	4·06	62·1	4·48	65	4·95
56·4	3·68	59·3	4·07	62·2	4·50	65·1	4·97
56·5	3·69	59·4	4·09	62·3	4·52	65·2	4·98
56·6	3·71	59·5	4·11	62·4	4·53	65·3	5·00
56·7	3·72	59·6	4·12	62·5	4·55	65·4	5·02
56·8	3·73	59·7	4·14	62·6	4·56	65·5	5·04
56·9	3·74	59·8	4·15	62·7	4·58	65·6	5·05
57	3·75	59·9	4·16	62·8	4·59	65·7	5·07
57·1	3·76	60	4·18	62·9	4·61	65·8	5·09
57·2	3·78	60·1	4·19	63	4·63	65·9	5·11
57·3	3·80	60·2	4·20	63·1	4·64	66	5·12
57·4	3·81	60·3	4·21	63·2	4·66		

saturated with water by shaking up equal quantities of ether and water in a Winchester and allowing to stand over night. A stopper is placed in the bottle, and it is shaken vigorously for half-a-minute, then it is placed in a vessel of water kept at a temperature of between 17° and 18° C., shaking gently from time to time. The ethereal solution of fat will rise to the

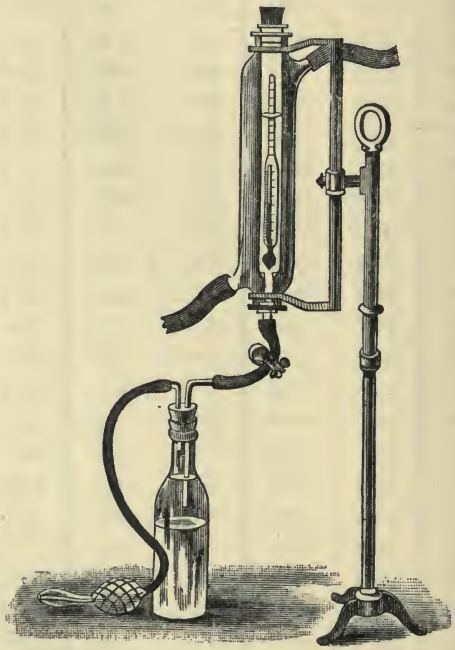

FIG. 46.

surface. When the bottle, with its contents, has attained the temperature of the water, the stopper is removed, and the india-rubber stopper shown in the figure is introduced. The longer glass tube is adjusted so that it terminates inside the ether layer. By opening the clip and gently pressing the blowing bulb, the ethereal solution is passed up into the water-

jacketed tube, which is surrounded by water at from 17° to 18° C. Here it rises until the hydrometer floats. The clip is now tightened up, and the graduation where the lower surface of the meniscus crosses the stem of the hydrometer is read off. The temperature is also taken.

311. **Calculation.**—Very frequently the graduation on the hydrometer omits the first decimal place, which is always 7. Thus the numbers would be set down from 43 to 66, meaning from ·743 to ·766. If the temperature be exactly 17·5, then the percentage of fat may be read off by reference to the table. Should the temperature be different, a correction must be applied. This is done by adding or subtracting the number of degrees above or below 17·5 from the *third* place of decimals in the specific gravity. (This is the unit place in the graduation.) Thus, supposing that the reading of the hydrometer is 53·5, and the temperature 19·2, the difference of the temperature from 17·5 is 1·7, and the specific gravity of the solution is ·7535. If we add on the number of degrees difference to the third place of decimals, we get ·7552 ; or if we add it to the units place of the graduation, we get 55·2 ; and on reference to our table we find that this represents 3·52 per cent. of fat (for table see pages 184 and 185).

Babcock's Centrifugal Method.

312. **Apparatus.**—The special apparatus required for this method is, firstly, a centrifugal machine, and, secondly, separating bottles. The machines in use are very various in structure, but the most common form is shown in fig. 47. The one thing essential to the proper working of the method is that the bottles may be whirled round at a rate of not less than 600 revolutions per minute. Any machine which will do this may be used. The bottles are made to hold 40 to 45 c.c. of milk, and the

necks are long and graduated, each division representing ·04 c.c.

313. **The Operation.**—Measure out 18 c.c. of milk into one of the bottles, and add 17·5 c.c. of sulphuric acid (S.G. 1·82). The liquid will become hot and dark in colour. Place the bottle in the machine, and turn it at as high a speed as possible for six or seven minutes. It is best to whirl the bottles directly after adding the acid, otherwise they may cool down and require

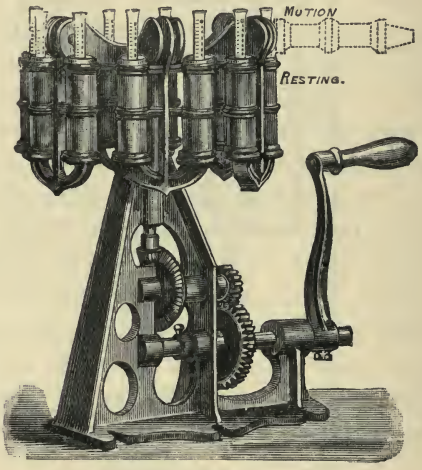

FIG. 47.

heating again to get the fat in a liquid condition. As soon as the bottles have been sufficiently whirled, fill them up to the base of the neck with hot water. Whirl them again for about two minutes, add more hot water to the top of the graduations, and whirl for a minute more. Stand the bottles upright in water kept at 55° C. for a few minutes, and read off the volume of fat.

314. **Calculation.**—Each division of ·04 c.c. is equal to ·2 per cent. of fat if exactly 18 c.c. of milk be used and the

temperature be 55° C. At this temperature the specific gravity of fat is ·9.

A small correction should be made for the specific gravity of the milk, but it is customary, when testing milk, to have a pipette graduated to hold exactly 18 c.c. of milk of normal density—viz., 1·03.

315. *Remarks on the Results of Milk Analysis.*—The two methods used in tampering with milk are the addition of water and the removal of cream. In calculating the extent to which either of these operations has been carried on, the analyst assumes the milk to be of the lowest probable quality before adulteration, and states his results calculated on this assumption as 'minimum' adulteration. The minimum standard for pure milk is generally agreed upon as 9 per cent. 'solids not fat' and 3 per cent. fat, though the 'Somerset House' standard is rather lower.[1] To calculate *added water*, let a be the percentage of solids not fat. Then the percentage of added water will be *at least*

$$100 - \frac{100a}{9}.$$

To calculate the percentage of fat removed from milk which has been skimmed, let a be the percentage of solids not fat and b the percentage of fat; then the *minimum* amount of fat removed from 100 parts of the original milk

$$= \frac{3a}{9} - b \text{ parts.}$$

[1] The introduction of the 'Adams' process gave rather higher percentages of fat than had been obtained before. Hence the percentage of 'solids not fat' became lower. The 'Somerset House' analysts apparently accept the lowered value of 8·5 instead of 9·0 for the 'solids not fat.'

BUTTER ANALYSIS

In the ordinary commercial analysis of butter, estimations are made of *water*, *fat*, *curd*, and *salt*, though as a rule the fat is estimated by difference. When the presence of foreign fat—*i.e.*, fat not derived from milk—is suspected, the fat undergoes further manipulation.

316. **Water.**—Five grams are weighed out in a flat porcelain dish of the same shape and size as that used for the determination of 'total solids' in milk. The dish is placed in a steam oven until all the globules of water which gather beneath the fat on melting have disappeared. The dish is then re-weighed. The loss is taken as water.

317. A *rapid method* which, in skilful hands, gives good results is performed by placing the dish with the weighed quantity on a sand bath, and stirring constantly with a short glass rod which has been weighed with the dish. By holding a perfectly clean polished watch glass over the hot fat from time to time, it can be seen whether steam is rising from the dish, as steam will dim the surface of the glass. The operation only takes a very few minutes.

318. **Curd.**—Mix the dry fat from the last operation with about 10 c.c. of ether. Filter the liquid so formed either through a weighed filter or, better, through counterpoised filters, such as are used in the determination of potassium described in paragraph 34.

Wash the filter and its contents with ether until, on evaporating a drop of the filtrate, no residue is left. Dry the filter in a water bath, and weigh. The weight gives curd plus ash.

319. **Ash.**—Transfer the filter paper containing the curd and ash to a weighed platinum dish and ignite over an Argand at the temperature used in the determination of $CaCO_3$ (see

paragraph 45). When the ash is quite white, weigh the dish again. By subtracting the weight of ash from the weight of curd plus ash obtained in the last experiment, the weight of curd is found. Of course it must be remembered that the weight of the ash from the filter has to be subtracted from the total ash.

Generally speaking, almost the whole of the ash is salt. This may, however, be determined by dissolving in water and estimating the chlorine with standard $AgNO_3$ solution, as described in paragraph 69.

320. Enter the results as follows:

—	I	II	III
Water . . .	10·15	9·53	11·2
Curd . . .	·65	·47	3·1
*Ash . . .	1·97	2·16	2·0
Fat	87·23	87·84	83·7
	100·00	100·00	100·0
*Containing salt .	1·61	1·93	Not determined

Estimation of Foreign Fats in Butter

321. **Butter Fat.**—All pure fats are compounds of the trihydric alcohol glycerin with monobasic organic acids. As glycerin is always present, the identification of any fat depends on the identification of the acid which it contains. Unfortunately for the analyst, there are very many of these so-called 'fatty' acids which resemble one another so closely as to make their separation a matter of great difficulty. Another difficulty arises from the fact that *pure* fats are seldom or never found in nature. In the investigation, therefore, of such natural fats as 'butter fat' or 'margarine,' experiments must be made on the mixed compounds of glycerin and a number of fatty acids.

Milk fat differs from all other natural fats in that it contains a considerable percentage of the so-called 'lower' fatty acids—*i.e.*, acids having a comparatively small molecular weight. Many of these *lower* acids are volatile at the temperature of boiling water, and are soluble in water.

These three properties—*i.e.*, low molecular weight, volatility in steam, and solubility in water—are used for the detection and estimation of those fats peculiar to butter.

322. **Koettstorfer's Method.**—The molecular weight of any acid may be determined by weighing the quantity which will combine with 56 grams of KHO. As it would be unscientific and inconvenient to speak of the average molecular weight of the fatty acids in butter, it is usual to express this peculiar property as a *Koettstorfer number*, which is the number of milligrams of KHO which are neutralised by the fatty acids in 1 gram of butter fat. In this method a weighed quantity of butter fat is heated with an excess of standard alcoholic potash. After the reaction is complete, the excess of potash is estimated by means of standard hydrochloric acid.

The solutions required are seminormal hydrochloric acid, which may be prepared by one of the methods given in Part II., and alcoholic potassium hydrate.

Alcoholic Caustic Potash. Thirty-two grams of caustic potash are weighed out roughly and dissolved in a litre of strong alcohol. This solution, if made from methylated spirit, very rapidly discolours and alters in strength. Students are advised to make up only small quantities as they may be required. In laboratories where large numbers of butter samples are analysed the alcohol is specially prepared. Fifty grams of potash are dissolved in a 'Winchester' of methylated spirit and left to stand for at least a week. The spirit is then distilled. After this treatment it may be used for making solutions of caustic alkalis, which will only alter very slowly.

Melt up about 10 grams of butter in a beaker and filter it. The easiest way of doing this is to place a filter funnel with a short stem in the mouth of a 4-oz. conical flask, place a paper in the funnel, and keep the whole arrangement in a steam oven whilst the filtration proceeds. The fat is thus kept fused, so that it runs through the filter, leaving the curd, salt, and moisture behind.

Weigh out accurately about 2 grams of the butter fat thus prepared in an 8-oz. flask of the shape shown in fig. 11. Add exactly 25 c.c. of the alcoholic potassium hydrate, and warm on a water bath, shaking occasionally until saponification is complete. Oily drops will remain on the surface of the liquid until the reaction is ended. Whilst this is going on, measure out another 25 c.c. of the alcoholic potash into a clean flask. Add a drop of phenol-phthalein solution and titrate with the seminormal acid.

When the butter fat is completely dissolved, add a drop of phenol-phthalein and run in the seminormal acid until the red colour just disappears. Less acid will be required in this case, as some of the potash will have been neutralised by the 'fatty acids.'

323. **Calculation.**—From the first titration one can calculate the weight of potash in each c.c. of the alcoholic potash solution. By subtracting the volume of acid required after heating with butter fat from the volume required for the 25 c.c. of original alcoholic potash, we may calculate the quantity of alkali used by the butter. Knowing the weight of butter fat used in the experiment, it is easy to find the number of milligrams of potash required by each gram of butter. A concrete example will make this plain:

Weight of butter fat = 2·193;

25 c.c. alcoholic KHO required 22·1 $\frac{N}{2}$ HCl;

25 c.c. alcoholic KHO after saponification required

$$4{\cdot}2 \frac{N}{2} HCl;$$

1 c.c. $\frac{N}{2}$ HCl neutralises ·028 gram KHO;

$\therefore$ Amount of alkali used $= (22{\cdot}1 - 4{\cdot}2) \times {\cdot}028$

$= 17{\cdot}9 \times 28 = 501{\cdot}2$ milligrams.

This divided by weight of fat $= \frac{501{\cdot}2}{2{\cdot}193} = 228{\cdot}1$.

The Koettstorfer number for pure butter fat varies from 221·5 to 233, averaging 227·25. The number given by oleomargarine is about 195·5. In the example just quoted, the material was pure butter fat. Had the number fallen below 222 or 223, it would have been viewed with suspicion, whilst had it fallen below 221·5 it would certainly have been adulterated.

An approximate idea of the percentage of foreign fat may be obtained from the formula:

$$(227{\cdot}25 - n) \times 3{\cdot}17,$$

where n is the Koettstorfer number found by experiment.

Should the number indicate that the butter has been adulterated, it is advisable to use one of the more definte methods described below.

324. **Hehner's Process.**—Weigh out about 4 grams of the butter fat so obtained in a tared 8-oz. conical flask; add 10 c.c. of saturated alcoholic potash. Heat gently on the water bath, shaking from time to time, until the whole of the fat has turned into a soap. The end of the reaction is easily seen from the fact that the unsaponified fat floats as a yellow oily drop on the surface of the liquid. This drop gradually diminishes, and finally disappears. When the saponification is complete, dilute with 50 c.c of water and allow the alcohol *entirely* to

evaporate on the water bath. Now pour the contents of the flask into a separating funnel (preferably made of thin glass, see fig. 48). Wash the flask well with hot water, and add the washings. Whilst the liquid in the separating funnel is still hot, add hot dilute hydrochloric acid (1–3) until the liquid is acid. Shake well, and allow to stand over night. This will separate all the fatty acids, which will collect in a wax-like film above the water. This long standing is necessary to allow the complete separation of the insoluble acids, which, when once thoroughly collected on the surface of the water, give no trouble in the subsequent washings. When the separation has taken place, shake the apparatus to detach the film from the walls of the bulb, and run off the liquid by means of the stopcock below. Now pour about 50 c.c. of boiling water into the bulb, and shake to wash the fatty acids. They will melt and rapidly collect on the surface of the water, which will be left perfectly clear, and may be run off. This washing must be repeated several times until the whole of the washing liquid, together with the original acid liquor, measures 300 c.c. In the final washing run off the water as completely as possible, then run the acids into a tared shallow dish. Wash out the acids which adhere to the funnel with a little ether. Place the dish, with its contents, in the water bath, and heat until it ceases to lose weight.

Fig. 48.

325. **Calculation.**—All animal fats contain about 95·5 per cent. of insoluble fatty acids. Butter fat contains on the average 87·5 per cent. It is, therefore, easy to calculate the approximate percentage of foreign fat in a sample of butter by the formula

$$x = 12{\cdot}5\ (a - 87{\cdot}5),$$

where x = percentage of foreign fat and a = percentage of insoluble fatty acids found.

The working out of this formula is as follows :

The difference between the percentage of these acids in butter fat and in animal fat is $95{\cdot}5 - 87{\cdot}5 = 8$.

It is, therefore, on this 8 per cent. that we must base our calculation.

If an excess of 8 % (over 87·5 %) means 100 % foreign fat,
then ,, ,, 1 % ,, ,, $\frac{100}{8}$ % ,,
$\therefore$,, ,, N % ,, ,, $\frac{100\,N}{8}$ % ,,

Supposing that we have found a per cent. insoluble fatty acids ; then

$$N = (a - 87{\cdot}5),$$

$\therefore$ the percentage of foreign fat present $= \frac{100(a - 87{\cdot}5)}{8}$,

which equals $12{\cdot}5\ (a - 87{\cdot}5)$.

326. **Reichert Meisl Method.**—It was stated in paragraph 321 that butter fat differed from most other natural fats, in that it contained a certain quantity of *volatile* fatty acids. This quantity is usually stated as *the number of c.c. of decinormal alkali* (barium hydrate) *required to neutralise the volatile acids in* 5 *grams of fat.* The fat is first saponified by heating with a solution of soda in glycerin, then the acids are set free by dilute sulphuric acid, and the volatile portion is distilled off. The acidity of the distillate is estimated by means of standard barium hydrate. The solutions required are :

Caustic Soda Solution. Fifty grams of caustic soda is dissolved in a small quantity of water and the solution diluted to 100 c.c. It is then mixed with 500 grams of pure glycerin.

Dilute Sulphuric Acid. The ordinary dilute sulphuric acid must be diluted until 5 c.c. just neutralises 2 c.c. of the glycerin-caustic-soda solution.

Decinormal Baryta Solution. This must be prepared by dissolving about 18 grams $Ba(OH)_2$ in a litre of water, and standardising with decinormal sulphuric acid as described in paragraph 64.

327. **The Process.**—Five grams of the butter fat is weighed in an 8-oz. conical flask; 10 c.c. of the glycerin solution is added, and the mixture is heated on a wire gauze until it ceases frothing, and the solution becomes clear. It is then allowed to cool, and 5 c.c. of freshly boiled distilled water is added. When solution is complete, 50 c.c. of the sulphuric acid is poured in, and the flask at once attached to a condenser. It is as well to place a piece of pumice or a piece of clay pipe-stem in the liquid, as it is apt to 'bump' during the distillation. The flask is now heated until 110 c.c. of the distillate has been collected. This must be filtered through a dry filter paper into a 100-c.c. flask.

The 100 c.c. thus collected is titrated with the decinormal baryta.

328. **Calculation.**—Add one tenth to the number of c.c of baryta used. If exactly 5 grams of fat has been weighed out, at least 26 c.c. of baryta should be required. Other fats give very small quantities of volatile acid, using about half a c.c. of decinormal baryta. This method is therefore the most useful and definite one when the percentage of foreign fat is to be determined.

Remarks on the Results of Butter Analysis.—The water in butter should not exceed 12 per cent. The curd and salt together should be less than 8 per cent. The curd should not exceed 4 per cent.

The keeping power of a butter depends on several circumstances, such as its general condition, but a butter containing large quantities of nitrogenous matter (curd) will turn rancid

sooner, all other conditions being equal, than one containing smaller quantities.

The fat should not fall below 80 per cent.

CHEESE ANALYSIS

The determinations ordinarily made in cheese analysis are *water*, *fat*, *casein* (*nitrogenous matter*), and *ash*.

329. **Water.**—Grate a piece a cheese on a bread grater until a sufficient quantity of gratings has been collected, then weigh out 5 grams of the material in a dish, and heat in the steam oven until no further loss takes place. Loss of weight = moisture.

330. **Fat.**—This is estimated in Soxhlet's apparatus as shown in fig. 38 and described in paragraph 140, but the special precaution is necessary that the cheese must be *quite dry*. The best method is to use the portion in which the moisture has been determined, removing it completely from the drying dish to a cartridge case of filter paper, and extracting as usual.

331. **Casein.**—Usually estimated by difference. Should a direct determination be necessary, it may be made by estimating the nitrogen by the acid process (paragraphs 92–95) in about half a gram of the cheese, and multiplying the percentage of nitrogen by 6·25.

332. **Ash** may most easily be determined in the portion which has been extracted, or 5 grams may be weighed into a platinum dish, and burned over an Argand at as low a temperature as possible.

The salt may be determined by dissolving the ash and titrating with decinormal $AgNO_3$.

The phosphates may be determined by the method described in paragraph 246.

333. **Adulteration of Cheese.**—Margarine is frequently

added to cheese made from poor milk. This may be determined by examining a portion of the fat in the manner described for the determination of foreign fats in butter.

Cheese is occasionally coloured with chromate of lead or salts of copper. These may be tested for in the ash by any qualitative method.

PART IX

WATER ANALYSIS

334. It is not very often that the agricultural analyst is called upon to analyse water. In this chapter, therefore, only that part of water analysis which is most useful is described. For information on such subjects as the analysis of gases contained in water, and the combustion method of analysing the solid matters, students are referred to larger text books.

335. In the statement of results two methods are at present in vogue. Some chemists state the number of grains of each substance contained in a gallon of water, considering a gallon of water to weigh 70,000 grains. Others state their results in parts per 100,000 of the water. In this chapter all results are worked out in grains per gallon. Parts per 100,000 may be calculated by dividing the grains per gallon by ·7.

ANALYSIS OF WATER FOR DRINKING PURPOSES

336. Before proceeding to the analysis proper, notes should be taken as to the colour, taste, and smell of the water.

The *colour* is best seen by filling a tall narrow glass cylinder, free from colour, with the water, placing it on a white tile, and looking down through it.

The *taste* and *smell* are best noted when the sample is slightly warmed.

337. **Estimation of Suspended Matter.** — This operation is unnecessary unless the water be distinctly turbid.

Wash a 6-inch disc of filter paper with distilled water free from ammonia. When about 2 litres has passed through, test the last portion for ammonia by Nessler's test (see page 203). If the water has ceased to dissolve ammonia, dry the paper in the air oven at 100° C. until it is of constant weight.

Shake up the sample of water, measure out 2 litres, and filter through the prepared paper. Collect the filtrate in a clean bottle (Winchester quart). Next wash thoroughly with distilled water, rejecting the washings, and dry in the air bath, as before, until it ceases to lose weight. The weight of suspended matter in 2 litres of the water is thus found. Calculate this into grains per gallon.

Next, cutting up the filter, place in a weighed platinum dish, and ignite over an Argand until all carbonaceous matter is driven off. Cool in a desiccator, and weigh. On subtracting the weight of the dish and the filter ash, we obtain the weight of inorganic suspended matter in 2 litres of the water.

338. **Microscopic Examination.**—In cases where suspended matter is present it is usual to make a microscopic examination. In this case a quantity of the water is left in a tall cylinder, and the undissolved matter allowed to settle. The supernatant water is carefully poured off, and the mud at the bottom placed on a slip of glass and examined by the microscope. For information as to the microscopic appearance of sediments, see Hassal's 'Food and its Adulterations.'

339. **Total Solids in Solution.**—Should the water have been filtered, this estimation is made in the filtered portion.

Measure out 500 c.c. of the water in a graduated flask, and fill an accurately tared platinum evaporating basin about half full of water from the flask. The water may be evaporated over a water bath, or, better, over a rose burner protected by

a lamp screen, as shown in fig. 49. The burner must be turned down as low as possible. The water will then evaporate slowly and without ebullition. As it evaporates it must be filled from time to time until the whole 500 c.c. has been placed in the basin. The evaporation is now carried on until only about 20 c.c. is left in the dish. Then remove the dish to a water bath until apparently dry. When no further evaporation takes place, heat in the air bath at 110° C. until its weight is constant. The residue, after weighing, must be saved for the nitrate estimation.

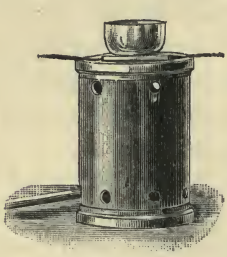

FIG. 49.

340. **Estimation of Nitrogenous Matter.**—The nitrogen present in water may be in one or both of two forms known respectively as 'free ammonia' and 'albuminoid ammonia'—the free ammonia being either ammonia or ammoniacal salts, and the albuminoid ammonia being obtained from the organic nitrogen.

For the estimation of these two constituents the following solutions are necessary:

Nessler's Solution. Dissolve 16·5 grams of potassic iodide and 6·5 grams of mercuric chloride in 400 c.c. of ammonia-free water. Boil and stir until all is dissolved. Now add cold saturated solution of mercuric chloride until the precipitate of mercuric iodide just becomes permanent. Now add 80 grams of caustic potash or 60 grams of caustic soda, allow to cool, and dilute to 500 c.c. Finally, to ensure sensitiveness, add a few more drops of mercuric chloride solution, and allow the precipitate to settle. This solution is kept in a well-stoppered bottle. A little should be decanted off for immediate use into an 8-oz. bottle fitted with a perforated cork through which passes a pipette with 1 or 2 c.c. marks on it.

Alkaline Permanganate Solution. Boil together in a large basin 200 grams of caustic potash, 8 grams of potassic permanganate, and a litre of water until the solids are completely dissolved. This should be kept in a well-stoppered Winchester quart bottle.

Standard Ammonium Chloride Solutions. Two solutions are usually prepared, one ten times as strong as the other. Dissolve ·117 (really ·11688) gram of pure crystallised NH_4Cl in a little water, and make up to 500 c.c. with ammonia-free water. Label the bottle containing this 'Strong NH_4Cl solution.' One c.c. will contain ·000074 gram of NH_3, or, when the ammonia is estimated in 500 c.c. of water, 1 c.c. = ·01 grain of NH_3 per gallon. For the 'weak solution' take 50 c.c. of this strong one, and dilute to 500 c.c. The NH_4Cl should be tested by estimating the nitrogen therein.

Water Free from Ammonia. It may happen that the ordinary distilled water supplied in the laboratory is free from ammonia. This may be tested by nearly filling a testing cylinder with the water, adding 2 c.c. of Nessler's solution, and stirring. If, after standing for five minutes, no yellow colouration appears in the water, it is sufficiently pure for use. Should the slightest pink, brown, or yellow appear, the water must be re-distilled as follows :

Place as much of the water as can conveniently be boiled in a large flask. Add about a gram of recently ignited soda crystals. Connect with a condenser, and distil. Test 20 c.c, of the distillate from time to time for ammonia. As soon as no further ammonia comes over, collect the water in a clean Winchester and keep it very carefully stoppered. In this operation it is very necessary to use *soda crystals*, as the bicarbonate always contains ammonia, often in considerable quantities.

341. **Free Ammonia.**—Place 50 c.c. of the water

under examination in a cylinder of clear glass standing on a white tile, and add 2 c.c. of Nessler's solution. Allow it to stand five minutes. Meanwhile, place in another similar cylinder 50 c.c. of ammonia-free water. Add from a burette ·1 c.c. of 'dilute' NH_4Cl solution, and treat with Nessler as before. Should the colouration in the two cylinders be about the same, 500 c.c. of water must be used for the determination. Should it be darker in the first cylinder, less must be used.

Fit up a flask and Liebig's condenser of the form ordinarily used for distilling. The condenser is usually made with a glass inner tube. In many laboratories a block tin tube is preferred on account of the superior conductivity of the metal, which allows of a much shorter condenser being used, and thus economises space. Pour into the flask about 250 c.c. of ammonia-free water, and add a gram of freshly ignited soda crystals. Distil for a few minutes to wash the apparatus, testing the distillate a little at a time with Nessler's solution, until it is quite free from ammonia. Now pour 500 c.c. of the water undergoing analysis into the flask, and distil, collecting the distillate in a cylinder. When 50 c.c has collected, change the cylinder for a fresh one, and estimate the ammonia in the 50 c.c. of distillate as follows : Add 2 c.c. of Nessler's solution, and place on a white tile. Now make a comparison cylinder by running ·2 c.c. of 'weak' NH_4Cl from a burette into 50 c.c. of ammonia-free water in a clean cylinder. Add 2 c.c. of Nessler, and stir. Place the two cylinders side by side, and compare. Should the comparison cylinder show the fainter colour, a fresh one must be made, using rather more NH_4Cl. On no account must a further amount of NH_4Cl be run into the liquid containing Nessler's solution. By making up several comparison cylinders one will be found of the same tint as the distillate. The amount of NH_4Cl solution in this is noted, as the two cylinders will then contain equal quantities of ammonia.

By the time this test is finished another 50 c.c. will have distilled over. The ammonia in this must be estimated in the same way. The third 50 c.c. will probably contain no ammonia. If it should, it must be estimated, and all the results added together.

342. **Albuminoid Ammonia.**—The solution of 'aikaline permanganate' whose preparation was described in paragraph 340 will act on organic matter, liberating the nitrogen, mostly in the form of ammonia. This ammonia is known as 'albuminoid ammonia.'

To the liquid left in the flask after the last operation add 50 c.c. of the alkaline permanganate; distil, and estimate the ammonia in each 50 c.c. of the distillate, exactly as in paragraph 341, until it ceases passing over. When the water is being distilled with alkaline permanganate it shows a great tendency to 'bump.' This can be lessened by putting a few pieces of clean platinum wire in the flask.

343. **Estimation of Oxygen consumed by Organic Matter.**—In the absence of nitrites, sulphuretted hydrogen, or other inorganic reducing agents, a very good idea of the amount of organic matter in the water may be obtained by the action of a standard solution of potassium permanganate on the acidified water.

Permanganate Solution. Weigh out accurately ·395 gram of pure permanganate of potash; dissolve in water, and make up to a litre. Each c.c. of this solution will contain ·0001 gram of available oxygen, or, as is very frequently assumed in stating results, 1 c.c. of the solution corresponds to ·0008 gram of organic matter.

Sodium Thiosulphate Solution. Dissolve 10 grams of sodium thiosulphate in a litre of water. This solution alters in strength when it is kept for some time, but as it is standardised whenever it is used, the alteration is of no consequence. For

each determination, 10 c.c. of the stock solution is diluted to 100 c.c.

Sulphuric Acid. Mix 50 c.c. strong H_2SO_4 with 150 c.c. water. When cool, add a drop or two of the standard permanganate solution. If, on standing for a few minutes, the acid does not remain pink, add a few more drops until the acid has a faint permanent colour.

344. **The Estimation.**—Carefully clean two 16-oz. flasks and measure into one of them 250 c.c. of the water undergoing analysis. Into the other measure 250 c.c. distilled water. In each place 10 c.c. permanganate solution and 10 c.c. sulphuric acid (prepared as in paragraph 343). Allow them to stand for four hours at 80° F.

After this time add to each a few drops of a saturated solution of potassium iodide, and a drop of starch solution ; run in the dilute sodium thiosulphate solution from a burette until the blue colour entirely disappears.

345. **Calculation.**—The volume of permanganate solution used must be calculated from the difference between the volume of thiosulphate used by the distilled water, and that used by the sample—*i.e.*, $\frac{x-y}{x}$ = volume of permanganate used, where x is the number of c.c. of thiosulphate used by the distilled water and y the number used by the sample.

The weight of oxygen for 70,000 parts is therefore

$$\frac{x-y}{x} \times \frac{\cdot001 \times 70{,}000}{250}$$

$$= \frac{(x-y)\,0{\cdot}28}{x} \text{ grains per gallon.}$$

346. **Estimation of Hardness.**—The hardness of water may be defined as its soap-destroying power, and is due to the salts of calcium and magnesium which it contains in

solution. It is estimated by acting on a measured quantity of water with a standard solution of soap. Some chemists, however, prefer to estimate the quantities of calcium and magnesium salts by a more scientific method, which will be found described in paragraph 351.

For estimation by the soap method (Clarke's process) the following solutions must be prepared :

Standard Calcic Chloride Solution. Weigh out accurately 1 gram of powdered Iceland spar ; dissolve this in dilute HCl, taking the precautions described in paragraph 10. Evaporate to dryness on the water bath ; add water, and evaporate again until no HCl remains. Wash into a litre flask, and make up to the 1000-c.c mark.

Soap Solution. This may be prepared in either of the two following ways :

(*a*) Weigh out about 10 grams of Castile soap cut up into shavings, dissolve in a litre of 35 per cent. alcohol, and adjust this as described in paragraph 347.

(*b*) Mix in a mortar 150 grams of lead plaster and 40 grams of dry potassium carbonate. When thoroughly mixed, treat with 50 c.c. of methylated spirit. Rub well round the mortar until a thick cream is formed. Dilute to about 400 c.c. with alcohol, and allow to stand in a tall cylinder so that the lead carbonate may settle. Filter off, and adjust the liquid to standard strength.

347. **Standardisation of Soap Solution.**—Pour some of the soap solution prepared as above into one burette, and some of the calcium chloride solution into another. Measure out into a 6-oz. stoppered bottle 10 c.c. of calcic chloride solution and 60 c.c. of water which has been boiled and allowed to cool so as to expel all carbonic acid. This solution will be equivalent to a water having 10 grains per gallon of calcium carbonate (10 parts in 70,000). Now run a c.c. of soap

solution into the bottle. Replace the stopper, and shake vigorously. A lather will be formed, which may or may not disappear on standing. Should it disappear, add another c.c., and repeat the operation until a permanent lather is formed. Note the quantity of soap solution required, and repeat the operation, running in 0·1 c.c. at a time when the correct quantity is nearly reached. When the amount has been correctly determined, calculate the dilution necessary to bring the solution to such a strength that 10 c.c. of the $CaCl_2$ solution diluted to 70 c.c. with water requires just 11 c.c. of soap solution. A calculation of this kind has been described in paragraph 62. Dilute to the extent which the calculation shall direct with alcohol (35 per cent.), and with the new solution so formed repeat the experiment. The solution will not give quite the result expected, and will probably have to be diluted again after making a fresh calculation. Repeat this alternate titration and dilution until 11 c.c. of soap just gives a lather with 10 c.c. of calcic chloride and 60 c.c. of water.

348. **Total Hardness.**—To determine the total hardness, measure 70 c.c. of the water under examination into the stoppered bottle and run in soap solution, as described in the last paragraph, until a permanent lather is formed which will not subside in three minutes. Read off the number of c.c. of soap required. It requires 1 c.c. of the soap to produce a permanent lather with 70 c.c. of water ; therefore we subtract 1 c.c. from our reading, and enter our result as degrees of hardness. Thus, supposing that 9·5 c.c. had been used, then we should say the total hardness of the water was 8·5 degrees, or that 1 gallon of it contained salts of calcium and magnesium equivalent in soap-destroying power to 8·5 grains of calcic carbonate.

349. **Permanent Hardness.**—Measure out 250 c.c. of the water, and boil gently for half-an-hour. Cool, dilute with

boiled distilled water until the volume is again 250 c.c., measure out 70 c.c. into the stoppered bottle, and estimate the hardness as before.

350. **Temporary Hardness** is obtained by subtracting the 'permanent' from the total hardness.

HEHNER'S METHOD FOR ESTIMATION OF HARDNESS

351. By this process the carbonates of calcium and magnesium, which have an alkaline reaction on methyl orange, are estimated by titrating with decinormal sulphuric acid in the presence of that indicator. Since the *temporary hardness* is due to these carbonates, it may be directly calculated from the titration of 350 c.c. of water.

To estimate the *total hardness*, add to 350 c.c. of the water 50 c.c. of decinormal sodium carbonate solution, and boil for half-an-hour. Filter, dilute to the original bulk, add a drop of methyl orange, and titrate with decinormal sulphuric acid. Thus the number of c.c. of sodium carbonate solution used to precipitate the sulphates of calcium and magnesium may be estimated. Each c.c. corresponds to 1 grain $CaCO_3$ per gallon.

352. **Nitrates.**—The nitrates in water are estimated by dissolving the 'total solid' matter (see paragraph 339) in 2 c.c. of dilute HCl, and placing in the nitrometer, together with 5 c.c. strong sulphuric acid, as described in paragraph 114.

REMARKS ON ANALYSIS OF DRINKING WATER

353. From the results of each of the determinations which have been described certain deductions may be made.

Total Solids. For drinking purposes the quality of the solid matters is of far more importance than their quantity. But

for certain technical purposes this determination is of considerable importance. When water is required for the purpose of raising steam, the greater the quantity of solid matter the greater the quantity of 'boiler scale' that will be produced. Again, in many manufactures where soap is used it is important that the water be as free as possible from solid matter. On the other hand, for brewing it is necessary that the water contain a certain quantity of sulphate of lime.

Ammonium Salts. These are represented by the free ammonia, and are almost always of animal origin. Seeing that ammonia is one of the first products of the decomposition of animal matter, the presence of large quantities of ammonia in water points to the fact that it has been *recently* contaminated with sewage in some form or other. It must be remembered, however, that the ammonium salts are not in themselves injurious, and that their presence in a water does not render it unfit for drinking purposes. It rather puts us on our guard, and directs us to look for other more harmful substances.

Free Ammonia may be present in quantities varying from ·0005 grain per gallon, or even less in spring waters, to 2 grains per gallon in shallow well waters. Sewage may contain 8 grains per gallon.

As a rule, water should contain less than ·01 grain per gallon.

Albuminoid Ammonia. This is the substance which, more than all others, should be absent from drinking water, as it is generally due to unchanged sewage. It should never exceed ·008 grain per gallon.

Oxidisable Matter. This, again, is an indication of the organic impurities in water, not necessarily, however, of animal origin. In upland surface waters the oxygen absorbed should not exceed ·3 grain per gallon. In other waters it should not exceed ·14 grain per gallon.

Chlorides. The quantity of chlorine in water is of very little importance, but should not exceed 1 grain per gallon.

Nitrates. Like ammonium salts, the nitrates in drinking water are not harmful in themselves, but their determination is useful in that it gives us an idea of the amount of sewage contamination which the water has, at some time or other, undergone. Nitrates are the *last* oxidation products of sewage, and hence they indicate contamination of less recent date than that indicated by free ammonia. The quantity present in water varies from nothing in spring or shallow well waters to 4 grains per gallon in deep wells.

Hardness. Here all the remarks will apply that have been made concerning total solids, except that the hardness, unless very excessive, cannot be considered injurious in drinking waters.

APPENDIX I

THE ATOMIC WEIGHTS (APPROXIMATE) AS USED IN THIS BOOK

Name	Symbol	Weight
Aluminum	Al	27
Barium	Ba	137
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35·4
Chromium	Cr	52
Copper	Cu	63
Fluorine	F	19
Iron	Fe	56
Magnesium	Mg	24
Manganese	Mn	55
Molybdenum	Mo	96
Nitrogen	N	14
Oxygen	O	16
Phosphorus	P	31
Platinum	Pt	194·5
Potassium	K	39
Silicon	Si	28
Silver	Ag	108
Sodium	Na	23
Sulphur	S	32
Zinc	Zn	65

APPENDIX II

Factors for Calculation of Equivalents

Amount of	Multiplied by	Gives equivalent amount of
NH_3	3·882	$(NH_4)_2SO_4$
NH_3	3·147	NH_4Cl
NH_3	5	$NaNO_3$
N	1·214	NH_3
N	4·7	$(NH_4)_2SO_4$
N	6·071	$NaNO_3$
K_2PtCl_6	·193	K_2O
K_2O	1·85	K_2SO_4
K_2O	1·585	KCl
K_2O	2·146	KNO_3
$Mg_2P_2O_7$	·64	P_2O_5
P_2O_5	2·183	$Ca_3(PO_4)_2$
P_2O_5	1·4	CaP_2O_6
P_2O_5	1·648	$CaH_4(PO_4)_2$
$CaCO_3$	·56	CaO
CaO	1·845	$Ca_3(PO_4)_2$
CaO	1·786	$CaCO_3$
CaO	2·43	$CaSO_4$
NaCl	·53	Na_2O
$Mg_2P_2O_7$	·36	MgO

INDEX

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