Practical Manual

MANAGEMENT OF PROBLEM SOILS AND WATERS

APS 513 2(1+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

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CONTENT

Exercise No. 1

Objective: Preparation of soil saturated paste and saturation extract

Principle:

The saturation percentage (SP) equals the weight of water required to saturate the pore space divided by the weight of the dry soil. Saturation percentage is useful for characterizing soil texture. Very sandy soils have SP values of less than 20 percent; sandy loam to loam soils have SP values between 20 and 35 percent; and silt loam, clay loam and clay soils have SP values from 35 to over 50 percent. Also, salinity measured in a saturated soil can be correlated to soil salinity at different soil-water contents measured in the field. As a general rule, the SP soil-water content is about two times higher than the soil-water content at field capacity. Therefore, the soil salinity in a saturation extract is about half of the actual concentration in the same soil at field capacity.

Therefore, mixing of soil with water to make the saturation paste as suggested by United State National Resources Planning Board (1942) and adapted by U.S. Salinity Laboratory Staff (1954) was also found most suitable for extracting the salt from soil for salinity appraisal and other uses.

Procedure:

This exercise is divided in two parts viz. **A.** Preparation of saturation paste and **B.** Preparation of saturation extract. The description is given here-

A. Preparation of saturation paste:

1. Weigh 100 g air dried and processed soil sample in a 250 ml Plastic Beaker.
2. Fill the burette with distilled water.
3. Add known volume of distilled water to the soil while stirring with spatula.
4. Consolidate the soil water mixture time to time by gentle tapping the moisture box on the working table.
5. At saturation, soil paste glistens as it reflects light and fall freely when the spatula with saturated soil is tapped.
6. At this stage mix the sample again and keep for one hour.
7. After one hour, if glistening disappears then again add more distilled water and prepare saturated paste.
8. Note the final burette reading.

Observation:

1. Weight of soil: _____g
2. Volume of distilled water used for preparation of saturated paste: _____ml
3. Saturation percent of soil (SP):_____%

$$SP = \frac{Total\ weight\ of\ water}{Weight\ of\ the\ oven\ dry\ soil}\ x\ 100$$

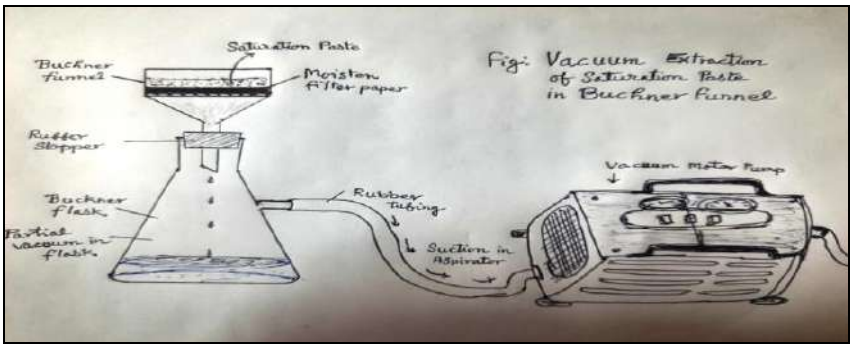


Fig: Vacuum Extraction of Saturation Paste in Buchner Funnel

Fig. Vacuum extraction of saturation paste in Buchner funnel

B. Preparation of saturation extract:

1. Place the filter paper on the Buchner funnel
2. Keep the Buchner funnel on the filter flask and connect it with vacuum pump.
3. Transfer the saturation paste into the Buchner Funnel.
4. Start the vacuum extraction of paste by starting the vacuum pump.
5. Collect the saturation extract in the filter flask.
6. Stop vacuum extraction if air begins to pass through filter paper.
7. Transfer the saturation extract in the volumetric flask after knowing its volume.

Precautions:

1. Do not use Pyrex glass if boron is to be determined.
2. Add 1000 ppm sodium hexametaphosphate solution @ 1 drop per 25 mL of extract before stoppering and storing, if CO_3^- and HCO_3^- are to be determined.
3. If soil contains more amount of free gypsum, allow to increase the EC up to 1-2 mmhos/cm (dSm^{-1}) standing the extract for several hours.
4. For salinity appraisal, extract few minutes after the preparation of saturation paste.
5. For the estimation of chemical constituents keep the saturation paste for 4-16 hours before extraction.

Exercise No. 2

Objective: Determination of pHs of saturation extract and soil water suspension

Principle:

The pH is a very important property of soils as it determines the availability of nutrients, microbial activity and physical condition of the soil. pH is the negative logarithm of the hydrogen ion activity; in very dilute solutions pH be expressed as concentration, in gram mole per liter.

$$pH = \log 10\ 1/a^{H+} = -\log_{10} a^{H+}$$

Soil pH below 7, the H^+ concentration exceeds OH- and the range is acidic. When OH- concentration is more than H^+ pH lies between 7 to 14 and the range is alkaline. pH is a sort of voltage measurement and to cover the entire range 0-14. A potential measurement in the range of +420 to -420mv is needed since a potential difference of 59.1 mv is developed for a difference of one pH unit. The pH of water and soil could not harm the plant growth directly. pH highly affects the efficiency of coagulation and flocculation process.

The pH of the saturated soil paste has been widely recognized as an index to distinguish alkali soils from the normal and/or saline soils. In normal and saline soils, the pH_2 values are usually higher than pHs by 0.2-0.5 units. The most striking difference being in alkali soil where pH_2 values may be higher than pHs by about 1.0 unit.

Procedure:

Saturation paste is prepared by adding distilled water to the soil and mixing till it starts glistening and slides on spatula as taken in 250 ml clean beaker as in earlier exercise number. The 1:2 soil water suspensions are prepared by taking 20 g soil and 40 ml distilled water in 100 ml beaker. The suspension is shaken at regular intervals for half an hour. The pH of the suspension should not be treated as pHs (pH of the saturation paste).

Allow the pH meter to warm for 10 minutes before recording pH. Adjust pH meter at room temperature and calibrated by known pH of buffer solutions of pH 4.0, 7.0 and 9.2. Take the beaker of saturation paste and dip the electrodes into it and note the pH reading. After each determination the electrodes must be washed with distilled water and wiped out by ordinary filter paper.

Take10-20 ml saturation soil extract into a very small beaker (50ml). Insert calibrated glass electrode into the extract and pHs can be measured. It requires saturation and extraction of 400–500 g soil.

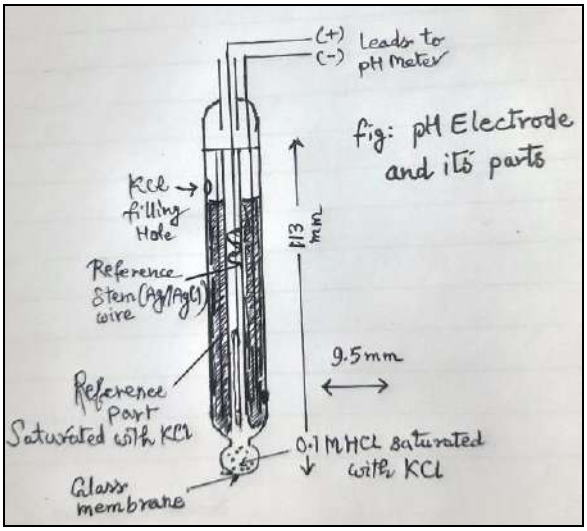


Fig: Glass electrode and pH meter

Precautions:

i. Soil water suspension should be shaken well intermittently for 30 minutes.
ii. The glass and reference electrode of pH meter should always remain dipped in water.
iii. Buffer solutions should be prepared accurately and stored well in glass container. It is desirable to prepare fresh buffer solutions after few days.
iv. Connect the pH meter to the stabilizer to avoid the fluctuations in pH readings.
v. Adjust the temperature knob of pH meter at room temperature for correct pH determination.

Interpretation of results of soil pH:

Rating:

<4.5 very strongly acidic; 4.5-5.5 strongly acidic; 5.5-6.5 slightly acidic; 6.5-7.5 Neutral Suitable for crop growth, 7.5-8.5 slightly alkaline, 8.5-10.0 strongly alkaline; >10.0 very strongly alkaline.

Interpretation: acidic soil needs lime; alkaline needs gypsum

Observations: Reading of pH meter is_____

Result: pH of saturation paste / 1:2 soil water suspensions is_____

Exercise No. 3

Objective: Determination of soil pH in 0.01M $CaCl_2$ solution.

Principle:

Standard measurement of soil pH in $CaCl_2$ is probably most commonly used method. As mentioned by Peech (1965), Davey and Conyers (1988) and Conyers and Davey (1988), the use of $CaCl_2$ has some advantages for pH measurement.

1. The pH is not affected within a range of the soil to solution ratio used.
2. The pH is almost independent of the soluble salt concentration for non saline soils.
3. This method is a fairly good approximation of the field pH for agricultural soils.
4. Because the suspension remains flocculated, errors due to liquid junction potential are minimized.
5. No significant differences in soil pH determination are observed for moist or air dried soil. and
6. One year of storage of air dry soil does not affect the pH.

Reagent:

Calcium chloride 0.01M: Dissolve 2.940g of Calcium Chloride dihydrate $CaCl_2 2H_2O$ with double distilled water in a 2 litre of volumetric flask. The electrical conductivity of the solution must be between 2.24 and 2.40mS cm^{-1} at 25°C.

Procedure:

Weigh 10 g of air dried mineral soil (<2mm) or 2 g of organic soil into a 30 ml beaker and add 20 ml of 0.01 $CaCl_2 2H_2O$. Note the solution soil to solution ratio used. Include duplicate quality control sample in each batch. Stirr the suspension immediately for 30 minutes. Let stand for about 1 hour. Immerge a combined electrode into the clear supernatant and record the pH once the reading is constant. Note both the glass membrane and the porous Salt Bridge must be immerged.

Comments:

The pH and electrical conductivity of the $CaCl_2$ should be fairly constant i.e. pH in the range of 5.5-6.5 and the electrical conductivity around 2.3mS cm^{-1} at 25°C if the pH is outside of this range , it should be adjusted with HCl or $Ca(OH)_2$ solution. If the electrical conductivity is not within the acceptable range, a new solution must be prepared.

Result: Soil pH in $CaCl_2$ solution is _____.

Exercise No. 4

Objective: Determination of EC of saturation extract and soil water suspension

In general, there are two extraction methods used for soil salinity are saturated paste (SP) extract and soil-water extracts ($EC_{1:2.5}$, $EC_{1:5}$). Soil salinity determination using a measurement of $EC_{1:2.5}$ generally preferred because it is a simpler procedure than the standard saturated paste extract (EC_e). The EC of SP extract (EC_e) is recommended as a standard laboratory method for estimating the EC of soil and considered to be the best indicator of plant response to salinity compared with more dilute soil-water extractions. However, unlike the SP extract method, soil-water extracts are less connected to natural soil conditions.

Principle:

Amount of total soluble salts (salinity) in a sample is generally expressed in terms of its electrical conductivity. It is measured with the help of EC meter works on Ohm's law. The most common unit of EC is dSm^{-1} (deci Siemen per meter) which is equal to milli mhos/cm (older unit). Specific conductance or electrical conductivity is the conductance 1 cubic cm of solution measured between 2 electrodes placed 1 cm apart. It is expressed in m Mhos cm^{-1} or dSm^{-1}.

$$1\ dSm^{-1} \times 100 = 1 \text{ milli Siemens } m^{-1}$$

$$\text{Percentage of soluble salts in soil} = 0.064 \times EC \times SP/100$$

Where, SP the saturation percentage of soil and EC in dSm^{-1}.

$$\text{Salt content in mg/L (ppm)} = EC\ dSm^{-1} \times 640$$

$$\text{Osmotic pressure (atm)} = EC\ dSm^{-1} \times (-0.36)$$

Comment:

A saline or saline-alkali soil can be identified from its EC values. The increased values of soil EC confirm increase in soluble salt content in soil. Since the EC depends on the number of ions in the solution, it is important to know the soil/water ratio used. The EC also is dependent on the temperature of water. Thus, the measurement of EC at 25°C temperature is considered as reference. The EC of irrigation water also affects the plant growth.

As determining the EC of soil solution from a saturated soil paste is cumbersome and requires 400–500 g of soil sample for the determination, a less complex method is normally used. Generally, a 1:2.5 soil/water suspension is used for EC.

Apparatus required:

EC meter; physical balance, some beakers (100 ml), thermometer; filter paper.

Reagent required:

To prepare the standard (0.01N potassium chloride solution), dissolve 0.7456 g of AR-grade KCl (dried at 60°C for 2 hrs in oven) to in freshly prepared 1 litre distilled water. This solution has an EC of 1.4118 dSm^{-1} at 25°C.

Procedure:

Place 40 g of soil in a 250-ml Erlenmeyer flask, add 100 ml of distilled water, and shake on mechanical shaker for 1 hour. Filter through No. 1 filter paper. Wash the conductivity electrode with distilled water, and rinse with standard KCl solution. Pour some KCl solution into a 25-ml beaker, and dip the electrode in the solution. Adjust the conductivity meter to read 1.412 mS/cm, corrected to 25°C. Wash the electrode, and dip it into the soil extract. Measure the conductance. Note filtrate temperature by a thermometer. The conductance is EC of soil suspension multiplied with the temperature correction factor (Appendix…) and cell constant.

Cell constant = 1.4118/ Observed conductivity of KCl solution

Similarly, EC of saturated soil extract can be measured requires saturation and extraction of 400–500 g soil.

General interpretation of EC values:

Soil	EC (dS/m)	Total salt content (%)	Crop reaction
Salt free	0-0.2	< 0.15	Salinity effect negligible, except for more sensitive crops
Slightly saline	0.4–0.8	0.15–0.35	Yield of many crops restricted
Moderately saline	0.8–1.5	0.35–0.65	Only tolerant crops yield satisfactorily
Highly saline	> 1.5	> 0.65	Only very tolerant crops yield satisfactorily

Crop response:

That tolerance of plants to soil salinity also differs from one plant to another. A 50% decrement of yield on saline soil from that on non-saline soil reported. The Horticulture plants except date palm, all pulse crops are sensitive to salinity (ECe 1.5 – 3.0 dSm^{-1}); sunflower, groundnut, maize, sugarcane and rice are the semi tolerant crops (EC_e 3-5 dSm^{-1}) and cotton, sorghum, pearl millet, wheat, barley, mustard, safflower and sugar beet fall in the tolerant group (EC_e 5-10 dSm^{-1}). Amongst vegetable crops, kale,

asparagus, spinach are tolerant; tomato, broccoli, cabbage, cauliflower, lettuce, potato, carrot, onion, pea, squash and cucumber are semi tolerant; radish, celery and garden bean fall in the sensitive group.

Results: EC of soil saturation extract ----------and soil water suspension----------

Exercise No. 5

Objective: Determination of cation exchange capacity in given soil sample

Principle:

Cation exchange capacity in calcareous or non calcareous soil is preferably determined in 1 N ammonium acetate extract. CEC determined by saturation of soil with index cation (NH_4^+), removal by washing of excess cation, and subsequent replacement of the adsorbed cation by another cation (Na) and measurement of the index cation (NH_4^+) in the final extract (Richards, 1954).

Apparatus:

Flame photometer, Mechanical shaker and Centrifuge and centrifuge tube (50ml).

Reagents:

1. Sodium acetate solution (CH_3 COONa; Mol. Wt.136 = 12+3+12+32 +23 + 54) 1.0N: Dissolve 136g sodium acetate trihydrate in 950 ml distilled water and adjust pH approx. 8.2 by adding dilute acetic acid or sodium hydroxide to a volume of 1 litre.
2. Ethanol 95% or methyl alcohol
3. Ammonium acetate (NH_4OAc) 1.0M: Dissolve 77.09 g of ammonium acetate in dist. water and dilute to approx. 900 ml. Adjust pH to 7.0 with dilute ammonium hydroxide or acetic acid as required and make up the volume to 1litre.

Procedure:

Take 5.0 g of soil in 50 ml centrifuge tube. Add 25ml sodium acetate solution (1.0N), stopper tube and shake for 5 minutes. Remove stopper from tube and centrifuge at 2000 rpm approximately 10 minutes or until supernatant liquid is clear. Decant the supernatant as completely as possible and discard. Repeat the sample in this manner with 25 ml of sodium acetate 1.0N four times. Discard the supernatant each time. Add 25 ml 95% ethanol to the tube, stopper shake for 5 minutes remove the stopper and centrifuge until the supernatant clear (5minutes) Decant and discard the supernatant liquid. Wash the sample with 25 ml ethanol 3 times. Add 25 ml of 1.0 N sodium-acetate to the centrifuge tube stopper and shake for 5 minutes. Remove stopper from tube and centrifuge at 2000rpm approximately 10 minutes or until supernatant liquid is clear. Decant the supernatant liquid as possible as in 100 ml

volumetric flask. Repeat this extraction three times decanting into the same flask. This way ammonium ion will replace sodium ions which will come in the supernatant liquid. Dilute the liquid of volumetric flask up to volume and determine sodium concentration by flame photometer (As given below).

Observation:

Record reading for sodium solution as given exchangeable CEC determination.

Calculations:

$$\text{CEC in me/100g} = \frac{\text{Na conc. of extract in me/L}}{\text{Wt. of soil in g}} \times \frac{\text{volume of extract (ml)}}{1000}$$

$$= \frac{\text{Na conc.of extract in me/L (100)}}{\text{Wt. of soil in g}} \times \frac{\text{volume of extract (100 ml)}}{1000}$$

$$= \frac{\text{Na conc.of extract in me/L X 10 ml}}{\text{Wt. of soil in g}}$$

$$\text{CEC in me/100 g soil} = \frac{X}{\text{Wt. of soil in g}} \times 10 \text{ ml}$$

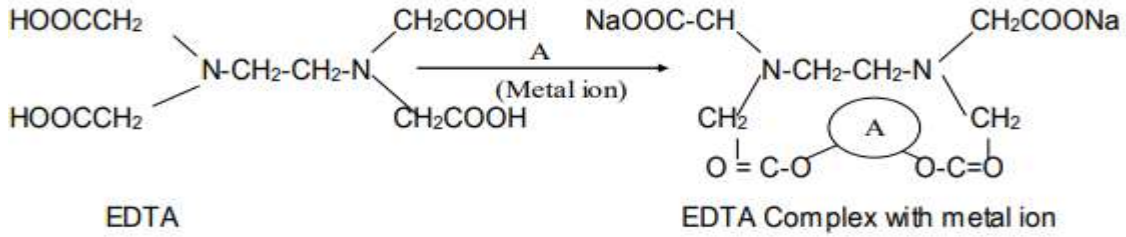
Where X is conc. of Na obtained in flame photometer.

Exercise No. 6

Objective: Determination of calcium by the versenate (EDTA) method in soil or irrigation water

Principle:

A known volume of the solution is titrated with standard versenate 0.01 N solution using murexide (ammonium purpurate) indicator in the presence of NaOH solution. The end point is a change of colour from orange red to purple at pH 12 when the whole of calcium forms a complex with EDTA.



EDTA EDTA Complex with metal ion

Apparatus required:

Mechanical shaker; porcelain dish, some beakers and volumetric/conical flask.

Reagents required:

1. EDTA solution (0.01N): Dissolve 2.0 g of versenate (disodium dihydrogen ethylene diamine tetra acetic acid) in distilled water and make the volume to 1 litre. Titrate it with 0.01N Ca solution and make the necessary dilution so that its normality is exactly equal to 0.01N.
2. Standard 0.01N Ca solution: Weigh accurately 0.5 g of pure calcium carbonate and dissolve it in 10 ml of 3N HCl. Boil to expel CO_2 and then make the volume up to 1 litre with distilled water.
3. Buffer solution: Dissolve 67.5 g of ammonium chloride in 570 ml of concentrated ammonium hydroxide, and make up to 1 litre.
4. Muroxide (Ammonium purpurate) indicator powder: Take 0.2 g of muroxide and mix it with 40 g of powdered potassium sulphate. This indicator should not be stored in the form of solution, otherwise it oxidizes.
5. Sodium diethyl dithiocarbamate crystals: These are used to remove interference by other metal ions.
6. Sodium hydroxide 4N: Prepare 16 percent soda solution by dissolving 160 g of pure sodium hydroxide in water, and make the volume up to 1 litre. This will give pH 12.
7. Extractant solution: 77.08 g Ammonium acetate (NH_4OAC) and make up to 1 litre of distilled water in a vol. flask.

Procedure:

1. Put 5 g of air-dried soil sample in a 150-ml conical flask and add 25 ml of neutral normal ammonium acetate (1:5 ratios). Shake on a mechanical shaker for 5 minutes and filter through whatman No. 1 filter paper.
2. Take a suitable aliquot (5 or 10 ml) and add 2–3 crystals of carbamate and 5 ml of 16 percent NaOH solution.
3. Add 40–50 mg of the indicator powder. Titrate it with 0.01N EDTA solution until the colour changes gradually from orange-red to reddish-violet (purple). Add a drop of EDTA solution at intervals of 5–10 seconds, as the change of colour is not instantaneous.
4. The end point must be compared with a blank reading. If the solution is overtitrated, it should be backtitrated with standard Ca solution; thus, the exact volume used is found.
5. Note the volume of EDTA used for titration.

Calculations:

If N1 is normality of Ca^{2+} and V1 is volume of aliquot taken and N2V2 are the normality and volume of EDTA used, respectively, then:

N1V1 = N2V2

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{\text{Normality of EDTA} \,.\, \text{Volume of EDTA}}{\text{ml of aliquot taken}}$$

Here, N1 (normality) = equivalent of Ca^{2+} present in 1 litre of aliquot. Hence, Ca^{2+} me/litre is:

$$= \frac{\text{Normality of EDTA} \times \text{Volume of EDTA} \times 1000}{\text{ml of aliquot taken}}$$

When expressed on soil weight basis, Ca^{2+} me/100 g soil is:

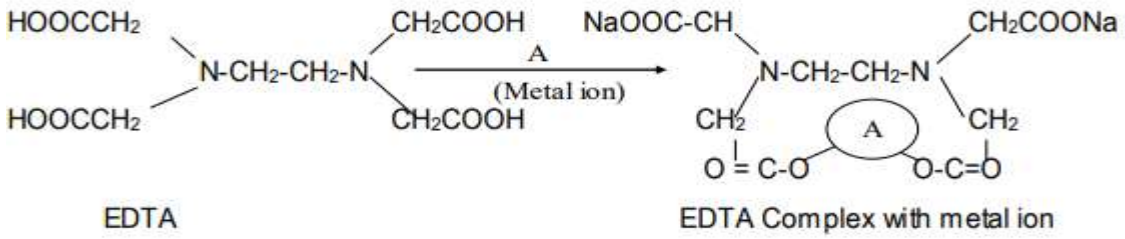
$$= \frac{100}{\text{wt.of soil}} \times \frac{\text{extract volume}}{1000} \times \text{Ca as me/ lit}$$

Exercise No. 7

Objective: Determination of hardness (calcium + magnesium) by the versenate (EDTA) method in soil or irrigation water

Principle:

Chelating agents like EBT (Erichrome Black T), EDTA (ethylene diamine tetra acetic acid) has tendency to form complex with metal cations especially with Ca and Mg. Buffer solution is added to increase the pH at 10 so that EBT will form complex with Ca and Mg. EDTA has more tendency to form complex, when the solution is titrated with EDTA, all the complex form with EBT will be broken and replaced by EDTA. Thus, knowing the amount of EDTA needed to form complex will give the amount of Ca and Mg present in the sample.



EDTA EDTA Complex with metal ion

Apparatus required:

Mechanical shaker, porcelain dish, beakers and volumetric/conical flask.

Reagents required:

1. EDTA solution (0.01N), Standard 0.01N Ca solution, Buffer solution; here we use EBT indicator instated of Muroxide indicator (Prepared as described in earlier exercise).
2. EBT indicator: Weigh exactly 0.5 g of EBT dye and 4.5 g of hydroxyl amine hydrochloride (NH2OH.HCl) and dissolve both in 100 ml of ethyl alcohol. Add 5 ml of 2% NaCN solution (or pinch of carbamate crystals) here, that keeps Cu, Zn, Fe, Mn, Co, Ni in their non-reactive complex form and $NH_2OH.HCl$ keeps Mn in its lower valency state(Mn^{2+}). Sometimes we ignore this as these ions are in fairly lesser amount.

Procedure:

1. Take 50 ml of irrigation water sample with the help of pipette in a conical flask or china clay dish and dilute it by 25 ml of distilled water. Either takes soil 5 g of air-dried soil sample in a 150-ml conical flask and adds 25 ml of neutral normal ammonium acetate (1:5 ratios).
2. Add about 2 ml of NH_4CI+ NH_4OH buffer to bring the pH at about 10.
3. Now add 3-4 drops of EBT indicator. Pinch of pure EBT indicator may be used here. It will give a wine red color.
4. Titrate it against EDTA till the color changes from red to bright blue. At the end point no tinge red color should remain in titrated sample.
5. Repeat procedure for blank.

Observations:

Parameters	Sample I st	Sample II nd
(a) Volume of EDTA used in titration		
(b) Volume of water sample taken		

Calculation:

Factor: 1ml N/100 EDTA = 0.00032g Ca + Mg

(c) Ca + Mg in irrigation water (g/L) = (b) step

(d) Ca + Mg in irrigation water (ppm) = (c) x 1000

(e) Ca + Mg in irrigation water (me/L) = (d)/ equiv. wt (32) =_____

Note:

Determination of magnesium in soil or irrigation water can be titrated with 0.01N EDTA using EBT dye as indicator at pH 10 in the presence of ammonium chloride and ammonium hydroxide buffer. At the end point, the colour changes from wine-red to blue or green. Where Ca is also present in the solution, this titration will estimate both Ca and Mg. Beyond pH 10, Mg is not bound strongly to EBT indicator to give a distinct end point.

Milli-equivalent (me) of Mg^{2+} = me (Ca^{2+} + Mg^{2+}) – me of Ca^{2+}

Results and Interpretation: _____

Exercise No. 8

Objective: Determination of Carbonate (CO_3^{2-}) and Bicarbonate (HCO_3^-) in soil and water

Principle:

When phenolphthalein is used an indicator, strong alkalis like KOH and NaOH are completely neutralized whereas weak alkalis like Na_2CO_3 or K_2CO_3 are neutralized to the stage of $NaHCO_3$ or $KHCO_3$ according to equation.

$$Na_2CO_3 + H_2SO_4 \rightarrow NaHSO_4 + NaHCO_3$$

The $NaHCO_3$ thus formed requires more H_2SO_4 to get completely neutralized according to the equation.

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2CO_2 + 2H_2O$$

It is evident from the above equation that the quantity of H_2SO_4 required in both the stages of neutralization of Na_2CO_3 is the same. The second stage of neutralization of Na_2CO_3 (i.e. the neutralization of $NaHCO_3$) can be indicated by methyl orange which can also indicate complete neutralization of alkali carbonate or bicarbonate. Thus, phenolphthalein and methyl orange are used one after the other during the course of titration in the same solution for evaluating mixtures containing carbonates or bicarbonates. Methyl orange when used jointly with phenolphthalein after the latter has decolorized indicated the quantity of acid required for the neutralization of bicarbonate only.

Reagents:

1. Phenolphthalein indicator: 0.25% solution of 60% ethyl alcohol.
2. Methyl orange indicator: 0.5% solution in 95% alcohol.
3. Standard H_2SO_4 (0.01 N)

Procedure:

1. Weigh 40g of soil sample in a 500 ml conical flask.
2. Add 200 ml double distilled water and shake for an hour in a shaking machine for equilibration.
3. Filter the suspension.
4. Pipette out 5 ml of extract or 5 ml of water sample (containing not more than 1 meq. Of CO_3^{2-} plus HCO_3^-) in a porcelain dish and add 2-3 drops of phenolphthalein indicator. Titrate against 0.01 N H_2SO_4 until pink color disappears (indicating phenolphthalein end point). This end point corresponds to the neutralization of the carbonate to the bicarbonate stage.
5. Record the ml of 0.01 N H_2SO_4 required for this process from burette reading.

6. Add 1-2 drops of methyl orange indicator to the colorless solution.
7. Titrate it again with 0.01 N H_2SO_4 stirring briskly, until the indicator turns orange indicating complete neutralization of the bicarbonate present
8. Note the titre value from the burette.

Calculations:

Weight of soil taken = 40 g

Volume of water added = 200 ml

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

Volume of 0.01 N H_2SO_4 required for the first titration (with phenolphthalein) = t_1 ml.

Total volume of H_2SO_4 required = t_2 ml (phenolphthalein plus methyl red)

Normality of H_2SO_4used = N

Therefore, meq. of H_2SO_4used in the first titration (with phenolphthalein) = $N \times t_1$

Meq.ofH_2SO_4 used (total) in the successive titration = $N \times t_2$

Hence,**meq. of CO_3^{2-}**per 100g of soil = $(N \times t_1) \times \frac{200}{V} \times \frac{100}{40}$

And **mg. of CO_3^{2-}**per 100 g of soil = $(N \times t_1) \times \frac{200}{V} \times \frac{100}{40} \times 30$

Likewise, meq ofHCO_3^- per 100g soil

$$= (t_2 - t_1) \times N \quad \frac{200}{V} \times \frac{100}{40}$$

And, mg of HCO_3^- per 100g soil = $(t_2 - t_1) \times N \times \frac{200}{V} \times \frac{100}{40} \times 61$

Note: 1 ml of 0.01 N H_2SO_4 = (0.01 meq. H_2SO_4)

$$= 0.00030 \text{ g } CO_3^{2-} = 0.00061 \text{ g } HCO_3^-$$

For Water Calculation:

Also meq. of CO_3^{2-} per litre of soil extract or water sample = $(N \times t_1) \times \frac{1000}{V}$

And; meq. of HCO_3^-per litre of soil extract or water sample = $(t_2 - t_1) \times N \times \frac{1000}{V}$

Exercise No. 9

Objective: Determination of nitrate contamination in ground water

Principle:

The NO_3-N is reduced to NH_3 by Devarda's alloy (Cu: Al: Zn:: 50: 45:5) in alkaline solution. The ammonia liberated is absorbed in known volume of 2 % boric acid solution. The amount of NH_3 absorbed is determined by titrating it with standard (0.1 N) sulphuric acid solution using mixed indicator. The end point is indicated by change of colour from sky blue to pink or wine red.

Reactions:

$Zn + 2NaOH \rightarrow Na_2ZnO_2$ (Sodium zincate) $+ 2H^+$

$Al + 2NaOH \rightarrow Na_2AlO_2$ (Sodium aluminate) $+ 2H^+$

$NO_3 + 9H^+ \rightarrow NH_3 + 3H_2O$

$3NH_3 + H_3BO_3 \rightarrow (NH_4)_3BO_3$ (Ammonium borate)

$2(NH_4)_3BO_3 + 3H_2SO_4 \rightarrow 3(NH_4)_2SO_4 + 2H_3BO_3$

(Boric acid)

Reagents:

1. Devarda's alloy: Mixture of metals in the ratio of Cu: Al: Zn:: 50: 45: 5.
2. Boric acid (2%): Dissolve 20 g H_3BO_3 in one litre volumetric flask, add about 900 ml distilled water and heat and swirl the flask until the H_3BO_3 is dissolved.
3. NaOH (5%): Dissolve 25 g loose alkali NaOH in water and dilute to one litre volume.
4. H_2SO_4 (6N): Dissolve 2.8 ml concentrated H_2SO_4 in distilled water and dilutes one litre. Standardize with 0.1N Na_2CO_3 using methyl orange indicator.
5. Mixed indicator: Dissolve 0.5g Bromocresol green and 0.1 g methyl red dissolved in 100 ml of 95 % ethanol. Adjust the pH 4.5 with dilute NaOH or HCl.

Procedure:

Pipette 25 ml of aliquot from water sample and transfer it to 1 litre of distillation flask. Add about 100 ml distilled water in distillation flask. Take 25 ml boric acid solution in a 250 ml beaker and add 4 to 5 drops of mixed indicator. Place the beaker containing boric acid and mixed indicator under condenser in such a way that tip of condenser should be dipped into the boric acid solution. Add 2 to 3 glass beads in the distillation flask. Add 2.0 g of Devarda's Alloy in distillation flask. Take about 25 ml of 2.5% NaOH solution and add into the distillation flask in such a way that it runs down from neck to the bottom without

mixing. Connect the splash head immediately and circulate the water in the condenser. Light the burner and start heating at once to avoid the danger of sucking back. Continue distillation till about 150 ml of distillate is collected in the beaker. Test for NH_3 using litmus paper. Wash the tip with distilled water. Remove the beaker first and then put-off the burner to prevent sucking back. Run a blank using same procedure without addition of water sample. Titrate the distillate with std. 0.1 N H_2SO_4 till the pink colour is observed. Calculate the percent of N of the given sample of water.

Observations:

1	Aliquot taken for distillation		25 ml
2	Burette reading with 0.1 N H_2SO_4 for the sample	S	_____ml
3	Burette reading with 0.1 N H_2SO_4 for the blank	B	_____ml
4	Net 0.1 required to react with NH_3 liberated from 25 ml of water sample	(S-B)	_____ml

Calculation:

1000 ml 1 N H_2SO_4 = 14 g N

1000 ml 0.1 N H_2SO_4 = 1.4 g N

1 ml 0.1 N H_2SO_4 = 0.0014 g N

$$\% N = \frac{(S - B) \times 0.0014 \times 100}{25}$$

$$\% N = (S - B) \times 0.0056$$

$$\% N = X = \_\_\_\_\_$$

Exercise No. 10

Objective: Determination of chloride in the soil sample or water

Principle:

Chloride (Cl^-) is determined in the soil/solution by titrating against $AgNO_3$ solution and potassium chromate (K_2CrO_4) is used as indicator. At the endpoint chocolate color or reddish yellow precipitate of silver chromate is formed.

Reaction:

$NaCl + AgNO_3 \rightarrow AgCl$ Silver Chloride (white) $+ NaNO_3$

$2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2KNO_3^-$

Procedure:

1. Place 20ml aliquot in a neat & clean volumetric flask of 250ml capacity.
2. Add 2-4 drop of K_2CrO_4 indicator in it.
3. Fill the burette with N/100 $AgNO_3$ solution.
4. Titrate the solution with N/100 $AgNO_3$ solution till white precipitate obtained.
5. When the white precipitate is converted to chocolate or reddish yellow precipitate, stop the titration and note the reading.

Observation Table:

S. No.	Volume of soil water extract taken	Burette reading		Volume of $AgNO_3$ used
		Ist	IInd	
1.	20ml			
2.	20ml			

Calculation:

$Ag\ NO_3 = NaCl = C1^-$ (35.5g $C1^-$).

170g $AgNO_3$ = 59.5g NaCl = 35.5 g $C1^-$

Because 1000 cc N NO_3= 35.5 g $C1^-$

So that, 1 cc N $AgNO_3$ = 35.5 /1000 g $C1^-$

1 cc N/100 $AgNO_3$ = 35.5 /1000 x 1/100 g $C1^-$

R cc N/100 $AgNO_3$ =35.5 /1000 x 1/100 x R g $C1^-$

20 cc solution contains = 35.5 x 1x R/ 1000x 100 gCl^{-1}

1 cc solution contains = 35.5 x 1x R/ 1000x 100 x 20 gCl^{-1}

1000 cc solution contains = 35.5 x 1x Rx 1000/ 1000x 100 x 20 gCl^{-1}

= ---------- gCl^{-1}/litre

Exercise No. 11

Objective: Determination of sodium (Na^+) in saturation extract or irrigation water

Principle:

Flame photometer is based on the principle of flame emission spectroscopy. Atoms / ions when subjected to high temperature, their valence electrons jump to high energy level absorbing energy, the absorbed energy is emitted as radiation energy of discrete wavelengths, characteristic of each element when the e- returns to its ground state, the intensity of radiation depend upon concentration of atoms in the solution. The emitted energy in the forms of photons is detected by phototube and amplified by amplifier and measured with galvanometer.

Irrigation water may have two major types of hazard *viz.* salinity and sodium hazard. The latter is expressed as the residual sodium carbonate (RSC) and sodium adsorption ratio (SAR). For working out the SAR value, sodium content is determined conveniently using flame photometer or simply by subtracting the Ca + Mg content from the total soluble salts. The subtraction method, though not so precise due to the presence of other cations like K, is often adopted to serve the purpose. The quantity of K^+ ions in water is generally low enough to be ignored for this the flame photometric determination of sodium is described here:

Instrument: Flame photometer

Regents:

1. Standard stock solution (100 me Na $litre^{-1}$): Dissolve 5.845 g of AR grade dried NaCl in distilled water and makes the volume to 1litre.
2. Working standard solutions of Na: Dilute 5, 10, 15, 20, 30, 40 and 50 ml portions of the stock solution (containing 100 me Na $litre^{-1}$) to 100 ml. in volumetric flasks to get working standards of 5, 10, 15, 20, 30, 40 and 50 me Na/litre concentrations.

Procedure:

1. Take 5or 10 ml of saturation extract (or irrigation water) sample into a 100 ml or 50 ml volumetric flask and makeup the volume with distilled water.
2. Calibrate the flame photometer with standard solution of 50 ppm Na concentration.
3. Insert the flame photometer tube into the diluted saturation extract and find the Na concentration on flame photometer.

4. If flame photometer does not give reading then we have to go for further dilutions with distilled water.

Observations and Calculation

∵ 1 Flame photometer reading = 0.5 ppm Na

∴ R Flame photometer reading = R x 0.05 ppm Na

∴ R of diluted solution= R x D × 0.05 ppm Na

Result: Na^+ content =…….. ppm

Exercise No. 12

Objective: Determination of potassium in saturation extract or irrigation water

Principle:

Potassium in saturation extract or irrigation water is commonly determined by flame photometer. It is rapid and reliable. Moreover, no special treatment of water sample is required except removal of suspended solids by filtration. This instrument works on the principle that the element, in question when excited in a flame, emits radiation of characteristic wavelengths. The intensity of emission line is proportional to the concentration of K in the solution. Potassium emits an yellow colour (404 millimicrons) flame when excited in the flame. The intensity of emission is proportional to the concentration of potassium in the sample.

Apparatus required:

Volumetric flasks 50,100 and 1000 ml, beakers 100 ml, flame photometer with K filter and filter papers.

Reagents required:

1. Ammonium acetate, approximately 1 N, To 700 or 800 ml. of water add 57 ml of concentrated acetic acid and then 68 ml of concentrated ammonium hydroxide. Dilute to a volume of 1 litre and adjust to pH 7.0 by the addition of more ammonium hydroxide or acetic acid.
2. Potassium chlorides, 0.02 N. Dissolve 1.491 g of dry potassium chloride in water and dilute to a volume of exactly 1 litre.
3. Potassium chloride 0.02 N in 1 N ammonium acetate. Dissolve 1.491 gm of dry potassium chloride in reagent A. Dilute to a volume of exactly 1 liter with additional A.
4. Lithium chloride (0.05 N). Dissolve 2.12 gm of dry lithium chloride in water and dilute to 1 liter.

Procedure:

Using reagents B and D, prepare a series of standard KCl solutions, each containing the same concentration of lithium chloride. Prepare a similar series of standard potassium solutions using reagents C and D, and use A for dilution. The concentrations of potassium chloride are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5 and 2.0 meq L^{-1}. Calibrate flame photometer with working standards over the concentration range 0 to 0.5 meq L^{-1} of potassium. Dilute the sample if the concentration exceed working range and consider the dilution factor during calculation.

Pipette an aliquot of the solution to be analyze containing less than 0.1 meq L^{-1} of potassium into a 50 ml volumetric flask. Add an amount of reagent D which when diluted to a volume of 50 ml, will give a

concentration of lithium chloride exactly equal to that in the standard potassium chloride solutions. Dilute to volume with water or with A, if ammonium acetate extracts are being analyzed, mix and determine the potassium concentration by use of the flame photometer and the appropriate calibration curve.

Calculations:

(me L^{-1} of K from calibration curve x 50) K in soil extract (me L^{-1}) = ---------- --- ml. in aliquot

Results:

K in soil extract (me $litre^{-1}$) = ---------- or

K in irrigation water (me $litre^{-1}$) = ----------

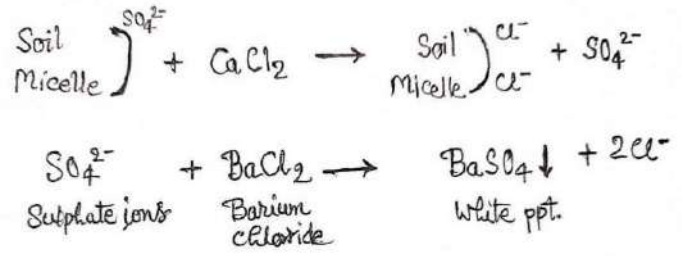
Exercise No. 13

Objective: Determination of available sulphur from soil sample

Principle:

When the soil solution is shaken with $CaCl_2$ (0.15 %), the chloride ions displace the adsorbed sulphate during extraction. The filtrate is analyzed for sulphur by turbidimetry method as outlined by Chesin and Yien (1950), in which turbidity produced due to the precipitation of SO_4^{2-} as $BaSO_4$ is measured on a spectrophotometer at a wavelength of 420 nm or corresponding to blue filter. The conditioning reagent is added to stabilize or suspend the $BaSO_4$ precipitate uniformly in the solution.

Equations:



Equipment and material required:

Weighing balance, spatula, measuring cylinder, conical flask, volumetric flask, glass rod, magnetic stirrer, beaker, reagent bottle, wash bottle, filter paper whatman no.1 and colorimeter or spectrophotometer.

Reagents required:

1. Extracting solution: Dissolve 1.986 g of calcium chloride dihydrate ($CaC1_2.2H_2O$) in distilled water and dilute to one litre.
2. Barium chloride ($BaCl_2$): 30 to 60—mesh crystals: Grind barium chloride crystals until they pass through 30-mesh sieve and are retained on a 60-mesh sieve.
3. Gum acacia solution (0.25%): Dissolve 0.25 g gum acacia in distilled water and dilute to 100 ml.
4. Standard sulphur solution (100 ppm S): 0.5434 g of the reagent grade potassium sulphate (K_2SO_4) in distilled water and dilute to one litre.

Procedure:

a**) Preparation of standard curve:**

Pipette out 0.25, 0.5, 1.0, 2.5 and 5.0 ml of 100 ppm S solution in different 25 ml volumetric flasks. Add in every flask 10 ml of 0.15% $CaCl_2$, solution and 1.0 g of 30-60 mesh $BaCl_2$, crystals. Swirl for one minute to dissolve the crystals and add 1 ml of 0.25% solution of gum acacia. Make up the volume in every flask with distilled water and shake well. Within 5 to 30 minutes after the development of turbidity read the standards on a colorimeter at 420 nm using a blue filter. Plot a standard curve showing relationship between concentration of S and turbidity/absorbance readings.

b) Analysis of test sample:

Weights 10 g air-dried soil and transfer it to a 150-m1 conical flask. Add 50 ml of 0.15 % $CaCl_2$ solution and shake for 30 minutes on an electric shaker. Filter the Suspension through Whatman No.42 filter paper. Pipette out 20 ml of the filtrate in 25 m1 volumetric flask and proceed further as in case of standard curve. Run blank with all the chemicals, except the soil. Find out sulphate concentration from the standard curve.

Precautions:

1. Reagents should be prepared accurately
2. Standard working solution should be prepared according to the need

Exercise No. 14

Objective: Estimation of boron in soils, plants and water

Principle:

Boron occurs as anion in soils and is required by plants in very small quantity. Water soluble B makes the estimate of its availability to plants. Total boron in soils varies from 20 to 200 mg kg^{-1} and available (water soluble) boron in soils ranges from 0.03 to 12 mg kg^{-1} respectively. The threshold value ranging from 0.1 to 0.5 mg kg^{-1} (water soluble B) depends upon the soil type, crops, and other factors, below which the response to applied boron may be expected. Some sensitive crops to boron deficiency are listed in table 1. Its availability is affected by soil pH. Deficiency of B is generally observed in old acid leached soils. Availability increased with the rise in soil pH having significant positive correlation with pH rising from 4.7 to 6.7. In neutral, saline and calcareous soils the B availability again decreases with the rise in soil pH having significant negative correlation with the rise in pH from 7.1 to 8.1. In calcareous soils B fixation occurs with the condensation of borate radical into long chains in the presence of Ca.

Table 1: Sensitivity of crop to Boron deficiency

Sensitive	**Medium**	**Low**
Alfalfa	Apple	Barley
Cauliflower	Cabbage	Beans
Rape seed	Carrot	Corn
Conifers	Clover	Grasses
Peanuts	Cotton	Oat
Sugarbeet		Turnip
Onion		Pea
		Potato
		Soybean
		Wheat
		Rice

In alkaline soils the availability of B is high and may be even toxic for plant growth. Besides this the low moisture availability also causes B deficiency. Irrigation water containing boron between 0.3 to 0.6 mg kg^{-1} can be used safely, whereas, irrigating soils with water containing 1 to 3 mg kg^{-1} B causes toxicity of B in plants.

Boron determination (Azomethine H Method):

Azomethine H forms coloured complex with H_3BO_3 in aqueous media. Over a concentration range of 0.5 to 10 µg B ml^{-1} the complex is stable at pH 5.1. Maximum absorbance occurs at 420 nm with little or no interference from a wide variety of salts. This technique is rapid, reliable and more convenient to use than traditional procedures employing carmin, curcumin or quinalizarin (John *et al.,* 1975).

Apparatus:

(1) Spectrophotometer (2) Poly-propylene tubes 10 ml capacity.

Reagents:

1. Distilled water
2. Buffer solution: Dissolve 250 g of ammonium acetate (NH_4OAc) and 15 g of ethylenediamine tetracetic acid (EDTA disodium salt) in 400 ml of distilled water. Slowly add 125 ml of glacial acetic acid and mix.
3. Azomethine H reagent: Dissolve 0.45 g of azomethine H in 100 ml of 1% L ascorbic acid solution. Fresh reagent should be prepared weekly and stored in a refrigerator.
4. Calcium hydroxide suspension: Add 0.4 g $Ca(OH)_2$ to 100 ml distilled water.
5. HCl (0.1N): Add 8.3 ml conc. HCl to 900 ml distilled water, mix, cool to room temperature and make up the volume to 1000 ml.
6. Calcium chloride (0.01M): Dissolve 1.11 g of anhydrous $CaCl_2$ in 900 ml distilled water and make up the volume to 1000 ml.
7. Boron standard solution: Dissolve 0.114 g of Boric acid (H_3BO_3) in distilled water and adjust the volume to 1000 ml. Each ml contains 20 µg B. Dilute 10, 20, 30, 40 and 50 ml of the stock solution to 100 ml with distilled water to have solution with B concentration of 2,4,6,8 and 10 µg of B ml^{-1} respectively. Include a distilled water sample for the 0.0 µg of B ml^{-1} standard solution.

Procedure:

Take 1 ml of aliquot of blank and diluted B standards into a 10 ml polypropylene tube; add 2.0 ml of buffer solution and mix. Add 2.0 ml of azomethine H reagent, mix and after 30 minutes read the absorbance at 420 nm on spectrophotometer. With the help of absorbance readings of standard solutions of different concentration of B the standard curve is drawn and a factor for concentration of B for 1 absorbance is calculated which is utilized to calculate B in the soils, plant or water sample.

Preparation of Extracts:

1. **Soil extracts:** The hot water soluble extraction procedure of Berger and Truog (1939) is being used widely with slight modification of adding dilute electrolyte (0.01 M $CaCl_2$) instead of water only. This provides clear, colourless extract which eliminates the need of charcoal for decolourzation. Beside this a negative error, associated with B adsorption by charcoal, is also removed. Place 20 g air dry soil in 250 ml low B flat bottom flasks and add 40 ml of 0.01 M $CaCl_2$ solution. Attach water cooled reflux condenser to the flask. Heat the flasks for 5 minutes and then cool and filter the suspension in plastic bottles. Transfer 20 ml aliquot to evaporating dish, add 2 ml $Ca(OH)_2$ suspension and evaporate the solution to dryness. Heat the evaporating dishes gently to destroy organic matter, cool to room temperature, add 5 ml 0.1N HCl. Triturate the residue with rubber policeman to ensure the complete dissolution of the residue (Bingham, 1982).

For analysis of B pipette 1 ml of the aliquot and proceed as for the standard curve.

2. **Plant digest:** Take 0.5 g plant sample in porcelain/platinum dishes Add 0.5 g $Ca(OH)_2$. Ignite the sample in the muffle furnace at 550°C for 4 hours to obtain white grey ash. Cool the dishes and moist the ash carefully with little distilled water and then add 5 ml 0.1N HCl. Transfer the content in to 25 ml volumetric flask mix and make up the volume to 25 ml with distilled water. For analysis of B take 1 ml of the aliquot and proceed as for the standard curve.
3. **Water analysis:** Take suitable quantity of water sample (containing 0.2 to 5.0 µg B) in porcelain dishes add 2 ml $Ca(OH)_2$ and proceed as described for soil extract. It is important to keep a definite volume of aliquot i.e. 1 ml of either soil, plant or water in final step of B determination.

Exercise No. 15

Objective: Estimation of redox potential in soil

The importance of pH as a “master variable" controlling chemical reactions in soils has been discussed in various equilibrium reactions. However, soils subjected to fluctuations in water content come under the influence of another master variable, the *reduction-oxidation (Redox) potential*. Under conditions of water saturation, the lack of molecular oxygen can result in a sequence of redox reactions that changes the soil pH. In this sense the redox state of the soil exerts control over the pH. The nature of redox reactions profoundly influence metal ion solubility and the chemical form of ions and molecules dissolved in soil solution.

For any electron transfer half reaction of general form is

Oxidized molecule + mH^+ + n electrons = reduced molecule

The Nernst equation can be written as;

$$Eh = E°_h - \frac{0.059}{N} \log \frac{(\text{reduced molecule})}{\text{Oxidized molecule X } (H^+)^m}$$

Where;

Eh = Potential for the half reaction (volts, V)

$E°_h$= staential state potential for the half reaction, (volts, V)

n = moles of electrons involved in the reaction as written

m = moles of protons involved in the reaction as written and the parenthesis denotes chemical activities of the reduced and oxidized molecules.

Redox potential measurement in soil by electrode:

Theory

The commonest method of measuring redox potential is to immerse a platinum (Pt) electrode along with a reference electrode into a solution. The electrodes are then connected to a potentiometer that measures the potential difference between the two electrodes. Reduced species in solution tend to donate electrons to the conducting Pt electrode, while oxidized species tend to accept electrons from the electrode. This creates electron flow in the electrode. However, to cause any detectable movement of electrons in the electrode, the reaction between the oxidized (ox) and reduced (red) form of an electron in solution must be shifted away from equilibrium. At the steady state of equilibrium, the forward

reaction rate equals the backward rate and the net electron flow (net current) is zero. Even at equilibrium, however, electron flow in either direction, termed as exchange current is not zero. A very small shift of the electrode potential away from its equilibrium value causes the half reaction to proceed either to the left or right, thereby creating a net current that can be measured. How precisely this measurement can determine the equilibrium potential of a particular half reaction depends on how steeply the net current deviates from near the equilibrium potential. The greater the magnitude of the exchange current, the more steep is the net current function.

This, in turn is a function of the concentration of reduced and oxidized species near electrode surface.

Required materials:

1. pH meter having Platinum (Pt) electrode
2. 25 ml Pipette
3. 50 ml polythene beaker
4. 100 ml wide mouth polythene bottle
5. Glass rod

Reagent required

Buffer solutions of reduced pH 4 and 9.2: Dissolves pH buffer tablets of 4.0 and 9.2 separately in 100 ml distilled water to prepare the buffer solutions of pH 4.0 and 9.2 and a fresh one is prepared if any mould formation is obtained. This is used to standardize the instrument.

Procedure

Take 10 g of reduced soil in a 50 mL polythene beaker. Add 25 mL of distilled water by a 25 mL volumetric pipette. Stirr the contents by a glass rod for 1 to 2 minutes. Then wait for 30 minutes with intermittent shaking to attain equilibrium between the oxidized and reduced species. Then measure the redox potential of the soil suspension after standardizing the Pt electrode. The soil suspension should be stirred just before measuring the potential. The electrodes should be washed properly just before and after measuring the redox potential. Express the results in mV.

Exercise No. 16

Objective: Determination of lime requirements

Principle:

Most of the cultivated grow well at neutral pH. Lime requirement is estimated to know the amount of lime required to bring the soil pH between 6.5-7.5. This amount varies mainly by pH, texture, buffering capacity of soil and nature of soil colloids. The method proposed by Shoemaker, Maclean and Prate (1961) (SMP) is generally used for estimation of lime requirement. In this method a definite amount of soil is shaken and brought in equilibrium with pH 7.5 buffer solution. Thus, the reserve H+ ions are brought into soil solution which result decrease of pH of buffer solution. This decrease in pH value of soil buffer suspension is calibrated for estimation of lime requirement.

Apparatus:

pH meter, automatic pipettes - 10 and 20 ml, beaker (50 ml) and balance.

Reagent: Extractant Buffer:

Dissolve 1.8 g of P-nitro phenol, 2.5 ml triethanolamine, 3.0 g potassium chromate (K_2CrO_4), 2.0 g calcium acetate and 53.1 g calcium chloride in a litre of water. Adjust pH to 7.5 with NaOH.

Procedure:

1. Take 5.0 g soil sample in a 50 ml beaker.
2. Add 5 ml distilled water and 10 ml extractant buffer.
3. Shake continuously for 10 minutes or intermittently for 20 minutes and read the pH of the soil buffer suspension with glass electrode. And find out lime requirement from given table.

TABLE: Lime requirement for different pH targets

Measured pH of soil buffer suspension ↓ pH →	Requirement in tonnes/ha as $CaCO_3$ for bringing soil pH to different levels		
	pH 6.0	pH 6.4	pH 6.8
6.7	2.43	2.92	3.40
6.6	3.40	4.13	4.62
6.5	4.37	5.35	6.07
6.4	5.59	6.56	7.53
6.3	6.65	7.78	8.99
6.2	7.52	8.93	10.21
6.1	8.5	10.21	11.66
6.0	9.48	11.42	13.12

Note:

1. The above values are in tonnes of pure $CaCO_3$ per $CaCO_3$ per hectare and the same may be converted to their equivalent of other liming materials available.
2. Practically, pH of acid soils may not be raised beyond 6.4/6.5.
3. The values of tones/ha can be converted tonnes/acre by dividing the factor 2.47.

Observations and calculations:

1. pH of soil sample= ……..
2. pH of soil buffer suspension= …….
3. Lime requirement from table provided:

   Lime requirement…….tonnes/acre

   Lime requirement…….tonnes/ha

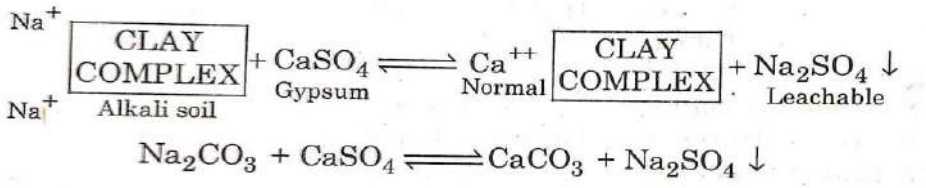
Exercise No. 17

Objective: Determination of gypsum requirement of soil

Alkali soils also called Sodic soils, Usar soils contain colloidal complex saturated with excessive amounts of exchangeable sodium. Under these conditions, calcium by cationic exchange is often used to replace sodium in alkali soils. Because of low cost and easily availability gypsum powder ($CaSO_4.2H_2O$) applied widely and intensively as an amendment for reclamation. That calcium helps to improve the physic chemical and biological properties of the alkali soils. The gypsum requirement of soils is determined by using the method proposed by Schoonover (1952).

Principle:

A known weight of the soil is shaken with a known excess volume of nearly saturated gypsum solution. The unutilized calcium left out in the solution is determined by titrating against standard EDTA solution using EBT indicator in the presence of NH_4Cl – NH_4OH buffer. The amount of gypsum utilized / required is calculated from the titre value.



When Gypsum is used as reclaiming agent, calcium replaces the exchangeable sodium and converts the clay back into calcium-clay (Ca-clay). Sodium sulphate goes into solution and then is removed by washing it out with water or leaching down with water with the help of artificial drains.

Apparatus:

Mechanical shaker, conical flask, burette with stand, pipette, filter paper, china dish and glass rod.

Reagents:

1. Saturated gypsum solution: Add 5 g of $CaSO_4$ $2H_2O$ to 1 litre of distilled water. Shake manually several times over a period of 1 hr for 10 minutes on a mechanical shaker and filter.
2. Eriochrome Black T indicator: Dissolve 0.5 g of Eriochrome Black T indicator and 4.5 g hydroxyl amine hydrochloride in 100 ml of 95 % ethanol.
3. EDTA solution (0.01 N): Dissolve 2.0 g of di sodium salt of ethylene diamine tetra acetate and dilute to 1 litre. Standardize this solution against 0.01 N calcium chloride solutions.
4. NH_4Cl- NH_4OH buffer: Dissolve 67.5 g of pure ammonium chloride in 570 ml of conc. ammonia

solution and dilute to 1 litre. Adjust the pH at 10 using dil. HCl or dil. NH_4OH.

Procedure:

1. Weigh 5.0 g of air dry soil in 250 ml conical flask.
2. Add 100 ml of the saturated gypsum solution to remove the Na from exchangeable complex to bring down to a reasonable level.
3. Shake for 5 minutes on mechanical shaker or by hand for several times for 30 min
4. Filter the contents through Whatman No. 1 filter paper. Entire quantity needs to be filtered.
5. Transfer 5 ml aliquot of the clear filtrate into a China dish.
6. Dilute to approximately to 25 ml with distilled water.
7. Add 1 ml of the NH_4Cl- NH_4OH buffer solution followed by 2 to 3 drops of EBT indicator.
8. Titrate against the 0.01N EDTA solution till the wine red color changes from purple to sky blue.
9. The titre value will give the volume of the EDTA required to react with the unutilized gypsum= (Sample reading S).
10. Also run a blank using 5 ml of the saturated gypsum solution to know the blank titre value = (Blank reading B).
11. Actual titre value = B-S ml

Calculation:

a. Wt of the soil taken = 5 g

b. Volume of saturated gypsum added = 100 ml

c. Volume of 0.01 N EDTA required to react with 5 ml of Gypsum solution = B ml of 0.01 N EDTA

d. Volume of EDTA required to react with unutilized gypsum solution=S ml of 0.01 N EDTA

e. Volume of EDTA required to react with utilized gypsum = (B-S) ml 0.01N EDTA

As per the law of equilibrium;

1000 ml of IN EDTA = 86 g of gypsum

$$(B-S)\ \text{ml of 0.01 N EDTA} = \frac{(B-S)\text{ml} \times 0.01}{1000} \times 86\text{g of gypsum}$$

$$\text{5 ml of extract requires} = \frac{(B-S)\text{ml} \times 0.01}{1000} \times 86\text{g of gypsum}$$

$$100ml\ extract\ requires = \frac{(B-S)\text{ml} \times 0.01 \times 100}{1000 \times 5} \times 86\text{g of gypsum}$$

$$= (B-S) \times 0.0172\text{g of gypsum}$$

Now; (B-S) ml x 0.0172 g of gypsum required for 5 g soil

So, 1 kg soil requires → (B-S) 0.0172 x 1000/5 g of gypsum

Then; 2.25 x 10^6 kg soil requires →2.25 x 10^6 x (B-S) x 0.0172 x 1000/5

==7.74 x (B-S) ton of gypsum

Result: The given alkali soil require ……t ha^{-1} of gypsum for its reclamation.

Exercise No. 18

Objective: Estimation of water stable soil aggregates

Principle:

The wet sieving method involves equilibrating a given amount of soil aggregates in a nest of stand sieving in water, for a given length of time, followed by the collection of aggregates plus the coarse materials, retained on each sieve and their weight. Finally, the soil mass, retained on each sieve, is dispersed in H_2O_2 and HCl, and passed through individual sieves to account for the coarse soil fractions, which, otherwise, might be included wrongly, while reporting the mean weight diameter, and the percent of the total aggregates, in different size fractions, of the soil mass.

Apparatus and equipments required:

Standard sieves-2 sets (5.0, 2.0, 1.0, 0.5, 0.2 and 0.1 mm); Yoder apparatus, physical balance, oven; desiccators; watch glasses (8 cm); wash bottle and moisture boxes.

Regents required:

Hydrogen peroxide and HCl (0.1 N).

Procedure:

Take about, 300 g of air-dry solid clods. Break them into smaller aggregates by pulling them apart with hand, such that they pass through 8.0 mm screen, and are retained on 5.0 mm screen. Do not break them too small. Large gravel or roots should be removed. Weight 50 g aggregates (5.0-8.0 mm) in three watch glasses. Keep one of them in oven at 105°C for water content determination, and use the other two for analysis in duplicate. Arrange two sets of six sieves (5.0, 2.0, 1.0, 0.5, 0.2 and 0.1 mm) in such a way that the uppermost sieve has the largest mesh size, and the sieve, at the bottom, should have the smallest mesh size.

A. Aggregate sample:

Spread sample aggregate evenly on the top sieve and spray 5-10 ml of salt-free water on them. Wait for 3-5 min., spray another 5-10 ml of water again, and wait for further 3-5 min. Transfer the nest of sieves to the drum of the sieve, shake and clamp them in position securely. Fill the drum with salt-free water up to a level slightly below the top screen, when the sieves are in the highest position (turn the pully of the shaker slowly with hand to attain the highest position). Lower the sieves to the lowest position, and wet the aggregates for 10 minute full more water in the drum so that the aggregates are just covered with water when sieves are in the highest position. Switch on the oscillator and let the sieves oscillate in

water for 30 min., with a frequency of 30-35 cycles/ min, through a stroke length of about 3.8 cm, and check that the aggregates on the top sieve remain immersed throughout the full stroke. Take out the nest of sieves, let the water drain for a few min in an inclined position, remove excess water from the bottom of screens with absorbent tissue and place them on paper sheets. Let the aggregates on each sieve dry and harden in air. Dry the soil in an oven at a temperature not higher than 75°C because high temperatures cause some soils to adhere to the sieves. Drying of the aggregate surfaces takes between 20 and 40 min, depending on the soil. When dry transfer the soil from each sieve separately to can boxes, dry overnight at 105°C in an oven and weigh.

B. Dispersed sample:

In order to determine how much of the soil, retained on the sieves, represents aggregates and how much is gravel or sand, transfer the aggregates of each to 250 ml breakers separately, and disperse them with H_2O_2 and HCl treatments. Pass the dispersed aggregates again through the same sieves on which they were retained earlier. Collect the unaggregated primary particles, 52 from each sieve, in can boxes, as per the procedure outlined in the preceding paragraph, and record their oven-dry weight. Calculate the percentage of aggregated soil particles on different sieves. Plot a graph between the accumulated percentage of the soil, remaining on each sieve on ordinate, and the upper limit of each size fraction on abscissa. Measure the area under the curve, which is a representative of the mean weight diameter (MWD or weighted diameter) of aggregates. Find out the mean weight diameter of aggregates in mm by computation also and report the results as MWD and percent aggregation.

Observations:

a. sample No.			I		II	
b. Air dry weight of sample =			50 g		50 g	
c. Water content in solids =			……%		……%	
d. Frequency of oscillation			..……..min		……..min	
e. Stroke length =			..……cm		……cm	
f. Oven-dry weight of the aggregated and the unaggregated particles=			……..g		……..g	
S. No.	Particle size range (mm)	Particle diameter (>mm)	Wt. of particles retained on sieves (g)			
			Before dispersion		After dispersion	
			Sample-I	Sample- II	Sample-I	Sample-II
A	B	C	D		E	
1.	> 5.0	5.0				
2.	5.0-2.0	2.0				
3.	1.0-0.5	1.0				

4.	0.5-0.25	0.5				
5.	0.25-0.10	0.10				

Calculations:

Sample No.	I	II
g. Oven-dry weight of sample [(100/(100+c)] x 50] =	…….g	…….g

h. Per cent Aggregation

Particle diameter (>mm)	Wt. of aggregated particles	Percent of total soil sample	Accumulated Percentage
	Sample-I Sample-II	Sample-I Sample-II	Sample-I Sample-II
C	F=(D-E)	G=(F100)/g	II

Mean weight Diameter (MWD) = $\sum_{i=1}^{n} X_i W_i$

Where,

n = 6 (number of size fractions, i.e. 5.0 to 0.1 mm)

X = the mean diameter of fraction

W = the proportion by weight of a given size fraction of aggregates: F/g

MWD of sample-I : = ---------- mm

MWD of sample-II: = ---------- mm

MWD from graph: Sample-I; Sample II = ---------- mm

Results:

1. Percent aggregation (mean) greater than 0.1 mm = ----------%
2. MWD (mean of two observations from calculations) = ----------mm
3. MWD (mean of two observations from graphs) = ----------m

TABLE : Correction factors for conductivity data at standard temperature of 25°C					
°C	**Ft**	**°C**	**ft**	**°C**	**ft**
8	1.488	22.6	1.051	29.2	0.921
9	1.448	22.8	1.047	29.4	0.918
10	1.411	23	1.043	29.6	0.914
11	1.375	23.2	1.038	29.8	0.911
12	1.341	23.4	1.034	30	0.907
13	1.309	23.6	1.029	30.2	0.904
14	1.277	23.8	1.025	30.4	0.901
15	1.247	24	1.02	30.6	0.897
16	1.218	24.2	1.016	30.8	0.894
17	1.189	24.4	1.012	31	0.89
18	1.163	24.6	1.008	31.2	0.887
18.2	1.157	24.8	1.004	31.4	0.884
18.4	1.152	25	1	31.6	0.88
18.6	1.147	25.2	0.996	31.8	0.877
18.8	1.142	25.4	0.992	32	0.873
19	1.136	25.6	0.988	32.2	0.87
19.2	1.131	25.8	0.983	32.4	0.867
19.4	1.127	26	0.979	32.6	0.864
19.6	1.122	26.2	0.975	32.8	0.861
19.8	1.117	26.4	0.971	33	0.858
20	1.112	26.6	0.967	34	0.843
20.2	1.107	26.8	0.964	35	0.829
20.4	1.102	27	0.96	36	0.815
20.6	1.097	27.2	0.956	37	0.801
20.8	1.092	27.4	0.953	380	0.788
21	1.087	27.6	0.95	39	0.755
21.2	1.082	27.8	0.947	40	0.763
21.4	1.078	28	0.943	41	0.75
21.6	1.073	28.2	0.94	42	0.739
21.8	1.068	28.4	0.936	43	0.727
22	1.064	28.6	0.932	44	0.716
22.2	1.06	28.8	0.929	45	0.705
22.4	1.055	29	0.925	46	0.694
Source: Richards (1954)					