

Practical Manual

# SOIL CHEMISTRY

APS-503, 3(2+1)



*For*  
**M.Sc. (Ag.) Soil Science**



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**Department of Soil Science**  
**College of Agriculture**  
**Rani Lakshmi Bai Central Agricultural University**  
**Jhansi-284003**

**Practical manual**

# **SOIL CHEMISTRY**

**APS-503, 3(2+1)**

**M.Sc. (Ag.) Soil Science**

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## Experiment No. 1

### Objective: Preparation of saturation paste and saturation extract of soil

#### Principle

Under laboratory conditions, the soil salinity can be determined by the (i) electrical conductivity (EC, dS m<sup>-1</sup>) of soil-water extracts, (ii) proportion and composition of salt species, or (iii) amount of total dissolved solids (TDS, mg L<sup>-1</sup>). The most common technique for the measurement of soil salinity is the laboratory analysis of aqueous extracts of soil samples. Ideally, the salinity of a soil solution measured at field water- content (usually at field capacity) is the best index because it is the salinity actually experienced by the plant root. But, it has not been widely used because (i) it varies throughout the irrigation cycle as the soil water-content changes; and (ii) the methods for obtaining soil solution samples at typical field water-contents are too laborious, time- consuming, and cost-intensive to be practical. As a result, soil solution extraction is made at saturation or higher water-contents and the most commonly used is the aqueous extracts of saturated soil paste.

The soil solution extracts of higher soil: water ratios (e.g. 1:1, 1:2 and 1:5 soil: water) have also been used because of comparative ease in extraction vis-a-vis soil saturation paste extraction. The strong linear relationships exist between the EC<sub>e</sub> and the EC 1:1 and EC 1:5 values ( $R^2 > 0.93$ ), but the relationships between extracts of higher soil: water ratios and saturation paste are often imprecise and inaccurate. The soil: water ratio used for extraction influences the solute partitioning the gas, liquid, and solid phases of soil. Therefore, the ratio needs to be standardized for a proper interpretation. The extracts of higher soil: water ratios affect the solubility of less soluble salts such as gypsum (CaSO<sub>4</sub>) or lime (CaCO<sub>3</sub>). This is particularly true in the case of gypsiferous soil where the concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> remain nearly constant but that of other ions decreases with increased sample dilution.

#### Apparatus

- Plastic containers with lid (500-mL)
- Spatula
- Glass rod
- Vacuum-line extraction assembly consisting of a Buechner funnel, vacuum pump, vacuum flask, filter paper (e.g., Whatman No. 1 and 5), glass tubes or bottles for collecting and storing the saturation extract
- Electronic balance

#### Reagents

- 0.1% Sodium hexametaphosphate (NaPO<sub>3</sub>)<sub>6</sub> : Dissolve 0.1 g of (NaPO<sub>3</sub>)<sub>6</sub> in distilled water and make up the final volume to 100-mL.

#### Procedure

##### (a) Preparation of Saturation Paste

- Collect about 1 kg of homogeneously mixed representative soil sample.
- After air drying, grind the sample and pass through 2-mm sieve.
- Weigh about 500 g of air-dried soil of < 2.0 mm size in a plastic container fitted with a lid.

- Add distilled or deionized water in increments to moisten the soil and stir the sample with a spatula.
- Continue to add incremental volumes of water while stirring the sample with a spatula until the soil is water saturated.
- Allow the mixture to stand for about 2 h to permit the soil to imbibe the water and dissolve readily-soluble salts. Add more water if required to obtain a uniformly saturated soil paste.
- Check the preparation of saturation paste using the following criteria. At saturation, (i) the soil paste glistens, (ii) the saturated paste flows slightly when the container is tipped, (iii) the paste slides smoothly off the spatula, and (iv) if a depression is made on the soil surface, no water collects in it and the depression fills slowly by flow of the paste under gravity. It may be ensured that there are no dry clumps of soil and the soil paste is homogeneous.
- Close the container with lid and allow the sample to stand (preferably overnight) in cooled conditions, preferably at 4 °C. Next morning take out the saturated paste from the cold storage and let the paste attain the room temperature.
- Recheck the paste for saturation criteria. Free water should not collect on soil surface, nor should the paste stiffen markedly or lose its glisten. If the paste is too wet or stiffen, add accordingly more dry soil or water to make soil saturation paste. Stir the soil paste with a spatula to ensure that it is homogeneous.

**(b) Extraction of Saturation Paste**

- Transfer the saturated soil paste to a Buechner funnel fitted with a filter paper Whatman No. 1 and apply vacuum. The soil paste should evenly and completely cover the filter paper. As moisture is drawn from the soil paste, cracks may develop in the soil cake. If cracks are not checked in time, air passing through the cracks may prematurely dry the cake at the cracks or air travelling through the extraction flask may evaporate the extract. To overcome it, the extraction process should be monitored regularly and cracks if developed in the soil cake should be smoothed immediately with the spatula.
- Collect the saturation extract sufficiently enough for analysis in a bottle or tube.
- Colouration of the extract imparted by the dissolved organic matter does not affect its quality for the chemical analysis or conductance measurement. But, if the initial filtrate is turbid either discard it or filter it again. In such cases, a higher retentive filter paper such as Whatman No. 5 may be used.

The samples containing a substantial amount of clay may require a longer time for extraction or need the transfer of the unextracted soil paste to another extraction funnel because the soil paste at the bottom of the soil cake dries, sealing the extract above from getting through.

**Precautions**

- The soil sample should not be oven-dried before extraction. Heating the soil at 105 °C may convert a part of the gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to plaster of paris  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  which is more soluble in water.

- Special precaution should be taken in the preparation of saturation paste of peat and muck soils, very fine or very coarse textured soils. The peat and muck soils should not be dried following collection as their saturation water content changes upon dryness.
- In the case of fine textured soils, enough water should be added immediately with minimum mixing to bring the sample near saturation. This also minimizes the formation of clumps of soil during stirring.
- The coarse textured soils should not be over-wetted. The presence of free water on the surface of soil paste indicates over-wetting. Even a small amount of free water may cause appreciable error in the saturation paste water content.
- One drop of 0.1% sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub> solution per 25 mL of extract may be added before storage to prevent precipitation of  $\text{CaCO}_3$ .
- A few drops of thymol ( $\text{C}_{10}\text{H}_{14}\text{O}$ ) can be added to the paste to minimize microbial activity on the saturated extract during equilibration.

## Experiment No. 2

### **Objective: Determination of soil pH by using pH meter.**

The pH Measurement specifies the degree of relative acidity or alkalinity of an aqueous solution at a given temperature. Theoretically, pH is derived from the word "Pondus Hydrogenii" which means "Potential Hydrogen" or power of hydrogen ion, pH is represented in the form of an equation as the negative logarithm of the hydrogen ion concentration. The pH value which is a measure of the hydrogen (or hydroxyl) ion activity of the soil water system indicates whether the soil is acidic, neutral or alkaline in reaction. The pH value of the solution surrounding the soil particles fluctuates in the natural state because of changing soil: solution relationships brought about by climate, cultivation, crop growth and other factors.

**Working principle of pH meter:** The pH Meter measures the voltage of an electro chemical cell and based on the temperature sensor determines the pH of a solution. The overall potential or the voltage is the algebraic sum of the potentials of the measuring electrode, reference electrode and the liquid Junction. The reference electrode provides a stable voltage as it has a fixed concentration of potassium chloride solution which is a neutral solution. On the contrary, the potential of the measuring electrode depends only on the pH of the solution. The potential difference (voltage) between a glass membrane of measuring electrode and a reference electrode which is dipped in the sample solution to be tested is measured. When the two electrodes are dipped in the sample solution, ion-exchange process occurs, where in some of the hydrogen ions move towards the outer surface of the measuring electrode and replaces some of the metal ions inside it. The potential difference of glass electrode and sample solutions will be recorded in the galvanometer.

### **Suspension effect in soil pH measurement**

In the pH measurement the reference and indicator electrodes are immersed in a heterogeneous soil suspension comprising of dispersed solid particles in an aqueous solution. If the solid particles are allowed to settle down, the pH can be measured in the supernatant liquid or in the sediment. Placement of electrode pair in the supernatant normally gives a higher pH reading than placement of the same in the sediment. The difference in soil pH reading is called the 'Suspension effect'. In practice a measured quantity of soil is shaken with a convenient volume of water or salt solution under consistent conditions and the pH of the suspension is determined electronically on a direct-reading pH meter, using a glass electrode with a saturated KCl-calomel reference electrode. Usually soil : water ratio of 1 : 2.5 or 1 : 1 is used for routine analysis.

### **Reagents and Apparatus**

- **Standard buffer solutions**

At least, two buffer solutions must be used one at low pH range and the other at high pH range. The buffer solution most commonly used for low pH values is a 0.05 M solution of potassium hydrogen phthalate which has a pH of 4.001 at 20°C. The pH of this buffer varies with temperature from 4.000 at 15°C to 4.020 at 35°C. The reagent must be of highest purity and the water used for its solutions should be double distilled water. The buffer can be stored in well sealed Pyrex or polythene bottles but preferably should be freshly prepared every 2

weeks. For high pH buffer solution a 0.01M solution of borax is convenient and at 20°C has a pH of 9.22. This buffer if protected from atmospheric carbon dioxide can be kept for about a month. Three to four drops of toluene addition prevents growth of mould.

Standard certified buffer tablets/capsule are also available for a whole range of pH-values and these are most convenient. One tablet or capsule dissolved in a specified amount of water, usually 100 cc provides a solution of known pH to within about 0.02 of a unit. Buffer tablets or capsules of pH 4.0, 7.0 and 9.2 are mostly used now a days for instrument calibration.

- Glass electrode pH meter with calomel reference electrode and salt bridge.
- 50 ml or 100 ml beakers, short stirring rods and distilled water wash bottle.

### Procedure

- Weigh 20 g soil sample in a 100 ml beaker and add 50 ml of distilled water ( soil: water ratio of 1:2.5).
- Stir the suspension at regular intervals for 30 minutes.
- Measure the pH with the glass electrode stirring the suspension well just before immersing the electrode.
- Switch on the pH meter at least 15 minutes before for allowing it to warm up and standardize the glass electrode using standard buffers.
- Adjust the temperature compensation knob to the temperature of the test solution.
- Rinse the electrode with distilled water after each determination and remove water from the surface with a piece of blotting paper.
- Check the standardization process after every ten determinations.
- Record the pH value of the samples

### Applications of pH measurement

- pH measurement is very crucial parameters for soil evaluation.
- Major crops require pH 6.5 to 7.5 for their optimum growth.
- pH controls the availability of various nutrient in soil.
- It is also used in food industry especially for dairy products like cheese, curds, yogurts, etc.
- pH also identify the salt affected soil.
- pH level monitoring is essential in water quality for irrigation.

### Classification of soil pH

Soil Class	pH
Extremely acid	<4.5
Very strongly acid	4.5 – 5.0
Strongly acid	5.1 – 5.5
Moderately acid	5.6 – 6.0
Slightly acid	6.1 - 6.5
Neutral	6.6 – 7.3
Slightly alkaline	7.4 – 7.8
Moderately alkaline	7.9 – 8.4
Strongly alkaline	8.5 – 9.0
Very strongly alkaline	>9.0

## Experiment No. 3

### Objective: Determination of electrical conductivity of soil sample

#### Principle

The conductivity of a soil is precisely the specific conductivity at 25°C of a water extract obtained at a definite soil : water ratio. The electrical conductivity is measure on an electrical conductivity bridge and is normally reported in mmhos cm<sup>-1</sup>. A fairly quantitative estimate of the soluble salt content of solutions extracted from the soils can be made from their electrical conductance. Soil extracts obtained using high water to soil ratios are as less accurate measure of the solute content of the soil since more salts may be removed than are ever present in the soil, at field moisture contents. Usually soil : water ratio of 1 : 2.5 or 1.5 is used for routine measurement. Thus the soil: water ratio employed must be specified with the analysis

The cell constant 'k' of a conductance cell is determined by measurement of the electrical conductance 'C' of a standard KCl solution usually 0.01M KCl solution and use of equation

$$k = L/C$$

where L is the known specific electrical conductance mmhos cm<sup>-1</sup>

C is the conductance of the standard solution measured in a given cell (mmhos).

The measured conductance 'C' of a test solution in mmhos multiplied by the cell constant (k) gives the specific conductance, L mmhos/cm of the test solution. i.e.  $L = kC$

For soil classification purpose the conductivity of saturation extracts of soils is required. However, extraction of solution from a saturated paste is very difficult process. As an approximation, the conductivity of the water extracts from a 1: 2.5 soil:water suspension is determined and the conductivity of the saturation extract is calculated as  $EC \text{ (saturation extract)} = E.C \text{ (1 : 2.5 extract)} \times 250/\text{saturation percentage}$ .

This does not hold good for soil containing gypsum for which saturation extract must be obtained.

#### Reagents and apparatus

- 0.01M Potassium chloride prepared from AR grade salt and double distilled water [0.74569 g KCl in 1000 ml or prepare fresh from a stock of 0.2 (M) KCl solution (14.92 g of the salt in 1000 ml)].
- Conductivity bridge with dip type or pipette type conductivity cells.
- Beakers – 50 ml or 100 ml.

#### Procedure

- Weigh 20 g air dry soil, into a 100 ml beaker and add 50 ml distilled water.
- Stir at regular intervals for 1 hour.
- Allow to settle for 30 minutes and filter the supernatant through a dry Whatman No. 42 filter paper into a dry beaker.
- Measure the temperature of the soil extract, for future correction.
- Measure the conductivity of the extract with the conductivity bridge. The specific conductivity is obtained by multiplying the electrical conductance with the cell constant. To obtain the conductivity at the temperature of the extract multiply by the appropriate correction factor (ft)

obtained from below table.

**Temperature factors for correcting conductivity data on soil extracts to 25 °C**

Temperature °C	Correction factor	Temperature °C	Correction factor	Temperature °C	Correction factor
10	1.411	18	1.163	26	0.979
11	1.375	19	1.130	27	0.960
12	1.341	20	1.112	28	0.943
13	1.309	21	1.087	29	0.925
14	1.277	22	1.064	30	0.907
15	1.247	23	1.043	31	0.890
16	1.218	24	1.020	32	0.873
17	1.189	25	1.000	33	0.858

**Calculations**

Electrical conductivity of the extract at 25°C or (Lmmhos/cm) =  
 conductivity of the extract as measured (mmhos) × cell constant (cm<sup>-1</sup>) × temperature correction factor

% of salts in soil = 0.064 x Lmmhos/cm x  $\frac{\% \text{ of water in soil at extraction}}{100}$

For (10 g soil + 25 ml water or 20 g soil + 50 ml water) i.e. 1:2.5 soil : water ratio the above expression

$$\begin{aligned}
 &\text{will be, } 0.064 \times \text{Lmmhos/cm} \times \frac{\frac{25}{10} \times 100}{100} \\
 &= 0.064 \times \text{Lmmhos/cm} \times \frac{250}{100} \\
 &= 0.064 \times 2.5 \times \text{Lmmhos/cm} \\
 &= 0.16 \times \text{Lmmhos/cm}
 \end{aligned}$$

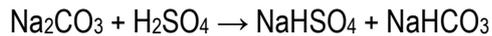
Or 0.32 x Lmmhos/cm for 1:5 soil: solution ratio

## Experiment No. 4

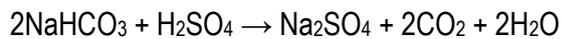
### Objective: Determination of carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) in soil.

#### Principle:

When phenolphthalein is used as an indicator, strong alkalis like KOH or NaOH are completely neutralized whereas weak alkalis like  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  are neutralized to the stage of  $\text{NaHCO}_3$  or  $\text{KHCO}_3$  according to the equation



The  $\text{NaHCO}_3$  thus formed requires more  $\text{H}_2\text{SO}_4$  to get completely neutralized according to the equation



It is evident from the above equations that the quantity of  $\text{H}_2\text{SO}_4$  required in both the stages of neutralization of  $\text{Na}_2\text{CO}_3$  is the same. The second stage of neutralization of  $\text{Na}_2\text{CO}_3$  (i.e. the neutralization of  $\text{NaHCO}_3$ ) can be indicated by methyl orange which can also indicate complete neutralization of alkali carbonate or bicarbonate. Thus phenolphthalein and methyl red are used one after the other during the course of titration in the same solution for evaluating mixtures containing carbonates and bicarbonates. Methyl orange when used jointly with phenolphthalein after the latter has decolorized indicates the quantity of acid required for the neutralization of the bicarbonate only.

#### Reagents

- Phenolphthalein indicator; 0.25% solution in 60% ethylalcohol.
- Methyl orange indicator; 0.5% solution in 95% alcohol.
- Standard  $\text{H}_2\text{SO}_4$  ; 0.01 (N)

#### Procedure

- Weigh 40 g of soil sample in a 500 ml conical flask.
- Add 200 ml double distilled water and shake for one hour in a shaking machine for equilibration.
- Filter the suspension.
- Pipette out 5 ml of the extract or 5 ml of water sample (containing not more than 1 meq. of  $\text{CO}_3^{2-}$  plus  $\text{HCO}_3^-$ ) in a porcelain dish and add 2-3 drops of phenolphthalein indicator. Titrate against 0.01(N) $\text{H}_2\text{SO}_4$  until the pink colour just disappears (indicating phenolphthalein end point). This end point corresponds to the neutralization of the carbonate to the bicarbonate stage.
- Record the ml of 0.01(N)  $\text{H}_2\text{SO}_4$  required for this process from the burette reading.
- Add 1-2 drops of methyl orange indicator to the colourless solution.
- Titrate it again with 0.01(N)  $\text{H}_2\text{SO}_4$  stirring briskly, until the indicator turns orange indicating complete neutralization of the bicarbonate present.
- Note the titre value from the burette.

## Calculations

Weight of soil taken = 40 g

Volume of water added = 200 ml

Let volume of aliquot taken from soil extract or water sample be V ml.

Volume of 0.1 (N) H<sub>2</sub>SO<sub>4</sub> required for the first titration (with phenolphthalein) = t<sub>1</sub> ml.

Total volume of H<sub>2</sub>SO<sub>4</sub> required = t<sub>2</sub> ml

(phenolphthalein plus methyl red)

Normality of H<sub>2</sub>SO<sub>4</sub> used = 0.01 (N) or N<sub>1</sub> (say)

Therefore meq. of H<sub>2</sub>SO<sub>4</sub> used in the first titration = N<sub>1</sub> × t<sub>1</sub>

meq. of H<sub>2</sub>SO<sub>4</sub> used (total) in the successive titration = N<sub>1</sub> × t<sub>2</sub>

Hence meq. of CO<sub>3</sub><sup>2-</sup> per 100 g of soil

$$= (N_1 \times t_1) \times \frac{200}{V} \times \frac{100}{40}$$

and mg of CO<sub>3</sub><sup>2-</sup> per 100 g soil

$$= (N_1 \times t_1) \times \frac{200}{V} \times \frac{100}{40} \times 30$$

Likewise, meq of HCO<sub>3</sub><sup>-</sup> per 100 g soil

$$= [(t_2 - t_1) \times N_1] \times \frac{200}{V} \times \frac{100}{40}$$

and mg of HCO<sub>3</sub><sup>-</sup> per 100 g soil

$$= [(t_2 - t_1) \times N_1] \times \frac{200}{V} \times \frac{100}{40} \times 61$$

**Note:** 1 ml of 0.01 N H<sub>2</sub>SO<sub>4</sub> = (0.01 meq H<sub>2</sub>SO<sub>4</sub>) = 0.00030 g CO<sub>3</sub><sup>2-</sup> = 0.00061 g HCO<sub>3</sub><sup>-</sup>]

Also meq. of CO<sub>3</sub><sup>2-</sup> per litre of soil extract or water sample

$$= (N_1 \times t_1) \times \frac{1000}{V}$$

and, meq of HCO<sub>3</sub><sup>-</sup> per litre of soil extract or water sample

$$= [(t_2 - t_1) \times N_1] \times \frac{1000}{V}$$

## Experiment No. 5

### **Objective: To determine the extractable calcium and magnesium in soil- Versenate (EDTA) method**

The Ca in solution is titrated with 0.01N EDTA using first the indicator ammonium purpurate (murexide) which at the pH of 12.0 change color from red to purple at the end point of titration. Ca + Mg in solution can be titrated with 0.01N EDTA using Erichrome Black T as indicator at pH 10.0 in the presence of Ammonium chloride-ammonium hydroxide buffer. At the end point color changes from wine red to blue or green. The Mg content is determined by the difference.

#### **Reagents required**

##### **For Ca determination**

- 0.01N Versenate (EDTA) solution: Dissolve 2.0 g of EDTA in distilled water and make the volume in to 1 liter volumetric flask.
- Sodium hydroxide (NaOH) (pH 10): 10 g of AR grade NaOH is dissolved in 90 mL of distilled water.
- Ammonium purpurate (murexide) indicator: 0.2 g of murexide is mixed with 40 g of powered potassium sulphate ( $K_2SO_4$ ).

##### **For Ca + Mg determination**

- 0.01N Versenate (EDTA) solution: Dissolve 2.0 g of EDTA in distilled water and make the volume in to 1 liter volumetric flask.
- Ammonium chloride-ammonium hydroxide buffer ( $NH_4Cl-NH_4OH$ ) (pH 10): Dissolve 67.5 g pure Ammonium chloride in 570 mL on conc. Ammonium hydroxide and made to 1 liter and adjusted to pH 10.
- Eriochrome black T indicator (EBT): Dissolve 0.5 g of EBT (Solochrome black) and 4.5 g of hydroxylamine hydrochloride AR grade in 100 mL of 95% ethyle alcohol.

#### **Procedure**

##### **Ca determination**

- Weight 10 g of soil sample in 150 mL conical flask, then add 50 mL of 1 N ammonium acetate solution and shake for 5 minutes, Filter through Whatman no. 1 filter paper.
- Pipette out 5 mL of soil extract in a porcelain dish (8 cm dia). Add about 25 mL distilled water to it.
- Add 5 mL of NaOH solution and then 50 g of murexide indicator, stirred well and the solution is titrated with standard 0.01 N EDTA till the color change from red to purple. The volume of EDTA used is noted.

##### **Ca + Mg determination**

- Same as Ca determination pipette out 5 mL of soil extract in a porcelain dish (8cm dia). Add about 25 mL distilled water to it.

- Add 1 mL of NH<sub>4</sub>Cl-NH<sub>4</sub>OH buffer solution and then 3-5 drop of EBT indicator, stirred well and the solution is titrated with standard 0.01 N EDTA till the color change from wine red to blue or green. The volume of EDTA used is noted.

### Mg determination

- The Mg content of the soil is determined from the difference between the contents of Ca + Mg and Ca.

### Calculations:

$$\text{Ca (me/L)} = \frac{\text{EDTA Used (ml)} \times \text{Normality of EDTA}}{5} \times 1000$$

$$\text{Ca (ppm)} = \text{Ca (me/L)} \times \text{equivalent wt. of Ca (20)}$$

$$\text{Ca+ Mg (me/L)} = \frac{\text{EDTA Used (ml)} \times \text{Normality of EDTA}}{5} \times 1000$$

$$\text{Ca+Mg (ppm)} = \text{Ca +Mg(me/L)} \times \text{equivalent wt. of Ca+Mg (32)}$$

$$\text{Mg (me/L)} = \text{Ca+ Mg (me/L)} - \text{Ca (me/L)}$$

$$\text{Mg (ppm)} = \text{Ca+ Mg (ppm)} - \text{Ca (ppm)}$$

### **Objective: To estimate the available potassium in soil by neutral normal ammonium acetate method (Hanway and Heidel, 1952)**

#### **Principle**

The readily exchangeable plus water soluble  $K^+$  is determined in the neutral normal ammonium acetate extract of the soil. The  $NH_4^+$  ion provides a sharp and quick separation from the exchange sites while other cations bring about a gradual replacement of either more or less amount of potassium which normally increases with the period of contact. Since,  $NH_4^+$  holds highly charged layers together just as K, the release of non-exchangeable K to exchangeable form is retarded during  $NH_4OAc$  extraction [Ammonium ions undergoes equilibrium fixation in the 2 : 1 layer silicates, particularly in the highly charged vermiculite interlayer spaces, in exactly the same way as  $K^+$ , by closure of the interlayer space. The ammonium ions thus fixed undergoes only slow exchange and is reluctant to nitrify,  $Na^+$  ions best replaces  $NH_4^+$  and  $K^+$  from slow exchange position]. Non-exchangeable K also has been found to contribute appreciably towards potassium availability to crops. The commonly used extractant for such purposes involve hot 1(N)HCl and boiling 1(N)HNO<sub>3</sub>. The procedure for determination involves either prior removal of exchangeable  $K^+$  or conditions made sufficiently vigorous to extract both exchangeable (including water soluble) and a portion of non-exchangeable forms from which the former is subtracted.

#### **Reagents required:**

- Neutral normal ammonium acetate solution; Dilute 60 ml glacial acetic acid (99.5%) and 75 ml concentrated ammonia solution (sp. gr. 0.91, 25%  $NH_3$ ) to one litre. Mix well, cool and adjust the pH to 7.0 with dilute acetic acid or ammonia solution.
- Potassium chloride solution : 1000 ppm stock solution; Dissolve 1.907 g of AR grade potassium chloride (dried at 60°C for 1 hr.) in distilled water and make up the volume to 1 litre.

#### **Procedure for potassium determination in soil**

- Weigh 5 g soil sample in a 25 ml conical flask.
- Add 25 ml of neutral normal ammonium acetate (pH = 7) and shake for 25 minutes.
- Filter immediately through a dry filter paper (Whatman No.1).
- Reject first few ml of the filtrate.
- Determine the potassium concentration in the extract flame-photometrically after necessary setting and calibration of the instrument.

#### **Standard curve for potassium**

- From the mother stock solution (1000 ppm K), prepare 2, 5, 10, 15 and 20 ppm K solutions in 50 ml volumetric flask by proper dilution.
- Construct the standard curve by plotting the flamephotometer readings along Y-axis and the different concentrations (ppm) along X-axis.

### Calculations

$$\text{Available K (Kg /ha)} = R - B \times \frac{25}{5} \times 2.24 = R \times 11.2$$

Where,

R = ppm of K in the extract, obtained from the standard curve (soil sample reading).

B = reading of blank sample (without soil)

### Interpretations

Low Potassium	Medium Potassium	High Potassium
< 135 Kg/ha	135 - 335 Kg/ha	> 335 Kg/ha

## Experiment No. 7

### Objective: Determination of exchangeable sodium in soil

#### Principle:

Sodium is readily excited in a flame producing an intense yellow light, the yellow colour is primarily due to radiation of 589.6 millimicron wavelength popularly known as D-line of sodium. Other less powerful radiations of different wavelength emitted are effectively blocked by a suitable yellow glass (Na-filter) allowing only the D-line emission to pass through. Thus, if a solution containing sodium ions is fed as a fine spray into a flame under controlled and standard instrumental conditions and the emitted light is passed through a Na-filter, the intensity of the D-line emission can be easily measured photoelectrically and related to the concentration of the sodium in the test solution. The flamephotometer is calibrated with a series of standard sodium chloride solution and then used to determine the unknown sodium concentration of the solution under analysis within the same range.

#### Procedure

- Analyze directly the ammonium acetate extract for Na<sup>+</sup> as same the K<sup>+</sup> in the flame photometer.

#### Standard curve for sodium

- Dissolve accurately weighed 2.542 g NaCl in distilled water and make up the volume to one litre. This gives 1000 ppm stock solution of Na<sup>+</sup>.
- From this prepare 1, 2, 3, 4, 5, 6, 7 and 10 ppm Na<sup>+</sup> by proper dilution.
- Adjust the gas and air pressures of the flamephotometer as per direction given in operation manual and set to appropriate filter.
- Adjust the flamephotometer reading to zero with blank (0 ppm) and 100 for the maximum (10 ppm).
- Construct the standard curve by plotting the flamephotometer reading along x-axis and concentrations along y-axis.
- Draw a mean line passing through the origin.
- From this graph obtain the sodium concentration of the sample under analysis in milliequivalents per litre or in ppm. If there is a dilution of the original sample, multiply by the dilution factor.
- Check the performance of the flamephotometer at frequent intervals by spraying some standard solutions and adjusting the sensitivity as necessary.

#### Calculations

$$\text{Exchangeable Na}^+ \text{ (ppm)} = R \times \frac{\text{volume of extractant}}{\text{weight of soil}}$$

where R = ppm of Na in the extract as obtained from the standard curve. R must include any dilution factor, if used.

also, 1 meq./l Na = 23 ppm Na

### Objective: Determination of cation exchange capacity of soil.

#### Principle

When a sample of soil is placed in a solution of a salt, such as ammonium acetate, ammonium ions are adsorbed by the soil and an equivalent amount of cations is displaced from the soil into the solution. This reaction is termed as 'cation exchange', and the cations displaced from the soil are referred to as 'exchangeable'. The surface-active constituents of soils that have cation-exchange properties are collectively termed as 'exchange complex' and consists for the most part of various clay minerals and organic matter. Soil mineral and organic colloidal particles have negative valence charges that holds dissociable cations and are thus called 'colloidal electrolytes. The cation exchange capacity determination involves measuring the total quantity of negative charges per unit weight of the material. Stated otherwise the total amount of exchangeable cations that a soil can retain is designated as the cation exchange capacity and is usually expressed as milliequivalents per 100 g soil or  $[\text{cmol}(\text{p}^+)\text{kg}^{-1}]$ . The determination of CEC is of fundamental importance in soil chemistry research. Adsorption, desorption and leaching of fertilizers, thermodynamic study of ion exchange; retention and release of nutrients, agrochemicals, soil pollutants, all depends upon the exchange capacity of the soil; CEC is also found to be an important parameter for soil classification. The cation exchange capacity is usually measured by leaching the soil or colloid with neutral normal ammonium acetate. Then the excess salt is removed by washing with 95% ethanol. The ammonium ion ( $\text{NH}_4^+$ ) is then determined by steam distillation with magnesium oxide in an alkaline medium. The ammonia evolved is adsorbed into a known quantity of the standard acid containing methyl red indicator and the excess acid back titrated with a standard alkali.

#### Reagents required:

- 1(N)  $\text{NH}_4\text{OAc}$  adjusted to pH = 7; Dilute 60 ml glacial acetic acid (99.5%) and 75 ml concentrated ammonia solution (sp.gr.0.91, 25%  $\text{NH}_3$ ) to 1 litre. Mix well, cool and adjust the pH of the solution to 7.0 with dilute acetic acid or ammonia solution. Alternatively, weigh 77.08 g  $\text{NH}_4\text{OAc}$  and dissolve in one litre distilled water and adjust the pH to 7 carefully with dilute acetic acid or ammonia solution.
- Ethanol 60%
- Ammonium chloride (AR)
- Magnesium oxide-carbonate free, freshly ignited (ignite at  $650^\circ\text{C}$  for 2 hours and cool in a desiccator over KOH pellets, store in tightly stoppered bottle)
- Standard  $\text{H}_2\text{SO}_4$  ; 0.1 (N)
- Standard NaOH ; 0.1 (N)
- Standard oxalic acid – 0.1 (N)
- Methyl red indicator
- NaOH; 45%
- Silver nitrate solution about 0.1 (M) : Dissolve 8.5 g  $\text{AgNO}_3$  in 500 ml water. Add 2 ml concentrated  $\text{HNO}_3$  and mix well.

## Procedure

- Transfer without loss 10 g of air dry soil sample accurately weighed in a 250 ml beaker and add 50 ml of neutral normal ammonium acetate solution.
- Stir occasionally for an hour cover with watch glass and leave overnight.
- Filter the contents through Whatman No. 44 filter paper receiving the filtrate in a 250 ml volumetric flask.
- Transfer the soil completely on to the filter paper and continue to leach the soil with 1(N) NH<sub>4</sub>OAc (using 20 ml at a time), allowing the leachate to drain out completely before adding a fresh aliquot.
- Continue the process, until the flask is full to the mark.
- Preserve this for estimation of exchangeable bases (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup> and Mg<sup>++</sup>). The residue left on the filter paper is intended for determination of cation exchange capacity of the soils.
- Wash the residue left on the filter paper with 60% alcohol to remove excess ammonium acetate. To ensure this add a pinch of solid NH<sub>4</sub>Cl to the residue on the filter paper and wash with alcohol till the filtrate is free from chloride (as tested with silver nitrate solution, the filtrate is perfectly clear when free from chloride). If the washing is to be interrupted such as for the night, attach a rubber tube to the tail of the funnel and pinch it tight with a clip when there is solution above the level of soil in the filter paper. i.e. in no case the soil should dry otherwise loss of ammonia may occur.
- Remove the soil with the filter paper into a 800 ml distillation flask and add about 200 ml of water and about 3 g MgO (one spoonful approximately).
- Add few glass beads and little liquid paraffin so as to avoid bumping and frothing during distillation.
- Pour 100 ml of 45% sodium hydroxide and immediately connect the distillation flask to the condenser and distill ammonia in a known excess of 0.1(N) H<sub>2</sub>SO<sub>4</sub> (say 25 ml) to which a few drops of methyl red indicator is added. (Continue distillation to collect about 150 ml distillate).
- Back titrate the excess of acid with 0.1(N) NaOH. Standardize NaOH versus oxalic acid and H<sub>2</sub>SO<sub>4</sub> versus standard NaOH.
- Perform a blank distillation without the soil on a similar volume of liquid.

## Calculations

CEC is normally expressed in milliequivalents of the cation per 100 g soil, presently as  $c \text{ mol}/(\text{pt}) \text{ kg}^{-1}$ . Milliequivalent means the equivalent weight expressed in milligrams. For instance 20 g of Ca<sup>2+</sup> represents 1 equivalent or 1000 milliequivalent Ca<sup>2+</sup>. Likewise 18 mg NH<sub>4</sub><sup>+</sup> would represent 1 milliequivalent (meq) of NH<sub>4</sub><sup>+</sup>.

Since 1000 ml of 1(N) acid or alkali = 1.0 g equivalent of any cation.

It follows that 1000 ml of 1(N) acid or alkali = 1000 milliequivalents of any cation.

Therefore, 1 ml 1(N) acid or alkali = 1 milliequivalents of any cation

$$\text{Cation exchange capacity} = \left[ (V_1 N_1 - V_2 N_2) \times \frac{100}{w} \right] c \text{ mol (pt) kg}^{-1}$$

Where,

$V_1$  = ml of standard acid taken initially for ammonia absorption

$N_1$  = normality of standard acid

$V_2$  = ml of standard base used in back titrating of excess acid

$N_2$  = normality of standard base

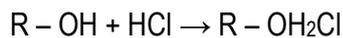
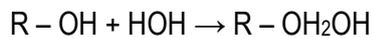
$w$  = weight of sample in g

## Experiment No. 9

### Objective: Determination of AEC in soil

Anion exchange capacity (AEC) is defined as the quantity of phosphate bound at pH 4 or 5.7. Many anions are often involved in anion exchange reactions viz.  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  etc. However, phosphate is usually very suitable for AEC estimation. Under low pH and high concentration, anions may be adsorbed and exchanged on soil colloids. The adsorption usually occurs on surfaces having a positive charge, viz. iron and aluminium hydroxides. The anion retention is related to the nature of anions and that of the soil surface together with amphoteric properties of organic colloids as well as iron and aluminium hydroxides. In highly acidic soil conditions phosphorus acid anions are retained directly on the surface of colloidal particles from the soil solution by adsorption phenomena. The mechanism of anion exchange may be illustrated as follows:

By the addition of a proton ( $\text{H}^+$  ion) to the  $-\text{OH}$  group linked to a sesquioxide clay particle (R) i.e.  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc.



By the addition of a proton to the functional groups of the organic fraction in acid soil



The study of AEC of soils helps in understanding the retention and release mechanism of important plant nutrient anions, viz. sulphate, phosphate, nitrate particularly in light textured soils of humid tropics.

### Principle

The method involves initial leaching of the soil with a solution of barium chloride- triethanolamine buffered at pH 8.1, followed by calcium saturation. The Ca-saturated soil is equilibrated with standard phosphoric acid solution and the quantity of phosphorus adsorbed is evaluated. From this adsorbed phosphorus plus phosphorus extracted initially the AEC of the soil is calculated using the formula.

AEC (meq./100 g soil) = [(extractable P + adsorbed P)] expressed as meq./100 g soil.

### Reagents required:

- Calcium chloride solution; Dissolve 50 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml of distilled water and adjust to pH = 8.0 with saturated  $\text{Ca}(\text{OH})_2$  solution.
- Triethanolamine solution; Dilute 90ml of triethanolamine to 100ml and adjust the pH to 8.1 with HCl. Dilute to 200ml and mix equal volume of distilled water containing 100g of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .
- Phosphoric acid solution [0.01 (M) in  $\text{H}_3\text{PO}_4$ ]
- Bray's (I) Reagent for P extraction [0.025(N)  $\text{NH}_4\text{F}$  in 0.03 (N) HCl].
- Dikman and Bray's reagent for colour development  $\text{KH}_2\text{PO}_4$ . stock solution of P for standard curve construction.
- Ethanol – 95%

## Procedure

- Weigh 10 g soil and leach with 100 ml of triethanolamine and wash 6 times with 95% ethanol.
- Leach the soil with 100 ml of CaCl<sub>2</sub> solution and wash again.
- Dry the calcium saturated soil at 45°C and weigh into a centrifuge tube sufficient to give a CEC of about 0.2 meq.
- Add 20ml phosphoric acid solution and shake for half an hour and let stand for 24 hours. Again shake for half an hour. Centrifuge and take 1 ml aliquot for P-estimation.
- In a separate soil sample, extract 'P' with Bray's reagent and determine 'P' colorimetrically using chloromolybdic acid reagent.

## Calculations

Weight of soil taken = 10 g

Volume of phosphoric acid solution added = 20 ml.

Volume of aliquot taken = 1 ml.

Let this 1 ml is made upto V ml. and concentration of P from standard curve = C ppm.

Hence first dilution =  $\frac{20}{10} = 2 \text{ times}$

Second dilution =  $\frac{V}{1} = V \text{ times}$

Total dilution = 2V times

Therefore, concentration of P in solution phase = (2 x C x V) ppm

Thus P adsorbed = [ P added (ppm) - 2 C.V ] = X ppm =  $\left[ \frac{X}{6.2 \times 10} \right] \text{ meq } 100g$

Also, extractable P = Y ppm =  $\left[ \frac{Y}{6.2 \times 10} \right]$

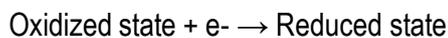
So, AEC (meq/100 g soil) =  $\left[ \frac{X+Y}{62} \right]$

### Objective: Measurement of redox potential (Eh) in soil

The reduction-oxidation status of a soil (redox potential) is used to characterize the degree of reduction or oxidation which is mainly related to the biological processes occurring in flooded soils under reduced conditions. The redox potential decreases as a consequence of soil flooding, followed by disappearance of soil O<sub>2</sub>. The aerated soils have redox potentials in the range of +400 to +700 mV. However, the seasonally flooded soils have a wider range of Eh as a result of prevalence of both oxidized (+400 to +700 mV) and reduced (as low as -250 to -300 mV) systems. The narrow range and poor reproducibility of Eh in well-drained (aerated) soils limit their practical applicability for characterizing aeration. The poor reproducibility is caused primarily by the lack of poisoning of the reduction-oxidation systems dominated by O<sub>2</sub>. The measurement of redox potential is mostly done for the flooded soils only.

### Principle

The Eh is measured by using platinum electrodes, as platinum is chemically inert but is an electrically conducting material. When a platinum electrode is introduced in the system, it registers the electron potential of the system which is measured in terms of voltage, produced across the cell, as a result of introducing a standard electrode of known potential in the soil-water system, nearby the platinum electrode. The voltage recorded in the pH meter is known as the redox potential. The electrode potentials are converted to the soil Eh by addition of 246 mV to account for the standard calomel electrode, relative to the standard hydrogen electrode. The redox potential for the reaction is given by:



At equilibrium, it is governed by the activity ratio of the reduced (Red) and oxidized (OX) couples, according to following (Nernst equation):

$$E_h = E_o + \left( \frac{RT}{nF} \right) \cdot \log \left[ \frac{ox}{Red} \right]$$

where, E<sub>o</sub> is the standard electrode potential; n is the number of electrons involved in the reaction; R is the gas constant; T is the absolute temperature and F is the Faraday constant; RT/F = 0.0593 at 25 °C.

If the activities of the oxidized and the reduced species are unity, the ratio becomes unity and consequently, E<sub>h</sub> = E<sub>o</sub>. Therefore, the standard redox (electrode) potential is defined as the E<sub>h</sub> of the system at which the activities of the oxidized and the reduced species are unity.

### Apparatus

- Platinum electrode,
- pH meter with a saturated calomel electrode,
- Beaker.

### Reagents required:

- (i) pH 4.0 buffer solution of quinhydrone in 0.1 M potassium hydrogen phthalate;
- (ii) 0.01 M CaCl<sub>2</sub> solution;
- (iii) 0.01 N HCl;
- (iv) 10% aqua regia.

### Procedure

- Attach a Pt-electrode to the glass electrode (plus terminal) of a pH meter having a millivolt scale and a saturated calomel electrode is connected to the negative terminal (to make a Pt-electrode, fuse both ends of the length of a Pt-wire into a glass tube, so that a loop extends beyond 3-4 cm).
- Add a few drops of mercury (Hg) inside the tube to make the electrical contact between the wire and the glass.
- Rinse the Pt-electrode, before each reading (not the reference electrode) in a 0.01 N HCl, followed by 10% H<sub>2</sub>O<sub>2</sub> and then rinse thoroughly with distilled water. Clean in aqua regia after a few hours of use.
- Adjust the potentiometer to read +210 mV when the electrodes are dipped in a buffer solution of pH 4.0.
- Add 30 mL of 0.01 M CaCl<sub>2</sub> to 10 g soil in a beaker. Stir until the soil and the solution are well mixed. Let it stand for 20 to 30 min with occasional swirling.
- Insert the electrode so that the reference electrode is in the upper half of the supernatant solution and the Pt-electrode is near the bottom of the suspension.
- Swirl for a few seconds, let it stand for at least 5 min without touching the cup, read  $E_o$  in mV.
- Measure the pH of the same suspension.

### Observations

Sample No.

- Observed redox potential,  $E$  (mV), of suspension:
- pH of the suspension.
- $E_h$  (mV)

### Calculations

$$E_h = (E_o + 246) + 60(R - 7)$$

where,  $E_h$ , is the value of the redox potential at pH = 7.0;  $E_o$ , is the observed potential in mV; 246 is the constant potential of the calomel half cell; 60 is the mV increase per pH at 25 °C and R is the pH of water sample or the suspension.

### Objective: Field measurement of redox potential (Eh)

The field measurements of Eh are widely used to estimate the intensity of oxidation or reduction of soils. This method is semi-quantitative but is used for predicting a number of important biogeochemical processes occurring in the soil such as activities of aerobic microorganisms at more oxidizing end to predictions of sulphate reduction and methane formation on the reducing end of the redox scale. The status of N, Mn and Fe systems can also be predicted from the properly measured redox potentials and pH values. The field measurements of redox potential can detect the aerobic and anaerobic conditions more rapidly than by any other measurement.

### Procedure

The redox potential measurements are made in the field using a portable pH/millivolt meter and a saturated calomel or silver/silver-chloride reference electrode. The method is as under:

- Push the reference electrode into the wet or moist soil to a short distance to ensure a good electrical contact.
- If the soil is relatively dry, break up a small volume of soil with a knife and add some water to form a paste and then install the reference electrode into it so as to provide a good contact with the soil solution.
- If the soil is dry or highly weathered, a dilute salt solution (i.e. 5 g KCl in 100 mL H<sub>2</sub>O) can be used to moisten the reference electrode hole and prevent the establishment of a junction potential between the reference electrode and the soil.
- Although the position of reference electrode in respect to the redox electrode may not be so critical, it is recommended to place the reference electrode within 2 m of the surface position of the redox electrode.
- Some reference electrodes may be submerged without problems, but it is preferred not to submerge the entire reference electrode where water is deep.
- If water is deeper than the length of the reference electrode, submerge only the working end of the reference electrode in the flood water.
- If the flooding is periodic, immerse the above-ground electrode lead, a thin film of salt or clay may coat the entire electrode lead after the water is receded. This coating may provide an additional electrical contact between the alligator clip attached to the top of the electrode and the soil surface, bypassing the platinum wire. To overcome this problem, the above-ground insulation on the electrode lead should be cleaned with a moist tissue and dried. It is very important to have a good electrical contact between the alligator clip and lead of the electrode. To ensure proper contact, gently scrap the exposed copper lead with a knife.
- A drift in the meter reading may be recorded when it is first connected to the electrodes in the field. If the electrodes are functioning properly, the rate of drift decreases rapidly within a couple of minutes. Now, the drift rate is low enough to record Ec reading (Ec is the direct meter reading using a calomel reference electrode).
- Well-poised soil systems tend to give minimal drift. This is typical of many reduced soils. The oxidized soils and surface waters tend to be poorly poised and often exhibit considerable drift for longer periods.

- Sometimes, it is necessary to wait for this drift to slow to a low rate before recording a value from the meter and often it is not necessary to wait. For example, if a meter reading is drifting upward after the Eh (corrected Ec reading) is above 450 mV, the system is clearly oxidized regarding all redox components of interest and likely to contain dissolved O<sub>2</sub> in the soil solution. Thus, for interpretation purposes, it is not necessary to wait longer for the drift to stop.
- If the Eh reading is in the range of +100 mV and drifting upward, or -100 mV and drifting downward, it is advisable to wait for the drift to attain a lower level before recording a reading. This is necessary as several redox active components (Fe, Mn, NO<sub>3</sub>) are transformed in the redox range of +100 to +350 mV. Thus, it is necessary to know the soil redox potential more precisely.
- Likewise, if a downward drift is noted from around -100 mV, it is useful to know if a soil is sufficiently reducing (about -150 mV) for reduction of sulphate (SO<sub>4</sub><sup>2-</sup>) to sulphide. If the electrodes are temporarily installed, it is advisable to leave them overnight before taking a reading.
- Generally, electrochemists use a standard hydrogen electrode (SHE) as the reference electrode for the measurements of electrode potential. In an electrochemical cell, the contribution of SHE has been defined as zero millivolts.
- For field or routine laboratory work, the use of SHE is not convenient. The reference electrodes such as the calomel or silver/silver-chloride are commonly used.
- To convert a redox potential meter reading using a calomel reference electrode filled with a saturated KCl solution (Ec) to a value that would be obtained had the SHE been used as a reference electrode (Eh), the meter readings are adjusted by adding 245 mV to the Ec value.
- If a silver/silver-chloride reference electrode is used, the correction added to obtain an Eh value would be +199 mV. Though the correction factor is temperature dependent, corrections for field temperatures are generally not made as the error involved from this source is relatively small compared to other inherent errors in the system.

### Interpretation

Redox potential (mV) (Corrected to pH 7.0)	Status of soil
-300 to -100	Highly reduced
-100 to + 100	Reduced
+100 to + 400	Moderately reduced
+400 to +700	Oxidized

If Eh=0 mV, it means that the system is:

- Devoid of O<sub>2</sub>, and NO<sub>3</sub><sup>-</sup>,
- Fe and Mn compounds are in a reduced state, and
- Sulphate is stable with no sulphide injury and methane production.

## Precautions

- The reduced conditions prevail when the soil is flooded or waterlogged for a certain period of time. The physicochemical environment of soil changes with the biological and chemical reduction of inorganic soil components. The oxidized components are reduced by facultative anaerobes only on depletion of  $O_2$ .
- The reduced  $NO_3^-$  and higher oxides of Mn occur at high redox potential, i.e. Eh between +200 and +300 mV. The reduction of hydrated ferric oxide occurs at intermediate redox potential of Eh between +100 and -100 mV, whereas the reduction of sulphate occurs at low redox potential, from -300 to -100 mV.
- The relative proportion of oxidized components in soil generally control its redox potential. The presence of nitrates along with higher oxides of Mn tend to maintain Eh above +200 mV, while the presence of a significant amount of hydrated ferric oxide maintains the anaerobic conditions. When ferric oxide content of soil becomes very low, as in the case of degraded rice soils, silica and hydrated ferric oxide are depleted. Under such conditions, the reduction of sulphates leads to the formation of  $H_2S$  which is toxic to rice plants.
- The reduction of higher oxides of Mn and Fe increases the concentration of soluble Mn and Fe in soil, leading to its higher uptake by the rice plant to the toxic level in some soils. There is an optimum Fe/Mn ratio for a higher yield of rice. A very high Fe/Mn ratio is not conducive for obtaining a high yield.
- Under moderately reduced conditions, the recovery of added nitrogen to rice is low because of the losses of nitrogen by denitrification. However, in some soils, in which reduced condition causes a significant reduction in crop yield, addition of nitrates is recommended not as a N-supplement but for preventing the Eh becoming low.

### Objective: To determine zero point charge (ZPC)

Zero point charge (ZPC) is the value of pH at which the total net charge is nil or zero. This is also termed as point of zero charge (PZC). At this point as the inter particle forces are inactivated, the particles flocculate and do not move when an electric field is applied (i.e. electrophoretic mobility is nil). ZPC is important in formation of soil aggregates and the retention of ions. If the soil pH is raised above ZPC value, the charge becomes negative for which the cation exchange capacity is increased. If the soil pH is decreased below ZPC value, the charge becomes positive for which the anion exchange capacity appears. Measurement of ZPC helps in predicting the response of the soil to modifications in environmental conditions by cultivation, use of fertilizers etc.

The method developed by Block and de Bruyn (1970) and experimented by the Hendershot and Laukulich (1979) is discussed here.

### Principle

The method is based on the indirect measurement of point of zero salt effect (PZSE) by potentiometric titration of the net absorption of  $H^+$  and  $OH^-$  at different pH and different ionic force. As certain colloids are amphoteric in nature, the curves intersect at a given pH where the adsorption of protons is independent of the ionic force. This point is named as PZSE.

### Materials required

#### A. Equipment and other materials

0.5 mm diameter sieve, 50 ml beakers (9 nos.), bar magnetic agitator, pipette, measuring cylinder, balance, pH meter in which an automatic titrimeter along with recording tape is connected to a combined electrode.

#### B. Reagent:

- I. NaCl (0.2 M): 11.688 gm NaCl is dissolved in distilled water and the volume is made up to 1 litre.
- II. NaCl (0.05 M): 2.922 gm NaCl is dissolved in distilled water and the volume is made up to 1 litre.
- III. NaCl (0.01 M): 0.5844 gm NaCl is dissolved in distilled water and the volume is made up to 1 litre. (iv) NaCl (0.001 M): 100 ml of 0.01 M NaCl is diluted to 1 litre with distilled water.
- IV. HCl (0.1 M): 8.6 ml concentrated HCl is diluted to 1 litre by distilled water.
- V. NaOH (0.1 M): 4 gm NaOH is dissolved in distilled water and the volume is made up to 1 litre.

### Procedure

- 2 gm of oven dry soil sieved through 0.5 mm diameter sieve (or equivalent amount of air dry soil) is taken in 50 ml of 8 no. beakers numbered from 1-8.
- 40 ml of 0.001 M NaCl is added to 1 and 2 no. beakers and each beaker is agitated with a bar magnet for 5 minutes without stopping.
- After that, the pH is measured. This pH corresponds to zero point titration (ZPT).

- In beaker no. 1 using an automatic titrimer connected to a combined electrode, the titration is started with 0.1 M HCl solution by regulating the additions to 1 drop in every two minutes and the pH value is recorded. The titration is continued until pH value becomes 3.0. The approximate time taken for this titration is 2 hours.
- In beaker no. 2 using an automatic titrimer connected to a combined electrode, titration is started with 0.1 M NaOH solution by regulating 1 drop in every two minutes and the pH value is recorded. The titration is continued until pH value becomes 9.5-10.0.
- 40 ml of NaCl in beaker no. 3 and 4, 40 ml of 0.05 M NaCl in beaker no. 5 and 6, 40 ml of 0.2 M NaCl in beaker No. 7 and 8 is added.
- Then after agitation with a bar magnet for 5 minutes pH is measured, titration is continued with 0.1 M HCl until pH becomes 3 and with 0.1 M NaOH until pH becomes 9.5 to 10.0 as stated above.
- A blank (reagents without soil) test is carried out in beaker no. 9 to correct the result if necessary.

### Observation and Calculation

- a. Weight of oven dry soil = 2 gm
- b. Volume of 0.001 M NaCl added = 40 ml
- c. pH value after agitation = ZPT =
- d. Figure of the recorded tape
- e.  $pH_o =$
- f. ZPC =
- g. Specific adsorptions

### Remarks

The  $pH_o$  value corresponds to a point of maximum chemical stability. The measurement can be done on untreated soil as well as on samples that have been subjected to pre-treatment by (a) saturation of soil by 1 M NaCl (b) destruction of organic matter by sodium hypochlorite (c) elimination of oxides and hydroxides. The results are concluded as follows:

#### On untreated soil

- I. If the pH measured in water is higher than that measured in KCl ( $pH_{H_2O} > pH_{KCl}$ ), ZPC is located below ZPT.
- II. If the pH measured in water is lower than that measured in KCl ( $pH_{H_2O} < pH_{KCl}$ ) ZPC is above ZPT.

#### On pre-treated soils

- I. Destruction of organic matter by hypochlorite shows the depression effect of organic matter on ZPC as compared to the untreated soil samples saturated in  $Na^+$ .
- II. Higher the content of oxides and hydroxides, higher is the ZPC.
- III. The presence of silica and organic matter results in relatively low values of  $pH_o$ .

### Objective: Determination of variable charge

The variable charges or net proton charges originate from iron and aluminium oxides, alumina silicates, organic matter, edge charges and charges of surface functional groups. These charges can be nil, positive or negative. The variable charges are sometimes measured by titration with an indifferent electrolyte at different ionic forces. The pH at which the curves intersect is the point of zero salt effect (PZSE), this being a particular case in which variable charges become invariable. At this point, the concentration of salts has no effect on the pH, but it is not necessarily equal to ZPC. As soil pH determines the magnitude of the net charge, the variable charges can be roughly estimated during measurement of  $pH_{H_2O}$  and  $pH_{KCL}$ . The intersection of the two curves gives  $pH_o$ . The variable charge is given by the difference in density of charges between soil  $pH_{H_2O}$  and  $pH_o$ .

The method described here was developed by Uehara and Gillman (1981). As variable charge is given by the difference in density of charges between soil  $pH_{H_2O}$  and  $pH_o$ , (i.e. the intersection point of the titration curves with variable concentrations), it is determined by drawing a graph between volumes of 0.1 M HCl / 0.1 M NaOH added against pH of the suspension. The graph enables the increase in the density of negative charges (i.e. variable charges) between soil  $pH_{H_2O}$  and  $pH_o$ .

### Principle

A given weight of soil sieved through 0.5 mm diameter sieve is taken in 15 numbered 50 ml numbered (1 - 15) beakers and the soil is thoroughly mixed with 10 ml of distilled water. Then increasing quantities of 0.1 M HCl solution is added to 1 - 7 numbered beakers and increasing quantities of 0.1 M NaOH solution is added to 9 - 15 numbered beakers making the final volume to 20 ml with distilled water. Beaker number 8 is control. The beakers are allowed to stand for 4 days agitating occasionally. After 4 days of equilibrium the  $pH_{H_2O}$  is measured. The variable charge is estimated from the difference in density of charges between  $pH_{H_2O}$  and  $pH_o$  (which is the intersection point of the titration curves with variable concentration) by drawing a graph between the volume of 0.1M HCl/0.1 M NaOH added against pH of the suspension. If necessary, correction is made with the blank value.

### Materials required

#### A. Equipment and other materials:

0.5 mm diameter sieve, 50 ml beakers (15 numbers), pipette, measuring cylinder, polythene sheet, balance, pH meter, rubber bands, glass rod.

#### B. Reagents:

- I. HCl solution (0.1 M): 8.6 ml conc. HCl is diluted to 1 litre by distilled water.
- II. NaOH solution (0.1 M): 4 gm NaOH is dissolved in distilled water and the volume is made up to 1 litre.
- III. Buffer for pH measurement.

## Procedure

- 4 gm of oven dry soil sieved through 0.5 mm diameter sieve (or equivalent amount of air dry soil) is taken in 50 ml of 15 beakers numbered from 1 to 15.
- 10 ml of distilled water is added to the beakers and the soil is mixed thoroughly with distilled water. Increasing quantities (ie. 0.50, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 ml) of 0.1 M HCl solution are added to 1-7 numbered beakers and increasing quantities e. 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 ml) of 0.1 M NaOH solution are added to 9 - 15 numbered beakers. Beaker number 8 is control.
- The volume is finally made up to 20 ml with distilled water. Each beaker is covered with polyethylene sheet bound by rubber band.
- The beakers are allowed to stand for 4 days agitating occasionally.
- The pH of all the beakers are measured and recorded.
- Then 1 ml of 2.1 M KCl solution is added in each beaker and allowed to stand for 3 hours with intermittent stirring (on addition of 1 ml of 2.1 M KCl to 20 ml soil suspension, the final concentration of the KCl soil suspension will be 0.1 M).
- After 3 hours, the pH of 0.1 M KCl suspension of each beaker is measured and recorded.
- A graph is drawn between volumes (ml) of 0.1 M HCl / 0.1M NaOH added against pH of the suspensions of H<sub>2</sub>O and 0.1 M KCl.

## Observations and Calculation

- Weight of oven dry soil = 4 gm
- Volume of water added = 10 ml
- Volume of 0.1 M HCl / 0.1 NaOH added = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 ml of 0.1 M HCl in 1 to 7 numbered beakers and 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 ml of 0.1 M NaOH in 9 to 15 numbered beakers. Beaker number 8 is control.
- The final volume of all beaker is made with distilled water = 20 ml.
- Volume of 2.1 M KCl added to each beaker = 1 ml
- Soil pH recorded

	Beaker number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pH <sub>H<sub>2</sub>O</sub>															
pH <sub>0.1 MKCl</sub>															

- A figure is drawn between the volume (ml) of 0.1 M HCl / 0.1 M NaOH added against pH of the suspension of H<sub>2</sub>O and of 0.1 M KCl. The intersection of the two curves i.e. pH<sub>o</sub> =
- Variable charge = Charge density at pH<sub>H<sub>2</sub>O</sub> - Charge density of pH<sub>o</sub>

### Objective: Determination of permanent charge

Permanent charges originate from the lattice structure of silicate clays due to isomorphous substitution by ions of different valence. In most of the cases permanent charge is negative. These charges are usually high in smectite type (2:1) clays and low in kaolinite type (1:1) clays and hydrous oxides. The method developed by Uehara and Gillman (1981) is used for determination of permanent charge in a soil.

### Principle

The determination of permanent charge in a soil is based on the absorption of ions at  $pH_0$ . At this point the absorption of cations and anions on surfaces are equal resulting nil density of the charge. Any excess adsorption of cations or anions at  $pH_0$ , constitutes a measure of the permanent negative charge and permanent positive charge respectively. For elimination of the specifically adsorbed ions and to render the medium homoionic, a pre-treatment of soil is carried out.

### A. Equipment and other materials Required:

0.5 mm diameter sieve, 50 ml beaker (15), pipette, measuring cylinder, polythene sheet, balance, pH meter, rubber bands, glass rod, 1000 ml conical flask, centrifuge.

### B. Reagents:

- I. KCl (1M): 149.12 gm KCl dissolved in distilled water and the volume is made up to 2 litre.
- II. KCl (0.2M): 14.912 gm KCl dissolved in distilled water and the volume is made up to 1 litre.
- III. KCl (0.1M): 0.7456 gm KCl dissolved in distilled water and the volume is made up to 1 litre.
- IV. KCl (0.002M): 200 gm of 0.01M KCl is diluted to 1 litre by distilled water.
- V. HCl (0.1M): 8.6 ml conc. HCl is diluted to 1 litre by distilled water.
- VI. KOH (0.1M): 5.6 gm KOH is dissolved in distilled water and the volume is made up to 1 litre.
- VII. NaOH (0.1M): 4 gm NaOH is dissolved in distilled water and the volume is made up to 1 litre.
- VIII.  $NH_4NO_3$  (0.5M): 40 gm  $NH_4NO_3$  is dissolved in distilled water and the volume is made up to 1 litre.

### Procedure

#### A. Preliminary treatment of soil

- This treatment is needed to eliminate the specific adsorbed ions such as  $SO_4^{2-}$ . For this 100 gm air dry soil already passed through 0.5 mm diameter sieve is taken in a 1000 ml conical flask.
- 500 ml of 1M KCl solution is added into the conical flask and it is shaken for few minutes in a reciprocating shaker.
- The pH of the suspension is adjusted to 7.5 with 0.1M KOH solution. The material of the flask is shaken for one hour in a reciprocating shaker.
- After shaking, it is allowed to stand for 1 hour and the supernatant is discarded.
- Again 500 ml of 1M KCl is added, the pH is adjusted to 7.5 with 0.1 M KOH solution, shaken for 1 hour, allowed to stand for 1 hour and the supernatant is discarded. This process is again repeated.
- The soil is washed with distilled water repeatedly until the conductivity of the liquid phase is equal to that of 0.0002 M KCl solution. This soil is dried in the air.

## B. Measurement:

- 4 gm previously treated soil (equivalent to soil dried at 105°C) is taken in 50 ml of 15 numbered beakers, numbered from 1 to 15 and the soil is thoroughly mixed with 10 ml of distilled water.
- Then increasing quantities of 0.1M HCl solution is added to 1 - 7 numbered beakers and increasing quantities of 0.1 M NaOH is added to 9-15 numbered beakers making the final volume to 20 ml with distilled water. Beaker number 8 is control.
- The beakers are allowed to stand for 4 days agitating occasionally. After 4 days of equilibrium the  $pH_{H_2O}$  is measured.
- Then 1 ml of 2.1M KCl is added in each beaker and  $pH_{KCl}$  is measured.
- The  $pH_o$ , is noted at the intersection point of titration curves with variable concentration by drawing a graph between volume of 0.1M HCl / 0.1M NaOH added against pH of the suspension
- If necessary, correction is made with the blank value [Saturation of K and elimination of the specifically adsorbed ions can modify the  $pH_o$  value as determined during estimation of variable charge].
- The soil residue is recovered. The beakers with the pH closest to  $pH_o$  are used for determination of the permanent charges. The residue soil is washed with 20 ml of 0.2M KCl solution and transferred in a 50 ml centrifuge tube.
- The tube is agitated for 1 hour and the supernatant is discarded.
- Then 20 ml of 0.01M KCl is added, agitated for few minutes and the pH is adjusted to the value closest to  $pH_o$  by using 0.1M HCl or NaOH solution.
- The tube is allowed to stand for 1 hour. After 1 hour o establishment of equilibrium it is centrifuged and the supernatant is drained out for analysis of  $K^+$  and  $Cl^-$ .
- The centrifuge tube containing the soil residue is weighed immediately after draining out of the supernatant to determine the value of 0.01M KCl solution retained by the soil. Let the value is V ml. The adsorbed  $K^+$  and  $Cl^-$  in the soil residue is removed by washing the residue soil five times with 20 ml of 0.5M  $NH_4NO_3$  solution through filtering.

## Observations and Calculations:

- I. Weight of soil taken = 4 gm
- II. Volume of KCl (0.2M and 0.01M) added = 20 ml
- III.  $K^+$  in the supernatant = A meq (Let)
- IV.  $Cl^-$  in the supernatant = B meq (Let)
- V. Volume of 0.01M KCl retained = V (Let)
- VI. Adsorbed  $K^+$  extracted into 100 ml of 0.05M  $NH_4NO_3$  = C meq (Let)
- VII. Adsorbed  $Cl^-$  extracted into 100 ml of 0.05M  $NH_4NO_3$  = D meq (Let)
- VIII. K adsorbed in soil [mmol(+) / kg] =  $(100 C - VB) \times 100/4 = X$  (Let)
- IX. Cl adsorbed in soil [mmol(+) / kg] =  $(100 D - VB) \times 100/4 = Y$  (Let)
- X. Permanent charge = Adsorbed  $K^+$  - Adsorbed  $Cl^-$  =  
=  $(X - Y)$  [mmol(+) / kg] or meq/100 gm soil.

**Remarks:** The sum of permanent charges and variable charges roughly corresponds to the cation exchange capacity of the soil measured by normal neutral ammonium acetate method.

## Experiment No. 15

### Objective: Determination of quantity – intensity (Q/I) relation of soil potassium

The Q/I relation of liable K relates the quantity (Q) of liable or immediately exchangeable K ion to its intensity (I) factor which is best measured as the chemical potential or the activity ratio of the potassium ion in the soil solution. Beckett (1964) gave the quantity - Intensity (Q/I) relation to obtain a clear picture of the potassium status of a soil. The potassium intensity in soil solution thus depends on the nature of the liable pool, the rate of release of fixed potassium and the rate of diffusion and transport of potassium ions in soil solution. Beckett estimated the immediate Q/I relationships for a number of soils and observed them to be linear over the activity ratios usually encountered. The form of immediate Q/I relationships regulates the uptake of potassium for short periods and also regulates the total potassium uptake. The potential buffering capacity of soil K, which is an intrinsic soil property, and which is not commonly affected by manuring and cropping can be known from Q/I relation of soil potassium.

### Principle

Under controlled temperature soil samples are shaken with aliquots contain varying concentrations of potassium (K) in calcium chloride ( $\text{CaCl}_2$ ) solutions of known strength in a given soil: solution ratio for a given length of time (usually for 12 hours). After equilibrating for 12 hours the solutions are filtered and potassium (K), sodium (Na), calcium (Ca), magnesium (Mg) and aluminium (Al) content in the filtrate are determined. For each suspension, the amount ( $\pm$  AK in meq/100 gm of soil) by which the exchangeable potassium content of the soil had changed is calculated from the difference between the potassium concentration of the initial and the resultant solutions. The activity ratios,  $a_k/\sqrt{a(\text{Ca}+\text{Mg})}$  of the resultant solutions were calculated using the Debye-Huckel equation modified by Guggenheim's (1950) expression for activity coefficients. The weighted average slope of the Q/I relationship curve is a measure of the potassium buffering capacity of soil potassium to maintain the potassium potential in soil solution.

### Materials required:

Flame photometer, horizontal shaker, volumetric flasks (50 ml), conical flasks (100 ml).

### Reagents:

#### I. Equilibrating solution of K (10 m mole/l) in 0.01 M $\text{CaCl}_2$ solution:

(a) Calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) solution (0.01 M): 1.47 gm of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  is dissolved in distilled water and diluted to 1 litre by distilled water.

(b) KCl (10 m mole K/l): 744.5 mg of KCl is dissolved in 0.01 M  $\text{CaCl}_2$  solution and the volume is made up to 1 litre by 0.01 M  $\text{CaCl}_2$  solution. This is a stock solution. From this solution various graded solutions like 0, 0.1, 0.2, 0.4, 1.0, 2.0, 3.0, 4.0 m mole K/l in 0.01 M  $\text{CaCl}_2$  solution are prepared.

#### II. EDTA and other solutions required for estimation of Ca + Mg

### Procedure

- 5gm of oven dry soil sieved through 20 mm diameter sieve (or equivalent amount of air dry soil) is taken in 100 ml of 8 conical flasks numbered from 1 to 8. 50 ml of each of the various graded potassium solutions like 0, 0.1, 0.2, 0.4, 1.0, 2.0, 3.0 and 4.0 m mol K/l is added to 1 to

8 number conical flasks respectively and the flasks are shaken for half an hour on a horizontal shaker and allowed them to equilibrate for 12 hours.

- The suspension is filtered and the filtrate of the equilibrium solution is analysed for K by flame photometer method and Ca + Mg by versenate titration method.
- In another set of experiment after addition of 50 ml of each of the various graded potassium solutions as stated above, it is thoroughly mixed with soil and then filtered and the filtrate is analysed for K by flame photometer and Ca + Mg by versenate titration method.
- The quality of loss (-AK) or gain (+AK) of K is calculated from the decrease or increase in concentration of K in the equilibrium solution, compared to the original or initial solution.
- A figure is drawn between + AK (on the y-axis) against the activity ratio (on the x-axis) [activity ratio is calculated by multiplying the concentration ratio by activity coefficient].
- The linear portion of the curve is extrapolated to the ordinate by drawing a tangent, from the point of abscissa where AK = 0.
- The curvilinear portion of the graph is also extrapolated to the ordinate.
- The slope of the linear portion of the curve is also measured.

### Observation and calculation

Parameters	Concentration of added K (m mol /l) in 0.1 M CaCl <sub>2</sub>															
	0		0.1		0.2		0.4		1.0		2.0		3.0		4.0	
	1		2		3		4		5		6		7		8	
	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii
(a) K Concentration																
(b) Ca+Mg conc.																
(c) Ionic strength																
(d) Act. Coeff. Of K																
(e) Act. Coeff. Of Ca and or Mg																
(f) Activity of K																
(g) Activity of Ca+ Mg																
(h) Activity ratio of K																
(i) Gain or loss of K																

### Parameters from Q /I plot:

- I. The concentration ratio (C.R. in mol/lit) is calculated by the following equation:

$$C.R.= \frac{K_E}{\sqrt{(Ca+Mg)_E}}$$

Where  $K_E$  = Potassium content of equilibrium solution in mol /l.

$(Ca+Mg)_E$ = Calcium plus magnesium content of equilibrium solution in mol/l.

- II. The activity ratio (A.R.) is calculated by multiplying the concentration ratio (C.R.) by activity coefficient.

$$A.R. = C.R. \times \frac{f_{K^+}}{[f_{(Ca^{2+}+Mg^{2+})}]^{-2}}$$

- III. Equilibrium activity ratio (AR, K in mol/lit): It is obtained from the intersecting point of the Q/I curve at the x-axis. Here K is neither gain nor loss (i.e.  $AK=0$ ). It is a measure of the intensity factor, I and is responsible for K nutrition of crops.
- I. Non-specific K ( $K_o$  in c mol (+)/kg): It is obtained by drawing a tangent from the point of ARe K axis where  $AK=0$ , i.e., by extrapolation of the linear part of the Q/I graph to the ordinate. It is that K held on non-specific planer sites of soil clays.
  - II. Specific K ( $K_x$  in c mol ( $P^+$ )/kg): It is obtained by subtraction of the non specific K from the liable K i.e.,  $K_x = K_1 - K_o$ . It is that K associated with specific sites.
  - III. Labile K ( $K_L$  in c mol ( $P^+$ )/kg): The curvilinear portion of the Q/I graph, extrapolated to meet the y-axis, gives the labile K which is a loosely held K.
  - IV. Potential buffering capacity ( $PBC^K$  in c mol/kg. mol<sup>-1/2</sup> l<sup>1/2</sup>): This is calculated as the linear slope of the Q/I curve i.e.,  $AQ/AI$ .
  - V. Potassium potential [ $K_o \times PBC^K$  in (c mol (+)/kg) mol/kg. mol<sup>-1/2</sup> l<sup>1/2</sup>]: It is the product of K held on non specific planer sites and the potential buffering capacity.

### Evaluation of the parameters from Q/I plot

Parameters	Concentration of added K (mol /l) in 0.1 M CaCl <sub>2</sub>															
	0		0.1		0.2		0.4		1.0		2.0		3.0		4.0	
	1		2		3		4		5		6		7		8	
	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii	i	ii
(a) C.R. in mol/lit																
(b) A.R.																
(c) AReK [in moles/lit]																
(d) $K_o$ [in c mol (+)/kg]																
(e) $K_x$ [in c mol (+)/kg]																
(f) $PBC^K$ [in c mol (+)/kg. mol <sup>-1/2</sup> l <sup>1/2</sup> ]																
(g) K-potential [(c mol (+)/kg mol <sup>-1/2</sup> l <sup>1/2</sup> )]																

**Interpretation:**

- (h) Higher the value of AReK, greater is the supply of K to crops.
- (i) Generally, higher the value of PBC<sup>k</sup>, greater is the capacity of soil to maintain K concentration for longer periods, although it often leads to low K intensity. A soil with a low value of PBC<sup>k</sup> needs frequent application of fertilizer as the soil fails to maintain K supply for a considerable period.
- (j) The deficiency and sufficiency or toxicity of potassium may be known from the value of K potential.

<b>K potential (kcal/mol)</b>	<b>Rating</b>
-4.0 to -3.5	Deficient in available K
-3.0 to -2.5	Adequate supply of available K
< -2.0	K-toxicity

## Experiment No. 16

### Objective: Determination of total potential soil acidity by BaCl<sub>2</sub> method

#### Principle

The total potential soil acidity includes all the acidity components including the weakly acidic R-COOH and R-OH groups on soil organic matter and partially neutralized Al-hydroxy polymers that may be present even in soils of pH > 7. The soil is leached with 0.5 (N) BaCl<sub>2</sub> and 0.055 (N) triethanolamine buffered at pH 8-8.2. This pH corresponds very nearly to the pH of complete neutralization of soil hydroxy-Al compounds. Barium ion effectively displaces the H<sup>+</sup> and Al<sup>3+</sup> ions and also causes hydrolysis of adsorbed Al-ions and dissociation of acidic R-COOH and R-OH groups, present in soil organic matter, which are neutralized by triethanolamine, which is a weak base. The leachate is titrated with a standard acid using bromocresol green- methyl red mixed indicator. A blank titration is also performed on the same volume of leachate.

#### Reagents

- 1(N) BaCl<sub>2</sub> solution
- 0.2 (N) HCl
- Buffer extractant of 0.5(N) BaCl<sub>2</sub> plus triethanolamine (pH 8-8.2); Dilute 25 ml of triethanolamine (sp.gr.1.126, normality 8) to 250 ml with water and adjust the pH to 8.0-8.2 with HCl (approx.90 ml 1(N) HCl is required for this partial neutralization process). Dilute the solution to 500 ml and then mix with 500 ml of 1(N) BaCl<sub>2</sub> solution. The final solution must be kept free of CO<sub>2</sub>.
- Bromocresol green-methyl red indicator; Dissolve 0.5 g bromocresol green and 0.1 g methyl red in 100 ml of 95% ethanol and adjust the pH to 4.5.

#### Procedure

- Weigh 10 g soil and take it in a 250 ml conical flask.
- Add 100 ml of extracting buffer solution and shake for half an hour and keep for overnight.
- Transfer the contents to a buchner funnel fitted with a Whatman No. 42 filter paper and carry out gently suction filtration.
- Rinse the conical flask with additional extracting solution so that no soil particle is left over in the flask.
- Now, transfer the leachate to a 250 ml volumetric flask and make up the volume with the extracting solution.
- Pour the leachate into a conical flask and add a few drops of mixed indicator into it. Titrate with 0.2 (N) HCl until the end point colouration (pink) is obtained.
- Perform a blank keeping all conditions identical excepting soil.

### Calculations

Let Volume of 0.2(N) HCl required for blank titration = B ml

Volume of 0.2(N) HCl required for sample titration = S ml.

Hence, meq. of total potential acidity =  $(B - S) \times 0.2$

Now 10 g soil has total potential acidity =  $[(B - S) \times 0.2]$  meq.

So 100g soil has total potential acidity =  $\left[ \frac{(B-S) \times 0.2 \times 100}{100} \right] meq$

Thus, total potential acidity  $[2 (B-S)] meq/100g$

### Objective: Determination of lime requirement of soil.

For satisfactory plant growth, the soil should have a pH between 6.5 to 7.5, though certain plants can grow well at low pH like tea and also at high pH like sugarbeet. In India acid soils are located mostly in eastern, southern and south central parts. Also some soils at higher elevations in north India are acidic. For sustained agricultural production and higher yields, through efficient soil management practices, it is essential to lime and acid soil, as it has considerable influence on soil environment, besides correcting soil acidity.

### Principle

In this method the soil is equilibrated with a pH 7.5 buffer solution, whereby the reserve  $H^+$  is brought into solution, which results in the depression of pH of the buffer solution, a note of which is made and interpreted in terms of lime required to raise the pH to a desired value.

### Reagents

Extractant buffer; Dissolve 1.8 g paranitrophenol, 3 g potassium chromate, 2 g calcium acetate, 53.1 g calcium chloride dihydrate ( $CaCl_2 \cdot 2H_2O$ ) and 2.5 ml triethanolamine in 1 litre of distilled water. Adjust the pH to 7.5 with NaOH.

### Procedure

- Determine the pH of the soil sample in 1 : 2.5 soil:water ratio.
- For this weigh 10 g soil and add 25 ml distilled water.
- Shake intermittently for half an hour and record the soil pH. If the pH exceeds 6.0 then this method is not applicable.
- If the measured pH is 6.0 or low then proceed as follows:
- Weigh 5 g soil in a 50 ml beaker.
- Add to it 5 ml of distilled water and 10 ml buffer solution.
- Stir continuously for 10 minutes or intermittently for 20 minutes.
- Determine the soil pH with the pH meter.
- Lime requirement is determined on the basis of soil-buffer pH ready reckoner given below.

The values in this table are given in tons of pure  $CaCO_3$  per acre required to bring the soil to the indicated pH and thus are required to be converted to their equivalents in the form of agricultural lime to be used. The figures are multiplied by a factor of 2.43 to express in tons per hectre.

<i>pH of soil- buffer suspension</i>	<i>Lime required to bring the soil to indicated (tons/acre of pure CaCO<sub>3</sub>)</i>		
	<i>pH 6.0</i>	<i>pH 6.4</i>	<i>pH 6.8</i>
6.7	1.0	1.2	1.4
6.6	1.4	1.7	1.9
6.5	1.8	2.2	2.5
6.4	2.3	2.7	3.1
6.3	2.7	3.2	3.7
6.2	3.1	3.7	4.2
6.1	3.5	4.2	4.8
6.0	3.9	4.7	5.4
5.9	4.4	5.2	6.0
5.8	4.8	5.7	6.5
5.7	5.2	6.2	7.0
5.6	5.6	6.7	7.7
5.5	6.0	7.2	8.3
5.4	6.5	7.7	8.9
5.3	6.9	8.2	9.4
5.2	7.4	8.6	10.0
5.1	7.8	9.1	10.6
5.0	8.2	10.1	11.2
4.9	8.6	10.6	11.8
4.8	9.1		12.4

### Objective: Determination of gypsum requirement of soil

#### Principle

Presence of large amount of sodium as high as 15% or more in the exchange complex results in high soil pH (> 8.0) for sodic (alkali) and saline-sodic soils which causes nutritional imbalances, depletion of soil organic matter, deterioration of soil physical health and also affects the soil biotic community. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is commonly used for soil amendment under such situation. A fixed weight of soil is equilibrated with a known amount of Ca solution, and the amount of Ca left in solution is determined by EDTA-titration. The difference between the amount of Ca added and Ca left in solution, gives the amount of Ca exchanged. Practically it has been observed that gypsum addition of about 1/3 of the value obtained by this method is satisfactory in most cases.

#### Reagents

- Ammonium chloride–Ammonium hydroxide buffer ; Dissolve 67.5 g of  $\text{NH}_4\text{Cl}$  in 570 ml of  $\text{NH}_4\text{OH}$  (sp.gr.0.86), and dilute to 1 litre.
- Saturated  $\text{CaSO}_4$  solution; Shake about 5 g  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  with 1 litre of distilled water for 15 minutes on a mechanical shaker and filter.
- Eriochrome Black T (EBT) indicator; Dissolve 0.5 g of EBT and 4.5 g of hydroxylamine hydrochloride in 100 ml of 95% ethanol.
- Standard EDTA solution 0.01N; Dissolve 2 g of disodium dihydrogen-ethylene-diamine- tetra acetate and 0.05 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in water and dilute to 1 litre. Standardise against standard Ca-solution.

#### Procedure

- Weigh 5 g of soil sample in a 250 ml conical flask, and add 100 ml of saturated  $\text{CaSO}_4$  solution.
- Shake for 5 minutes on a mechanical shaker and filter.
- Pipette out 5 ml of the extract into a 100 ml conical flask and dilute to about 25 ml with distilled water.
- Add 0.5 ml of the  $\text{NH}_4\text{Cl}$ - $\text{NH}_4\text{OH}$  buffer and 3-4 drops of the EBT indicator.
- Titrate with the standard EDTA solution until the colour changes from wine red to blue.
- Titrate in a similar way 5 ml of the saturated  $\text{CaSO}_4$  separately.

#### Calculations

Weight of soil taken = 5 g

Total volume of extract = 100 ml

Let volume of EDTA used for titration of x ml of gypsum solution be A ml (say) and volume of EDTA used for titration of y ml of sample aliquot be B ml (say)

Therefore, meq. of Ca/l in gypsum solution

$$= \left( \frac{A}{x} \right) \times 0.01 \times 1000 = P \text{ meq/l}$$

Meq. of Ca/l in sample solution

$$= \left( \frac{B}{Y} \right) \times 0.01 \times 1000 = Q \text{ meq/l}$$

Total meq. of Ca remained in soil after addition of 100 ml gypsum

$$= \left( \frac{(P-Q) \times 100}{1000} \right) = 0.1(P - Q)$$

Now 5 g soil contains  $0.1 \times (P - Q)$  meq

Hence 100 g soil contains  $\frac{0.1 \times (P-Q)}{5} \times 100 \text{ meq}$

$$= [ 2 \times (P - Q) ] \text{ meq/100 g}$$

Thus 1 kg soil requires  $[20 \times 20 \times (P - Q)] \text{ mg Ca}$

$$= 400 \times (P - Q) \text{ mg Ca.}$$

2.24 million kg soil requires  $\frac{400 \times (P-Q) \times 2.24 \times 10^6}{10^6}$

$$= 896 (P - Q) \text{ kg Ca}$$

Now 40 kg Ca is obtained from 172 kg gypsum

So,  $[896 \times (P - Q)] \text{ kg Ca}$  is obtained from  $\frac{172 \times 896 \times (P-Q)}{40 \times 1000}$

$$= [ 3.85 (P-Q) ] \text{ tons of gypsum}$$

Thus gypsum requirement of the soil =  $[3.85 \times (P - Q)] \text{ tons/ha.}$