Analytical Procedure.

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The various methods of analysis and estimations adopted during the course of the present work, have been described in the following pages (the values have been calculated on oven-dried soil basis).

**Estimation of total carbon**

In the estimation of total carbon in soil samples or in other carbonaceous energy-rich materials, such as, wheat-straw, molasses, sugar candy or lignite, the method of Robinson, McLean and Williams\(^1\) was followed.

Five grams of well dried and powdered soil were taken in a 500 ml. Kjeldahl flask, and 5 gms. of fused potassium-sulphate (to raise the boiling temperature of sulphuric acid) and a few crystals of copper sulphate (catalyst) were added to it. This flask was connected to three conical flasks, the first containing most of the standard iodine solution, the second containing a few ml. of standard iodine solution, while the third containing pure potassium iodide solution only. The last flask containing KI solution was connected to an efficient filter pump. A current of air purified by passing it through a solution of ferrous sulphate and then through concentrated sulphuric acid, was aspirated through the system, so that it passed through sulphuric acid, ferrous sulphate, Kjeldahl's flask, standard iodine in both the conical flasks and lastly through potassium iodide. The Kjeldahl's flask was heated over direct Bunsen flame for 4-5 hours.

The sulphur di-oxide evolved according to equation(1),
\[ C + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + 2 \text{SO}_2 + 2 \text{H}_2\text{O} \quad \ldots \quad (1) \]
was carried along with air current into iodine solution in the first and then in the second conical flask, where the reaction was completed.

\[ \text{SO}_2 + \text{I}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI} \quad \ldots \quad (2) \]
Any iodine vapour from the iodine solution, going with the air current were trapped by potassium iodide in the third conical flask.

The excess of iodine left over, after the reaction (2) was titrated against a standard sodium thio-sulphate solution. The value of iodine used up during these reactions and the amount of carbon present originally, can be calculated as under:

It follows from equations (1) and (2) that,

one atom of \( C \) \( \equiv \) 2 \( \text{SO}_2 \) \( \equiv \) 2 \( \text{I}_2 \)

or, 12 gs. of carbon by weight \( \equiv \) 508 gs. of iodine by weight

i.e., 3 gs. of carbon \( \equiv \) 127 gs. of iodine.

The values obtained by this method are believed to record a little less of carbon than present originally in the system. However, since, this method is employed in the first as well as in the subsequent determinations, the results obtained are comparative.

This method has been employed in all determinations of carbon except those in chapters II and V where organic carbon was estimated by Black and Walkley's rapid titration method.

**Estimation of total nitrogen:**
The total nitrogen present in the system, was estimated by
salicylic acid reduction method. Ten gms. of well powdered soil were taken in a 500 ml. Kjeldahl's flask and 30-35 ml. of concentrated sulphuric acid to which 1 g. of salicylic acid was previously dissolved, were added to it. A cold reaction as follows was allowed to take place for 30 minutes, with occasional shaking.

$$2 \text{KNO}_3 + \text{H_2SO}_4 = \text{K}_2\text{SO}_4 + 2 \text{HNO}_3$$

$$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_4\text{COOH} = \text{HO-C}_6\text{H}_3\cdot\text{NO}_2\cdot\text{COOH} + \text{H}_2\text{O}.$$  

5-10 gms. of sodium thio-sulphate were added in order to reduce the nitro group to form amino-salicylic acid.

$$\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_3 + \text{S}$$

$$3 \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_3\cdot\text{NO}_2\cdot\text{COOH} + \text{H}_2\text{O} = 3 \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \cdot \text{C}_6\text{H}_3\cdot\text{NH}_2\cdot\text{COOH}.$$  

When the foaming and the colour due to charred carbon had disappeared, 8 gms. of potassium sulphate and a few crystals of anhydrous copper sulphate were added, followed by a regular shaking, in order to ensure complete reduction of nitrate. After 3-4 hours of digestion, the mixture was cooled, diluted and again boiled in order to break any cement-like material which is generally formed during the digestion process.

This was filtered, washed and made up to a certain volume in a volumetric flask. An aliquot part of this solution was distilled with 40% solution of sodium hydroxide, till one third of the liquid had passed over.

The issuing gas,

$$(\text{NH}_4)_2\text{SO}_4 + 2 \text{NaOH} \rightarrow 2 \text{NH}_3 + 2 \text{H}_2\text{O} + \text{Na}_2\text{SO}_4,$$

was received in 25 ml 0.1 N hydrochloric acid, containing a few drops of methyl red.
The excess of acid after the reaction was titrated against 0.1 N sodium hydroxide.

A blank experiment was carried out exactly in the same manner using 0.2 g. of cane sugar, in place of soil, so as to allow corrections for any nitrogen contained in the reagents.

The percentage of nitrogen in the soil was calculated as, \((B - T) \times N \times 0.14\), where
- \(B\) = blank titration, in ml of standard alkali,
- \(T\) = actual titration in ml of standard alkali,
- \(N\) = normality of the standard alkali.

**Estimations of ammoniacal and nitrate nitrogen:**

The determinations of ammoniacal and nitrate nitrogen were carried out by the methods followed by Dhar and Co-workers\(^4\). The values obtained by these methods were the same (up to the fourth place of the decimal) as those obtained by the water leaching (containing 10 drops of sulphuric acid) of nitrates and McLean and Robinson's\(^5\) method of ammonia determination.

**Estimation of ammonia:**

Twenty five gs. of soil from sampling spot or from jars, were directly treated with 100 ml. of a normal sodium chloride solution. The contents were stirred well and allowed to stand for half an hour. The supernatant liquid was decanted and filtered off through a Whatman No. 44 filter paper, fitted in a Buchner funnel. After a second washing with normal sodium-chloride solution, the whole mass of soil, was transferred to
the filter paper. The leaching was continued till the filtrate collected, approximated 500 ml. This was distilled with 3-4 gs. of magnesia, till 150-200 ml. of solution distilled over. The ammonia was absorbed in 10 ml. of 0.02 N hydrochloric acid. The excess of acid was titrated with 0.02 N sodium hydroxide, using methyl red as indicator.

A blank experiment was also made, using all reagents in quantities corresponding to the above.

Soils containing higher percentage of ammonia, were leached with a 15% solution of sodium chloride. In the case of alkaline soils where the extract was strongly coloured due to the dispersion of humified organic matter, a solution of normal sodium chloride containing 10 ml. of normal hydrochloric acid per litre was used.

The percentage of ammoniacal nitrogen corresponds to:

\[(B - T) \times N \times \frac{1.4}{W}\]

where

\(B\) = Volume of standard alkali used in blank titration.
\(T\) = Volume of standard alkali used in actual titration.
\(N\) = Normality of alkali used in titration.
\(W\) = Weight of the soil taken.

Estimation of nitrates:-

The soil sample, in small lumps (from sampling spot or from jars) was directly weighed and kept in an oven at 55°C for 12-16 hours, so that the soil could be leached with the minimum puddling. This was transferred to a Buchner funnel, fitted with a Whatman No.50 filter paper; and suffi-
cient distilled water containing 10 drops of concentrated sulphuric acid so as to cover the soil was added to it. The soil was leached after a few minutes, with successive volumes of distilled water, till the filtrate amounted to 600 ml. This was boiled with 1 g. of magnesia in order to expel ammonia leached from the soil, and the boiling continued till the volume was reduced to one third. It was cooled and 5 gs. of zinc dust, 70 ml. of 30% sodium hydroxide and 5 gs. of powdered iron were added in the above order. The flask was connected to the distillation apparatus and the reduction was allowed to proceed overnight, later for half an hour over a very small flame and then in the second half an hour, ammonia was distilled off and received in 10-30 ml. of 0.02 N hydrochloric acid, containing methyl red. The excess of acid was titrated with 0.02 N sodium hydroxide.

When much organic matter was present in the soil extract, 2.5 ml. of 3% sodium hydroxide and 10 ml. of 3% potassium permanganate were added and boiled for 2-4 hours. A further quantity of potassium permanganate solution was added (the colour disappeared after half an hour boiling), followed by 300 ml. of distilled water and 2 ml. of rectified spirit. This treatment was followed by reduction and distillation.

In all the experiments, determinations with blank sets using all the reagents in the same quantities as those used in actual nitrate determination, were carried out.

The percentage of nitrate-nitrogen corresponds to,
\[(B - T) \times N \times \frac{1.4}{W}, \text{ where}\]

\[B = \text{Blank titration in ml. of standard alkali.}\]
\[T = \text{Actual titration in ml. of standard alkali.}\]
\[N = \text{Normality of standard alkali.}\]
\[W = \text{Weight of the soil taken.}\]
Determination of Water Soluble Salts and Hydrogen Ion Concentration:

A soil extract was prepared, as recommended by C.S.I.R. Division of Soils, by adding 500 ml. of aerated distilled water to 100 gs. of air-dried soil (water-soil ratio = 1:5) in a pyrex glass bottle. The bottle was shaken in a mechanical shaker for an hour. After the contents had settled in a tall cylinder, the supernatent liquid was filtered through Whatman No. 44 filter paper. The filtration flask was rinsed with the first portion of the filtrate. The filtration was completed with a very light suction, and with due precaution not to allow any colloidal matter to reach the filter paper, since it was likely to pass in the filtrate.

The aliquot portions of this filtrate were taken for the determinations of total soluble salts, carbonates, bicarbonates, sulphates, chlorides and soluble calcium, magnesium, potassium and sodium.

For the determination of pH of the soils, the same water-soil ratio, 1:5, as recommended by C.S.I.R. Division of Soils, has been preferred. The pH of the soil suspension was directly obtained on the dial of the Beckman pH meter previously standardised, on immersing the calomel and glass electrodes in the soil suspension.

Total soluble salts:

100 ml. of the clear filtrate were pipetted out in a clear platinum basin and evaporated over a water bath. When
the volume was reduced to about 5 ml., 2 ml. of 20 volume hydrogen peroxide (free of salts), were added in order to oxidise soluble organic matter. It was then evaporated to dryness and was put in an electric oven at 110°C for an hour, cooled in a dessicator and weighed. In soil no. 19, the values for water soluble salts by this method and by adding up the figures as obtained in the determination of carbonates, bicarbonates, chlorides, sulphates, calcium, magnesium, potassium and sodium were approximately equal (0.2321 gs. per 100 gs. of oven dried soil). The total soluble salts, as reported, therefore, were obtained by adding up the values for the individual soluble salts.

Carbonates and bicarbonates:

To 100 ml. of the soil extract, in a porcelain basin, 2-3 drops of phenolphthalein were added. This was titrated with 0.1 N hydrochloric acid until the red colour showing the presence of carbonates, was just discharged. This corresponded to the neutralization of carbonates to the bicarbonate stage. To the solution, 2 drops of dimethyl yellow indicator were added, and titration was continued, till the solution just changed from yellow to red. The bicarbonates were completely neutralized at this stage.

The calculations used, are as follows:

\[
\% \text{ CO}_3^2- = \frac{V_1 \times 0.0060 \times \frac{1.000 \text{ ml.}}{100 \text{ ml.}} \times \frac{100 \text{ gs.}}{200 \text{ gs.}}}{V_1 \times 0.030}.
\]
\[
\% \text{ CO}_3 \cdot = (V_2 - V_1) \times 0.00061 \times \frac{1.000 \text{ ml.}}{100 \text{ ml.}} \times \frac{100 \text{ gs.}}{200 \text{ gs.}}
\]

\[
= (V_2 - V_1) \times 0.0305,
\]

where,

\( V_1 \) = Volume in ml. of 0.1 N acid used in first titration with phenolphthalein.

\( V_2 \) = Volume in ml. of 0.1 N acid used in second titration with dimethyl yellow.

Chlorides:

25-50 ml. of clear soil extract were taken in a porcelain basin and 3-4 drops of 1% solution of potassium chromate (indicator) were added to it. This was titrated with a \( \frac{\text{N}}{35.5} \) silver nitrate solution till all chlorides precipitated and the first faint tint of red silver chromate persisted.

A second basin containing the same volume of water as the soil extract with 3-4 drops of potassium chromate solution was used as standard for comparison.

The percentage of chlorine in the original soil corresponds to,

\[
\frac{\text{Volume of silver nitrate used}}{1,000} \times \frac{1,000}{\text{Volume of extract}} \times \frac{100}{200}
\]

\[
= \frac{\text{Volume of silver nitrate}}{2 \times \text{Volume of extract taken}}.
\]

Sulphates:

25-50 ml. of soil extract were taken in a beaker and were made just acidic to dimethyl yellow, with dilute hydrochloric acid. A slight excess of 5% solution of barium
chloride were added to the boiling solution, along the sides of the beaker. It was boiled, stirred cautiously avoiding scratches on the walls of the beaker, boiled again and allowed to stand overnight. It was filtered through a sintered glass crucible no. 4, and washed with hot water till free from chloride ions. The precipitate was ignited, cooled and weighed.

\[
\% \text{ of SO}_4^2- \times \frac{\text{Weight of the precipitate} \times 96 \times 1000}{233 \times \text{Volume of soil extract}} \times \frac{100}{200} = \frac{\text{Weight of the precipitate}}{\text{Volume of soil extract}} \times 206.
\]

The amounts of water soluble calcium, magnesium, potassium and sodium, were determined by the same methods as described for exchangeable calcium, magnesium, potassium and sodium in the soil extract.
Analysis of Mineral Constituents:

The methods, for the analysis of the mineral constituents present in the soils, as recommended by C.H. White\(^7\) and those by C.S. Piper\(^8\) and by the Association of Official Agricultural Chemists\(^9\), were adopted. The analysis was carried out in duplicate and repeated, till concordant values were obtained.

**Moisture content:**

10 gs. of the soil were transferred to a weighed silica basin, and placed in an electric oven at 100-105\(^{\circ}\)C for 12-16 hours for drying, after which, it was cooled and weighed.

The percentage of loss in the soil sample = loss in weight of the soil sample x 10, and this was the percentage of moisture content.

**Loss on ignition:**

The above soil sample, after the determination of moisture content, was ignited for 4-6 hours, till the colour of the soil turned reddish-brown or greyish-brown. It was then removed to a dessicator, cooled and weighed. This was repeated, till a constant weight was obtained.

The percentage of loss on ignition = Loss in the weight of the soil x 10.

**Preparation of hydrochloric acid extract:**

The hydrochloric acid extract employed for soil analysis, was prepared by the method, recommended by the Agricultural Education Association.\(^10\)
The soil left after the determination of loss on ignition, was digested with 100 ml. of concentrated hydrochloric acid (B.P. 110°C., S.G. 1.10) on a sand bath. After cooling the contents, 100 ml. of distilled water were added to it. This was filtered through a Whatman No. 42 filter paper. The filtrate together with the washings (to free the precipitate from chloride ions) were collected in a 500 ml. graduated flask.

The insoluble portion left on the filter paper, was silica, which was dried and weighed.

The percentage of silica in the sample = Weight of silica x 10.

(In most of the cases, while estimating the percentage of clay in soils, silica was determined as sand as recommended by C.S. Piper.)

The filtrate was made up to 500 ml. The sesqui-oxides, of iron, calcium, magnesium, phosphorus and potassium were determined in it.

**Sesqui-oxides:**

To 100 ml. hydrochloric acid extract, 2 gs. of solid ammonium chloride followed by dilute ammonium hydroxide were added (1:1) for precipitating sesqui-oxides. The mass was heated over a sand bath for an hour and filtered hot. The precipitate was washed with hot water, till free from chlorine ions, and the filtrate was collected along with the washings, in a flask for subsquent analysis. The precipitate was dried, ignited, cooled and weighed to a
constant weight.

The percentage of sesqui-oxides in the soil is weight of sesqui-oxide x 10 x 5.

Iron oxide (Fe₂O₃):

The precipitate obtained above for determining sesqui-oxides, was treated with 30 ml. of 30% sulphuric acid and 0.5 gs. of zinc dust, and was kept overnight (so as to allow the reduction of ferric to ferrous state). This was filtered through glass wool and titrated with \( \frac{N}{10} \) potassium permanganate solution.

The percentage of Fe₂O₃ in the soil was calculated as, ml. of \( \frac{N}{10} \) KMnO₄ used x 0.003.

Calcium oxide (CaO):

The filtrate left after precipitation of sesqui-oxides was reduced in volume to 100 ml., and was made alkaline with dilute ammonia. Warm solution of saturated ammonium oxalate was then added to the hot solution in slight excess for precipitating calcium. This was followed by stirring, boiling and leaving the solution for 4-6 hours for the precipitate to settle. The contents were filtered through Whatman No. 44 filter paper, washed with hot water to remove oxalate ions, and was dissolved in warm, dilute hydrochloric acid (1:4). From this, calcium was reprecipitated, allowed to stand overnight, washed free from oxalate ions and was dissolved in 30 ml. of 30% sulphuric acid. This was warmed and titrated
against a \( \frac{N}{10} \) solution of potassium permanganate.

The percentage of calcium oxide was calculated as,

\[ \frac{\text{ml. of } \frac{N}{10} \text{ KMnO}_4 \text{ used} \times 5 \times 10 \times 0.0023}{\text{Total ml.}} \]

**Magnesium oxide (MgO):**

The filtrate and the washings after calcium oxalate precipitation was concentrated and 5 ml. of concentrated hydrochloric acid and a drop of methyl orange were added to it. Magnesium was precipitated by just neutralizing the excess of acid and adding 10 ml. of a saturated solution of sodium-di-hydrogen phosphate, stirring and making it alkaline with dilute ammonia. After 4-6 hours, the precipitate was filtered through Whatman No. 44 filter paper, and washed free from phosphate ions. This was dissolved in (1:4) nitric acid, reprecipitated as above and kept overnight. The precipitate was washed, ignited, cooled and weighed to a constant weight.

The percentage of magnesium oxide in the soil, was calculated as,

\[ \text{Weight of the precipitate (Mg}_2\text{P}_2\text{O}_7 \times 5 \times 10 \times 0.36213.} \]

**Phosphoric acid (P\(_2\)O\(_5\)):**

50 ml. of the hydrochloric acid extract were evaporated over a sand bath, to dryness, cooled and diluted, and phosphate was precipitated by addition of a freshly prepared ammonium molybdate solution (50-100 ml.)

The precipitate was allowed to stand overnight, filtered,
washed (with 1% nitric acid and then with a 3% solution of potassium nitrate) free from acid ions.

The precipitate was dissolved in 10 ml. of \(\frac{N}{10}\) nitric acid, using phenolphthalein as indicator.

The percentage of phosphoric acid (P\(_2\)O\(_5\)) in the sample was calculated as,

\[
\text{Ml. of sodium hydroxide used} \times 10 \times 10 \times 0.000309.
\]

Potash (K\(_2\)O):

50 ml. of hydrochloric acid extract were evaporated to dryness on a sand bath, cooled and 1.5 ml. of glacial acetic acid were added to it. This was followed by the addition of 10 ml. of saturated sodium chloride solution and 5 ml. of 35% sodium nitrite solution. Potassium was then precipitated as cobalt-nitrite compound by vigorously stirring and adding 0.5 ml. of 20% cobalt nitrate solution to it. This was kept overnight, filtered through a Gooch crucible, the precipitate washed and was dissolved in a beaker containing a known volume of \(\frac{N}{10}\) potassium permanganate solution. This was acidified with 30% sulphuric acid, heated on a sand bath, and treated with \(\frac{N}{10}\) oxalic acid till the colour was discharged.

The excess of oxalic acid was back titrated with \(\frac{N}{10}\) potassium permanganate solution.

The percentage of potash (K\(_2\)O) in the soil was calculated as,

\[
\text{Ml. of } \frac{N}{10} \text{ potassium permanganate used} \times 10 \times 10 \times 0.000356.
\]
Base Exchange Capacity and Exchangeable Bases:

Preparation of soil extract:

Before leaching the soil with ammonium acetate or sodium chloride solution, removal of soluble salts, was effected as follows (Prescott, Sedro):

50 gs of soil were treated with 100 ml. of 40% alcohol, stirred and allowed to stand for half an hour. The contents were filtered through a Whatman no. 50 filter paper and washed with 40 alcohol (50 ml. portions), till free from chlorine ions. The soil was finally washed with absolute alcohol to facilitate drying and its easy removal from the funnel.

The soil was returned to the beaker and washed with water (125 ml. where the extraction was to be done with ammonium acetate) or with N sodium chloride solution (200 ml where the extraction was to be done with sodium chloride).

Leaching of the soil was carried out by both sodium chloride and ammonium acetate methods. Since the percentage of calcium carbonate in the soil was much above 0.3%, the extraction was made with a N solution of sodium chloride for exchangeable calcium (Piper, C.S., Soil and Plant Analysis, 158, 1950), and with a N solution of ammonium acetate (pH 7) for exchangeable potassium and sodium.

Leaching of the soil with normal sodium chloride solution (Hissink's method):

500 gs. of soil (after removal of soluble salts)
were treated with 200 ml. of a normal solution of sodium chloride. The contents were allowed to stand at room temperature with occasional stirring, and filtered through a Whatman no. 44 filter paper, with repeated additions of normal sodium chloride in 500 ml. portions, allowing the filtrate to drain completely each time.

The leachate was collected in a one litre volumetric flask. When exactly one litre of the leachate was collected, the flask was changed, and another litre of the extract was received in a second one litre volumetric flask.

Determinations of calcium and magnesium were carried out in the aliquot parts of these solutions.

Exchangeable calcium:

To 200 ml. of the extract, as prepared above, 2.5 ml. of concentrated hydrochloric acid, followed by 10 ml. of 30% hydrogen peroxide, were added. The contents were heated cautiously for 10 minutes, and 35 ml. of dilute ammonia (1:1) were added. This was heated very cautiously, as the remaining hydrogen peroxide was likely to decompose (hydrogen peroxide was used only where the filtrate was coloured dark due to the presence of dispersed carbon or humified organic matter. When the extract was not coloured, ammonia was added directly, there being no need of hydrogen peroxide addition).

From this solution, calcium was precipitated as oxalate with 10% ammonium oxalate solution, the precipitate
dissolved in (1:4) hydrochloric acid and reprecipitated exactly in the same manner, as in the estimation of calcium in the hydrochloric acid extract described on page 37.

The same procedure was followed with another 200 ml. portion of sodium chloride extract, collected in the second volumetric flask.

The amount of exchangeable calcium in m. e. per 100 gs. of soil, was calculated as follows:

Since, 1 ml. of 0.05 N K\text{MnO}_4 \equiv 0.05\text{ milligram equivalent calcium}

the amount of calcium = Volume of K\text{MnO}_4 used \times 0.500.

When 50 gs. of soil were originally extracted with one litre of sodium chloride and 200 ml. of it were taken for the estimation of calcium.

The difference in the values of calcium in the first litre and second litre, corresponds to the value of exchangeable calcium in the soil.

**Exchangeable Magnesium:**

The filtrate left after the first precipitation of calcium in the sodium chloride extract was collected in a beaker and was evaporated on a water bath until its volume was reduced to 200 ml., and then the filtrate from the second precipitation of calcium was also collected in the same beaker. The sodium chloride crystals formed, were dissolved by boiling. To this solution 5 ml. of 1% solution of sodium phosphate (\text{Na}_2\text{HPO}_4\cdot12\text{H}_2\text{O}) were added. The precipitate
thus obtained, was dissolved in dilute nitric acid (1:4) and magnesium was reprecipitated as phosphate, exactly in the same manner as followed in the determination of magnesium from hydrochloric acid extract of the soil (page 38). The precipitate was ignited and weighed as magnesium pyrophosphate (Mg$_2$P$_2$O$_7$).

The amount of exchangeable magnesium in m.e. per 100 gs. of soil was calculated as follows:

Weight of the Mg$_2$P$_2$O$_7$ precipitate $\times$ 179.5,
when 50 gs. of soil were originally taken for preparing one litre of sodium chloride extract and 200 ml. were originally taken for estimation of exchangeable calcium.

**Exchangeable potassium and sodium:**

For the estimation of potassium and sodium, ammonium acetate extract of the soil was prepared, by the method proposed by Schollenberger.$^{15}$

**Preparation of normal ammonium acetate solution (pH 7):**

A 2N solution of acetic acid and a 2N solution of ammonia were prepared by diluting 576 ml. of glacial acetic acid (S.G. 1.052) and 540 ml. of concentrated ammonia (S.G. 0.88) separately, to 5 litres. These were standardised by a tenfold dilution and titration of a small volume against a $\frac{1}{10}$ N alkali and acid solution respectively, using methyl red as indicator.

Exactly equal volumes of these 2N solutions of ammonia and acetic acid were mixed to prepare a N solution of
ammonium acetate. This was checked with a Beckman pH meter and was generally found to have a pH value 7.0. When the solution was not found to be close to pH 7.0, a little of 2N ammonia or acetic acid were added, in order to obtain the desired pH value. Precaution was taken to bring the solution exactly to pH 7.0, though it may not be strictly normal.

Preparation of ammonium acetate extract of the soil (Schollenberger's method):

After removal of soluble salts, the soil was transferred to a 400 ml. beaker, and 250 ml. of N ammonium acetate solution, as prepared above, was added to it. The contents were stirred and allowed to stand overnight at room temperature. The solution was decanted and filtered through Whatman No. 44 filter paper on a Buchner funnel, and the soil was quantitatively transferred to the filter paper using a jet of normal ammonium acetate. The leaching was continued with small quantities (about 50-60 ml.) of ammonium acetate solution, allowing the filter to drain between each addition, till the filtrate amounted to one litre. The filtration was facilitated by applying a slight suction by running the filter pump, and the filtrate was collected in a filtration flask. It was then transferred to a volumetric flask, 2 ml. of formalin (A.R.) were added to it, in order to prevent the growth of mould, and the volume was made up to the mark. This solution was reserved for the determination of exchangeable potassium and sodium in the original soil.
Total base exchange capacity:

The soil left on the filter paper, after leaching the exchangeable cations with N ammonium acetate, was washed repeatedly with 60% alcohol, till free from ammonium acetate. This was determined by adding a small quantity of ammonium chloride to the first lot of alcohol used for washing, and then leaching with alcohol until the filtrate gave no test for chloride. The alcohol washing were discarded. The adsorbed ammonium ions were removed by washing once with 0.1N potassium sulphate and then with N potassium sulphate till about 1 litre of leachate collected in the filtration flask. This volume of filtrate could normally displace all adsorbed ammonium ions from light to medium soils, but with heavy soils more of potassium sulphate was required. Complete displacement of adsorbed ammonia was ensured by distilling off the last lot of potassium sulphate leachate, with magnesia till no ammonia was reported in the 0.05N hydrochloric acid solution. All ammonia is taken to be displaced from the soil at this stage.

The leaching of ammonia is somewhat slow, especially in heavy soils. It was, therefore, very essential to start with tenth normal potassium sulphate to avoid the precipitation of sulphate by alcohol retained in the soil. The filtrate thus obtained was made up to the mark.

An aliquot part of the solution was transferred to a one litre distillation flask and 2-3 gs. of magnesia were added.
The flask was connected to the nitrogen distillation set and the evolved ammonia was absorbed in excess of the measured amount of 0.05N hydrochloric acid. The excess of hydrochloric acid remaining unused was titrated against 0.05N sodium hydroxide solution, using methyl red as indicator.

When the leachate was more than one litre, the leachings in excess of one litre were distilled separately from the aliquot, with magnesia. This was added to the amount of ammonia present in the first leachings of one litre.

The total amount of ammonia adsorbed by the soil and displaced by potassium sulphate, corresponded to the total base exchange capacity. The total base exchange capacity of the soil was calculated as,

\[ \text{Amount of ammonia absorbed by soil in mgs. } \times \text{0.00017 m.e. per 100 gs. of soil.} \]

**Analysis of exchangeable bases in the ammonium acetate extract**

200 ml. of ammonium acetate extract were taken in a silica basin and evaporated to dryness on a water bath. Ammonium acetate was destroyed by gentle ignition. The basin was cooled and 4 ml. of concentrated hydrochloric acid and 15 ml. of water were added. The contents were warmed on a water bath till solution was complete. This solution was then transferred to a tall 150 ml. beaker, the basin being washed with hot water. Determination of calcium and magnesium was carried out in this solution.
Removal of iron, aluminium and manganese:

To the above solution, 5 ml. of 3% ammonium per-
sulphate were added, the solution heated to boiling and then
8-10 ml. of dilute ammonia (1:1) were added in slight excess.
This was filtered hot through Whatman No. 41 filter paper.
The precipitate was washed with hot water several times and
the filtrate together with washing were reserved for the
determination of exchangeable calcium and magnesium, as de-
scribed on page 44-45 in the sodium chloride extract.

Exchangeable potassium:

150 ml. of the ammonium acetate extract were pipe-
tted out in a silica basin and ammonium acetate was destroy-
ed as before. After ignition, 15 ml. of hot water were added
to the ignited mass which was broken, stirred, warmed and
then filtered through a Whatman No. 44 filter paper. All solu-
able salts were extracted by the repeated treatment of the
ignited mass as above. The filtrate was collected, 6 drops
of concentrated hydrochloric acid were added to it, and it
was evaporated to dryness on a water bath.

When cold, this was taken up with 1.5 ml. of glaci-
al acetic acid and then 10 ml. of saturated solution of
sodium chloride, 5 ml. of 35% sodium nitrite and then 5 ml.
of 20% cobalt nitrate were added at intervals of 5-10 minutes
in the above order, in the similar manner as during the
estimation of K₂O in hydrochloric extract of the soil.
A similar treatment of the precipitate with a known volume of acidified 0.05N permanganate and 0.05N oxalic acid in excess, the unused oxalic acid being titrated back with 0.05N permanganate, was followed in a similar way.

The amount of exchangeable potassium in m.e. per 100 gs. of oven dried soil was calculated as follows:

\[
K_2O \text{ (in mgs.)} = 0.354 \times \text{volume of } 0.05N \text{ KMnO}_4 + \\
0.00034 \times (\text{volume of } 0.05N \text{ KMnO}_4)^2 \\
= \text{Volume of } 0.05N \text{ KMnO}_4 \times (0.354 + \\
0.00034 \times \text{Volume of } 0.05N \text{ KMnO}_4)
\]

The values for the latter factor \((0.354 + 0.00034 \times \text{volume of } 0.05N \text{ KMnO}_4)\) for all titrations, from 1-48 ml. were utilized from the table suggested by C.S. Piper.

To calculate the amount of exchangeable potassium in m.e. per 100 gs. of oven dried soil the amount of potash found in the blank experiment, was deducted from the value as obtained above, and the weight of \(K_2O\) (in mgs.) thus obtained, was multiplied by 0.283.

Potassium was determined in ammonia free atmosphere as traces of ammonia are readily absorbed, specially during the evaporation of acidified solution.

**Exchangeable sodium:**

100 ml. of the ammonium acetate extract were taken in a silica basin and the ammonium acetate was destroyed as before. The basin was removed from the water bath and
cooled. Then, it was taken with 6 ml. of cold distilled water. In cases where the solution was not very turbid, no filtration at this stage was necessary as it did not interfere and was corrected later. Where the mass was filtered, the same operation of evaporating it to dryness and taking with cold water was repeated.

To the above solution 15 ml. of uranyl magnesium acetate were added and the mass was stirred for 4th of a minute till a precipitate was formed. The basin was covered and was allowed to stand for 30 minutes. It was never left at this stage for more than 2 hours, as a small amount of potassium would be precipitated along with the sodium salt in presence of the former, in excess in the solution. The precipitate was filtered through a small Gooch crucible charged with asbestos, washed twice with 2 ml. of uranyl magnesium acetate, and five times with 96% alcohol saturated with the triple salt. Ultimately the precipitate was transferred to the Gooch crucible quantitatively. This was dried in an electric oven at 105°C for not more than an hour, cooled and weighed as \( \text{Na} (\text{UO}_2)_3 \text{Mg} (\text{CH}_3\text{COO})_9 \cdot 8 \text{H}_2\text{O} \). After weighing, the crucible was washed with hot water and again weighed in order to detect if there was any insoluble residue which was not removed before the sodium precipitation, the difference corresponded to uranyl magnesium acetate compound.

A blank determination was carried out with all the
reagents.

The amount of exchangeable sodium in m.e. per 100 gs. of oven dried soil was calculated as follows:

Weight of the precipitate after making the necessary correction from the blank experiment x 13.04.
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