CHAPTER 4

ANALYSIS OF SOIL AND WATER
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COLLECTION AND PREPARATION OF SAMPLES

(i) Soil Samples:

The method adopted for the collection and preparation of samples of soil is described on page 76.

(ii) Water Samples:

The method adopted for the collection of samples of water is described on page 78.

ANALYSIS OF THE SAMPLES OF SOIL AND WATER

(i) Soil Samples:

The following determinations were generally carried out with soil samples, adopting standard procedures from available literature 1 .....12.

1 Analysis of water extract (1:5) of soil for various cations and anions and determination of pH and electrical conductivity.

2 Alkaline Earth Carbonates.

3 Organic Matter.

4 Mechanical Analysis.

5 Gypsum.
(ii) Water Samples:

Samples of water were analysed adopting standard procedures from literature 1 ... 12. The following determinations were generally carried out:

1. pH.
2. Electrical conductivity.
3. Dissolved solids.
4. Sodium.
5. Potassium.
6. Calcium.
7. Magnesium.
8. Chloride.

No attempt was made to estimate Boron and Nitrate.

ANALAR chemicals were used throughout the work.

All the measuring apparatus like the burette, the pipette etc. and the weight box were calibrated before use.

COLLECTION AND PREPARATION OF SOIL SAMPLES:

Samples of soil were generally collected from virgin land. The surface layer up to 3 inch was collected separately in some cases. Samples were taken up to 3-4 ft. depth. Normally the sampling was done with a cylindrical
auger, but whenever necessary representative layers of the profiles were sampled after digging a square pit 3' x 2' x 3' (4'). The various portions of a particular depth interval were intimately mixed, and about 2-3 lbs. of the representative sample was placed in a numbered brown paper bag, which in its turn was kept in a khaki calico bag bearing the same number. A record slip was kept in each bag, showing the location of the site and description of various profile features. The approximate distance between two sites was ½ to 1 mile in the Runm area; at other places the sites were selected in view of change in vegetation or of distinct profile features met with.

The method adopted to prepare soil samples was slightly modified for convenience from standard procedures.

About half the original sample was retained for observation of structure, colour etc. The remaining sample was put in sun-shine for air drying and subsequently ground in an iron mortar without crushing ultimate particles. The ground sample was shifted in sieve with round holes 2 mm. in diameter and the coarse material again returned to the mortar for further grinding. The process was repeated until most of the sample, except stones, gravels and organic residue (if any), was reduced to adequate fineness. The bulk sample was thoroughly mixed. Particles bigger than 2 mm. in
size were weighed and reported as stones and gravels. The sample thus prepared was stored in labelled ground-glass stoppered bottles.

**Collection of Water Samples:**

Water samples were collected in thoroughly clean amber-coloured bottles of about 2 lb. capacity, properly corked, sealed and numbered. A general description of the site, the depth of the source etc. were recorded in a day to day diary. Samples of water were brought to the laboratory and analysed at the earliest.

**Methods of Analysis:**

It would be convenient to discuss the methods of analysis in the following order:

(i) Methods of water analysis.

(ii) Methods of soil analysis.

(1) **Methods of Water Analysis:**

1. **pH Determination of the Water Samples and the Water Extract (1:5) of the Soil.**


The pH was determined by the Lovibond all purpose comparator using Phenol Red and Thymol Blue discs, and occasionally checked with the Beckmann H2 model pH meter working on mains. The pH meter was previously standardized
using various buffers.

2 Electrical Conductivity of Water Samples and 1:5 Water Extract of the Soil:


Procedure: The specific conductivity was determined by using a potentiometer (Leeds & Northrup, potentiometer 7651, U.S.A.) as conductivity bridge. The conductivity cell was platinized. A microphone hummer (Leeds & Northrup, 70029) was used to supply 50 cycle A.C. (230 volts). The conductivity was measured first without the use of end coils and finally using the end coils, utilizing the formula \( R = \frac{4500 + A}{5500 - A} \), where \( A \) is the reading of the bridge and \( R' \) is the observed resistance (vide: Leeds & Northrup, Direction Book Std. 10962, pp. 9-10).

The temperature variation was noted during and after the conductivity measurement of the sample. (Distilled water was used for preparing the water extract of soil samples).

Cell constant was determined by finding out the conductivity of N/10 KCl solution. Sp. conductivity of N/10 KCl was obtained from literature. A dip type conductivity cell was used throughout. The temperature correction was applied according to Table 15, p. 90. The sp. conductivity was calculated. All the results are represented at 25°C.

3 Dissolved Solids:

Ref: (1), p. 142.
Procedure: A suitable quantity of the water sample or the filtered water extract (1:5) of the soil was taken in a weighed dish and evaporated on a water bath, finally dried in an oven at 105°C for two hours. The dish was cooled and weighed.

An alternative method of determining dissolved solids was by measurement of the conductivity of the solution, as described earlier.

4 Sodium:

Ref: (1), p. 96, 144.

Reagents: Zinc uranyl acetate solution.

In order to prepare the reagent the solutions A and B prepared as follows, were heated and mixed.

Subsequently 2 ml. of 0.1N NaCl was added and kept overnight. (filtered before use.)

Solution A:

10 gm. uranyl acetate dihydrate + 6 ml. of 30 percent acetic acid + 50 ml. of distilled water.

Solution B:

30 gm. of zinc acetate dihydrate + 3 ml. of 30 percent acetic acid + 50 ml. of distilled water.

Ethyl Alcohol (95 percent) saturated with sodium-zinc-uranyl acetate precipitates (filtered before use).

Ether (anhydrous).
Procedure: A suitable quantity of the solution was evaporated to dryness in a Pyrex beaker on a water bath. The evaporate was treated with 2 ml. of distilled water and 20 ml. of zine uranyl acetate solution. The precipitates were transferred to sintered glass crucible grade 4, washed with reagent, followed by ethyl alcohol and ether, dried and weighed.

A small quantity of water was added to the crucible to dissolve triple-acetate and reweighed after drying.

The difference between two weights is the weight of sodium-zinc uranyl acetate, hexahydrate.

Calculations:

\[
\text{mg} \text{ of Sodium} = \frac{\text{Wt. of precipitates in gm.} \times 650.16}{\text{ml. of solution taken for estimation}}
\]

5 Potassium:


Reagents: Glacial Acetic Acid, Sodium Cobaltinitrite Solution (20 per cent), Sodium Hydroxide Solution (0.5N approx.), Sulphuric Acid (cone), Potassium Permangnate Solution (0.05N), Sodium Oxalate Solution (0.05N).

Procedure: A suitable quantity of the solution was acidified with 2 drops of glacial acetic acid. About 20-25 ml. of sodium-cobaltinitrite reagent was added and evaporated to dryness on a water-bath. The residue was extracted.
with 5 per cent acetic acid and transferred to a sintered glass crucible (grade 4). Precipitates were washed with cold water till free from acid. The precipitates were treated with sodium hydroxide, boiled and further treated with excess of acidified potassium permanganate solution. The amount of unused permanganate was found out by back titration with sodium oxalate solution.

Calculations:

\[
\text{N of Permanganate solution} \times \text{ml. of med. of Potassium} = \frac{\text{Permanganate used up}}{181.81} \times \text{ml. of solution taken for estimation}
\]

6 Calcium:


Reagents: Hydrochloric Acid (1:1), Ammonium Oxalate Solution (6%), Ammonium Hydroxide (1:1), Methyl Red (0.1%), Sulphuric Acid (6 N), Potassium Permanganate Solution (0.05 N), Sodium Oxalate Solution (0.05 N).

Procedure: Calcium was precipitated as calcium oxalate by adding ammonium oxalate solution to a slightly acidic solution. Subsequently it was made alkaline by ammonium hydroxide solution. Precipitates were filtered. The precipitates were dissolved in hydrochloric acid and reprecipitated to avoid contamination of magnesium. The precipitates were filtered through a sintered glass crucible (grade 4), dissolved in sulphuric acid and titrated against potassium permanganate solution.
Potassium permanganate solution was standardised against standard sodium oxalate solution.

**Calculations:**

\[
\text{meq. of Calcium} = \frac{\text{ml. of Permanganate solution} \times \text{Normality of Permanganate solution} \times 1000}{\text{ml. of solution taken for estimation}}
\]

7 Magnesium:

Ref: (3), p.454.

**Reagents:** Ammonium Acetate (solid), Oxine Solution (2 per cent in 2N Acetic Acid), Ammonium Hydroxide (7N), Hydrochloric Acid (3N), Potassium Bromate Solution (0.1N), Sodium Thiosulphate Solution (0.1N), Starch Solution, Potassium Bromide, Potassium Iodide.

**Procedure:** The filtrate after removal of calcium was concentrated if necessary and magnesium was precipitated as magnesium oxinate by adding oxine solution followed by ammonia. The precipitates were filtered through a sintered glass crucible (grade 3), washed the precipitates with hot water and dissolved in excess of hydrochloric acid and titrated against standard potassium bromate solution after adding 1 gm. of potassium bromide. The excess of bromate was found out by sodium thiosulphate solution adding potassium iodide and using starch solution as indicator. Sodium thiosulphate was standardised against
standard bromate solution.

Calculations:

\[ \text{meq/L of Magnesium} = \frac{\text{ml of Bromate soln. used up} \times \text{N of Bromate soln}}{\text{ml of solution taken for estimation}} \times 1000 \times 0.253 \]

8 Chloride:


Reagents: Silver Nitrate Solution (0.05N), Potassium Chromate Solution (2 per cent).

Procedure: A suitable quantity of the solution was titrated slowly against standard Silver Nitrate solution using potassium chromate as an indicator. A blank reading was taken and the necessary correction was applied.

Calculations:

\[ \text{meq/L of Chloride} = \frac{\text{N of Silver Nitrate Solution} \times \text{ml of Silver Nitrate required} \times 1000}{\text{ml of solution taken for estimation}} \]

9 Sulphate:


Reagents: Hydrochloric Acid (conc.), Barium Chloride (10 per cent).

Procedure: A suitable quantity of the solution was acidified
and boiled. To this solution slightly acidified hot barium chloride solution was added. The precipitates were filtered through ashless filter paper, washed, dried, ignited and weighed.

**Calculations:**

\[
\text{mg}^{\circ} \text{ of Sulphate} = \frac{\text{gm. Barium Sulphate} \times 8568.2}{\text{ml. of solution taken for estimation}}
\]

10 Carbonate - Bicarbonate:


Reagents: Sulphuric Acid Solution (0.02N), Phenolphthalein (0.25 per cent in 50 per cent alcohol), Methyl Orange (0.1 per cent in water).

**Procedure:** A suitable quantity of the solution was titrated against standard sulphuric acid using phenolphthalein indicator. This gives the alkalinity of solution as carbonate (phenolphthalein indicates the change from carbonate to bicarbonate). The bicarbonate obtained as above and bicarbonate originally present was obtained by titrating the same solution against standard sulphuric acid using methyl orange indicator. If the readings of phenolphthalein and methyl orange (total) are P and M ml. resp.,

\[
\text{ml. required by Carbonate} = 2P \quad \text{and}
\]

\[
\text{ml. required by Bicarbonate} = M-2P.
\]
Calculation:

\[
\text{meq. of Carbonate or Bicarbonate} = \frac{N \text{ of the acid} \times \text{ml. of acid required}}{\text{ml. of solution taken}} \times 1000 \times \text{ml. of solution taken for estimation}
\]

(11) Methods of Soil Analysis:

† Preparation and analysis of 1:5 (Soil:Water) Extract.

Ref: (2), p. 16-19.

Procedure: A 1:5 soil-water extract was prepared by mixing 1 part of soil and 5 parts of distilled water in a hard glass bottle and agitated for a period of one hour in a mechanical shaker. It was subsequently allowed to settle and the extract was sucked by mouth or with the help of vacuum suction whichever was convenient. Filtered before use, the extract was used for finding out the pH, conductivity, total solids and the proportion of various cations and anions.

As the soil to water ratio is fairly high, it was not necessary to correct for the moisture content.

The measurement of pH and electrical conductivity as well as the estimations of Na\(^+\), K\(^+\), Ca\(^{++}\), Mg\(^{++}\), Cl\(^-\), S\(_{O_4}\)^\(^-\), and CO\(_3\)^\(^-\) = HCO\(_3\)^\(^-\) have been carried out following the procedures described in section on Methods of Water Analysis.
2 Alkaline Earth Carbonates:

Ref: (1), p.105; (2) p.135.

Reagents: Hydrochloric Acid (0.5N), Sodium Hydroxide (0.25N), Brom Thymol Blue (sodium salt) indicator (0.04 percent).

Procedure: About 5 gm. of the soil was treated with 100 ml. of hydrochloric acid and was allowed to stand for one hour with occasional stirring, keeping it covered with watch glass. It was then filtered and a suitable volume of the filtrate was titrated against sodium hydroxide using brom thymol blue as an indicator. Reduction in the strength of acid indicates the amount of alkaline earth carbonates as calcium carbonate.

Calculations:

\[
\text{ml. of acid required for the amount of soil taken} \times \frac{\% \text{ of } \text{CaCO}_3}{50.44} = \frac{\text{gm. of soil taken}}{100}
\]

3 Organic Matter:


Reagents: Potassium Dichromate Solution (1N), Sulphuric Acid Conc. (containing 25 gm. Silver Sulphate per litre), Diphenylamine-Sulphonate (0.4 percent), Ferrous Sulphate (0.5N), Phosphoric Acid.
Procedure: For the estimation of organic matter, the sample was ground to pass a 0.5 mm. screen. About 10 gm. of the sample was treated with 10.0 ml. of dichromate solution and 20-30 ml. of sulphuric acid in an Erlenmeyer flask. It was allowed to stand for one hour, with occasional stirring. Heated to 150°C and cooled. The amount of dichromate used up was found out by titration against standard ferrous sulphate solution adding phosphoric acid and using diphenylamine indicator.

Calculations:

\[
\% \text{ Organic Carbon} = \frac{\text{ml. of H Dichromate soln. used up} \times 0.3}{\text{gm. of soil taken for estimation}}
\]

\[
\% \text{ Organic Matter} = \% \text{ of Organic Carbon} \times 1.72
\]

4 Mechanical Analysis:

Ref: (12), p.231; 241-244; (10), p. 5; (2), p. 47-49; (13), p.171.

Procedure: 20 gm. of the air dried soil was treated with an excess of hydrogen peroxide to decompose organic matter. It was subsequently treated with HCl (2N) to decompose alkaline earth carbonates. The soil was then filtered in a Buchner funnel and washed with water. The soil was taken up in a 1 litre beaker, 500 ml. of distilled water, and 10 ml. of 1 N sodium hydroxide were added and electrically stirred for a period of one hour.
The suspension was transferred to a tall cylinder (6.5 x 40 cm.) through a 70 mesh sieve. The residue was washed, dried and weighed. The weight gives the amount of coarse sand in 20 gm. soil.

The soil suspension was diluted to 1000 ml. and temperature of the suspension was noted. A suitable time-scale was prepared to take out various samples by the Pipette method with an automatic suction. The samples from 10 cm. depth were dried and weighed. These samples provide values for silt and clay in the soil taken.

The fine sand value was obtained by allowing the suspension to stand for a day. On removing all the silt and clay by the Beaker method, the final fraction at the bottom of the beaker gives the value of the fine sand for the soil taken.

The values were obtained in terms of percentage by calculation.

Moisture was determined separately as follows:

Exactly 2 gm. of the air dried sample of the soil was heated in an oven at 110°C for two hours and the loss in weight was considered the moisture.

Determination of Gypsum:

Ref: (1), p.102-104.

Reagents: Acetone, Distilled Water.
Procedure: 2.0 gm. of the soil was treated with 200 ml. distilled water and allowed to stand for two hours with intermittent stirring. 50 ml. of the above solution was concentrated and treated with adequate quantity of acetone for complete precipitation of gypsum. The precipitates were filtered and dissolved in a definite quantity of water. Gypsum was estimated by measuring the conductivity of this solution (or by estimating the Ca content in the solution). The amount of gypsum was found out from a standard curve prepared by using data from the International Critical Tables.

Calculations:

\[
\text{meq. of CaSO}_4 \text{ in aliquot} = \frac{\text{meq./l. of CaSO}_4 \text{ from conductivity reading} \times \text{ml. of water used to dissolve precipitate}}{1000}
\]

\[
\text{meq. of gypsum per 100 gm. of soil} = \frac{\text{meq. of CaSO}_4 \text{ in aliquot} \times 100}{\text{Soil : Water ratio} \times \text{ml. of soil water extract used}}
\]

6 Cation Exchange Capacity and Exchangeable Cations:

The ability of the soil to exchange ions with solutions in contact with it has been known for a long time. "Ion exchange occurs widely in nature, and its consequences have been known from the time of Aristotle who has remarked upon the use of sand filters for the
purification of sea and impure drinking waters. Many other naturally occurring materials such as silk, wool, cellulose, various minerals and cell membranes exhibit this phenomenon. Unquestionably, its most important manifestation is in soils where it plays an essential role in the inorganic nutrition of plants. It is from the study of soils, in fact, that much of the foundation for our modern understanding of the phenomenon has been derived. In 1850, the two agricultural chemists, Way and Thompson reported the first systematic observations on ion exchange with clays and their observation that the exchange of ions involved equivalent quantities and that certain ions are more readily exchanged than others have stood the test of time. During the last hundred years, rapid development has taken place in our understanding of the nature of the soil complex. The phenomenon of ionic exchange in soils is, however, of a complicated character and even, today, our knowledge of the subject is far from complete.

The early soil scientists were inclined to consider ionic exchange in soils, essentially, as a chemical process. Van Dommelen emphasized that the processes are more of the absorption exchange type and further stressed the importance of the colloidal concept of soils.

Gedrois published a series of investigations on the cation exchange in soils. He was of the opinion
that the exchange phenomena may be treated as an aspect of colloid chemistry. * We must look, therefore, upon the exchange of soil zeolitic cations for the cation in solution in contact with the soil, as upon a purely physical process, taking place only on the surface of solid particles, and its source of energy is the surface energy of the system." Mattson emphasised the importance of pH on cation exchange capacity.

The most significant advance was the clay mineral concept developed by Hendricks, Fry, Kelley, Dore and Brown. The cation exchange in soil is due to the crystal structure and lattice composition of the clay minerals. The crystal structure of clays has been established by Pauling and others. Knowledge of crystal structure and isomorphism enables one to understand the nature of cation exchange material. There are a number of clay minerals, whose general structures resemble the structures of mica and talc. They are characterized by a lattice structure. The inorganic cation exchange material of the soil is usually one of the clay minerals such as montmorillonite, hydrous mica, kaolinite and halloysite or the admixture of several clays. The clay particles are negatively charged and can be neutralised by any cation except hydrogen. Clays, however, hold different ions with different intensities. When a sample of clay saturated with calcium ions is treated with dilute aqueous
solutions of different salts of the same normality, ionic exchange takes place to different extents. In base exchange phenomena, any cation may be taken up by a soil and it can subsequently be displaced by any other cation.

**Methods of Studying Cation Exchange:**

The cation exchange capacity of a soil is defined as the total quantity of cations which it can absorb by cation exchange, usually expressed as milliequivalents per 100 gm. of the soil. The method to be used to determine ionic exchange will depend upon the nature of the soil. Various methods have been proposed from time to time.

In 1875 Pillitz adopted a method of studying ionic exchange in a soil by treating it with 1.4 N NH₄Cl until the leachate gave no residue on ignition. In 1877, Kellner studied the exchange capacity and the individual cations in the soil. In 1918, Gedroiz used a modified Kellner's method employing 1N NH₄Cl as follows: 25 gm. of dry pulverized soil is first shaken with 250 c.c. of NH₄Cl; then the sample is transferred to a filter and leached with 1 N NH₄Cl until the last portion of leachate gives no test for Ca. Metallic cations are then determined in the leachate.
Kelley and Brown (1924) first realised that utilisation of an acid salt like \( \text{NH}_4\text{Cl} \) will affect the pH of the solution. They utilised \( \text{NH}_4\text{Cl} \) neutralised with \( \text{NH}_4\text{OH} \). Their procedure was as follows: *Twenty-five grams of well-pulverized air-dry soil is shaken with \( N \ \text{NH}_4\text{Cl} \) neutralized to pH 7 with \( \text{NH}_4\text{OH} \). The sample is then allowed to stand several hours at 70°, after which the contents of the flask are thrown onto a filter and the soil is leached with neutral \( N \ \text{NH}_4\text{Cl} \) until one litre of the leachate is obtained. The filtrate is evaporated to dryness in the presence of concentrated \( \text{HNO}_3 \) in order to decompose \( \text{NH}_4\text{Cl} \). The residue is brought to dryness two or three times in presence of concentrated HCl. After filtering out the small amounts of silica; Ca, Mg, K and Na are determined.* Schollenberger discussed the advantages of using ammonium acetate instead of ammonium chloride.

The determination of cation exchange capacity becomes complicated in the presence of \( \text{CaCO}_3 \) as pointed out by Gedrois, who suggested a special procedure. He determined \( \text{CaCO}_3 \) in a sample of the soil before and after leaching with \( \text{NH}_4\text{Cl} \). The difference represents \( \text{CaCO}_3 \) dissolved by \( \text{NH}_4\text{Cl} \). To obtain the exchange capacity of the soil, the experimentally determined exchange capacity, using \( \text{NH}_4\text{Cl} \), must be corrected.
for dissolved CaCO₃ determined as above. Hissink²³ (1922) used NaCl instead of NH₄Cl. Hissink's method, however, has been adversely criticised by Chapman and Kelley²⁴ (1930). Determination both of total exchange capacity and exchangeable bases is perhaps more complicated with the saline soils which have been investigated in the present work. Kelley and Brown²⁵ (1925) state: "In view of the complexity of the system involved in soil; the ready reactivity and lability of some of the constituents; the presence in alkali soils of relatively high concentrations of soluble salts, whose determination may affect the exchangeable constituents to some extent; and the errors due to solubility effects, it is not reasonable to expect highly accurate results with any method." "Fortunately, no convincing evidence has yet been obtained showing that approximate results will not suffice, insofar as the solution of practical soil problems is concerned."²⁶

The following method was suggested by Kelley and Brown²⁷ (1934), in view of the uncertainties about the effects of carbonates, soluble silicates and CaSO₄. "Soluble Na and K were determined in 1 to 5 water extracts of the soil and again in extracts obtained by leaching a sample with N ammonium acetate. The water soluble Na and K were subtracted from the amounts found in the ammonium acetate extracts, the difference being considered exchangeable Na and K. The NH₄ absorbed
from ammonium acetate is also determined and the amount found represents the exchange capacity. This quantity less the sum of exchangeable Ca and Mg equals exchangeable Ca and Mg collectively. Thus, in this method no attempt is made to determine exchangeable Ca and Mg separately."

Most of the soils under investigation may be termed saline alkali and saline-non-alkali soils. The following constituents were present in varying proportions: Na⁺, Ca⁺⁺, K⁺, Mg⁺⁺, Cl⁻, SO₄⁻⁻, CO₃⁻⁻, HCO₃⁻, CaSO₄, CaCO₃, MgCO₃, and organic matter in small quantities.

The determination of exchangeable cations may be considered under following heads:

(a) Determination of CaCO₃;
(b) Determination of Gypsum;
(c) Determination of Soluble Salts;
(d) Total Exchange Capacity;
(e) Exchangeable Cations.

(a), (b) and (c) have already been described.

(d) Total Exchange Capacity (T.E.C.)

Ref: (2), p.169-189

(In the beginning the following method was adopted.)

Reagents: N Ammonium Acetate Solution (pH 7); 40% Alcohol; HCl 0.1N; NaOH 0.1N.

Procedure: 50 gm. of the soil was treated with 40% alcohol, and kept overnight to dissolve the soluble salts. The salts were removed by filtration. The process
was repeated a total of four times. After filtration the soil was treated with 250 ml. of N Ammonium Acetate, allowed to stay overnight. The extract was collected by filtration. The process was repeated and subsequently the extract collected was diluted to one litre. A suitable quantity of this extract was evaporated to dryness on a water bath and ignited in the muffle furnace to decompose the acetates to carbonates and oxides. When cold, the residue was treated with excess of standard HCl and the unused acid back-titrated against sodium hydroxide, using methyl red as an indicator.

Calculations:

\[
\text{T.E.C. in meq./100 gm.} = \frac{(V_a - V_b) \times N \times 1000}{V_e} \times \frac{100}{W}
\]

Where, 
- \(V_a\) = Vol. of std. HCl taken,
- \(V_b\) = Vol. of std. NaOH used in back titration,
- \(N\) = Normality factor,
- \(W\) = Weight of the soil taken,
- \(V_e\) = Volume of the extract taken.

The acetate extract was also used for estimation of cations, \(\text{Na}^+\), \(\text{K}^+\), \(\text{Ca}^{++}\), and \(\text{Mg}^{++}\).

(e) Exchangeable Cations:

A suitable quantity of the extract obtained in (d) was evaporated to dryness on water bath, the acetates
were decomposed to carbonates and oxides in the muffle furnace and taken up with hydrochloric acid.

From this solution calcium was estimated as described on p. 82. The filtrate was used for the estimation of magnesium as described on p. 83. The filtrate after removal of magnesium was used to estimate Na and K using the following method:

The filtrate after removal of Ca and Mg was evaporated to dryness, heated to dull redness to decompose the ammonium salts. The residue was taken up with a small quantity of hydrochloric acid in a silica crucible. The solution was evaporated to dryness and treated with conc. sulphuric acid and finally weighed as Na₂SO₄ + K₂SO₄.

Potassium was estimated separately from the extract as described on p. 81. Sodium was calculated by difference.

The above method of determining Na and K ions in soil was based upon experience in a pure inorganic laboratory. It had to be given up as the results obtained were erroneous, probably due to the imperfect removal of Ca and Mg and also the possibility of the soil material yielding soluble sodium salts. The results of determination of Ca and Mg also may be high, as Ca and Mg might have been derived from Ca and Mg carbonates or silicates. This would obviously introduce error in the value of total exchange capacity of the soil.
An alternative procedure adopted (after realizing the above errors) is as follows:

(d) Total Exchange Capacity


Reagents: N Sodium Acetate Solution, N Ammonium Acetate Solution, 95% Alcohol.

Procedure: 5.0 gm. of the soil was treated with 100 ml. N sodium acetate (pH 8.2), allowed to remain overnight and the clear extract was sucked up without disturbing the soil layer. The soil was further treated with two fresh lots of N sodium acetate and finally washed thrice with 95% alcohol to remove the soluble salts. The soil was then treated with N ammonium acetate (pH 7.0), for four times, each time using 50 ml. of the solution. The extracts were collected together and made up to 250 ml. A suitable quantity of the extracts was taken and sodium was estimated by the triple acetate method described on p. 80.

Calculations:

\[
\text{T.E.C. in meq./100 gm.} = \frac{\text{Na concn. of extract in meq.} \times 4}{\text{Wt. of sample in gm.}}
\]

(e) Exchangeable Cations:

Ref: (1), p. 101-102; (6) p. 89.
Reagents: N Ammonium Acetate.

Procedure: 5.0 gm. of the soil was taken in a 30 ml. test-tube treated with 20 ml. of N ammonium acetate (pH 7) and centrifuged. The supernatant liquid was taken out in a 100 ml. measuring flask and the soil was again treated with fresh lots of ammonium acetate and the extract collected. Various extracts collected were finally made upto 100 ml. Suitable quantities of the extract were taken for the estimation of Na$^+$ and K$^+$ and estimated as described on pp. 80-81.

Calculations:

Exchangeable cations:  
\[
\text{Exchangeable cations in (Na and K) in meq./100 gm.} \quad = \quad \text{(soluble cations in meq./100 gm.)} - \text{(soluble cations found out from 1:5 extract of the soil)}
\]

Exchangeable Ca$^{2+}$Mg$^{2+}$ = (Cation exchange capacity in meq./100 gm.) - (exchangeable Na in meq./100 gm. exchangeable K in meq./100 gm.)

The above procedure was selected, in view of the limited resources of the laboratory.

The cation exchange capacity was determined following the procedure recommended by the U.S. Salinity Laboratory. However, Ca$^{2+}$Mg$^{2+}$ was determined as a difference between cation exchange capacity and exchangeable sodium plus potassium, following Kelley and Brown.

The flame photometer was not available in the laboratory and hence Na and K were determined by chemical
methods. Another important difference in procedure was of the determination of soluble salts from 1:5 extract of the soil, instead of from the saturation extract, which is a method more recently adopted, by the U.S. Salinity Laboratory. The 1:5 extract method has been adopted by Kelley and Brown. The method is quite satisfactory except for soils which contain considerable quantity of gypsum. When such a soil is treated for soluble salts with water (1:5), then, along with soluble salts, as Kelley (1939) and Reiteneir (1948) have remarked, one is bound to get additional Na from absorption complex and Ca and Mg by hydrolysis of Ca and Mg silicates. The saturation method will no doubt decrease the chances of the constituents of the soil complex going in solution. There is, however, some difficulty of judging "saturated paste." The following is the criteria to judge the saturation point. "At saturation, the soil paste glistens as it reflects light, flows slightly when the container is tipped and the paste slides freely and cleanly off the spatula." The definition lacks precision. Again, it is doubtful, whether the method gives reliable and reproducible results in the presence of CaSO₄ and NaCl as soluble salts. When a saturation paste is made, the more soluble NaCl may dissolve to a greater extent than the difficultly soluble CaSO₄. Hence the saturation paste in contact with the soil complex will exchange part of its sodium with the calcium of the soil complex, which will result in decreasing the
sodium ion content in saturation extract. This will ultimately result in giving high values for exchangeable sodium in the soil complex than actually present.

The detailed results about cation exchange are given in Tables X, XII, XV, XVIII, where an attempt will be made to assess the reliability of the results.

Methods of soil investigation need continuous revision and no finality can be claimed for any particular procedure.
REFERENCES

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