PRACTICAL MANUAL

COURSE NO. SSAC-242

Practical manual : SSAC-242

Problematic Soils and their Management

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CERTIFICATE

This is to certify that Mr./Miss……

Reg. No……., a student of **B.Sc.(Agri) degree, semester IV** has completed all the practical exercises of the course **Problematic Soils and their Management (SSAC-242),** Credit : 2 (1+1) satisfactorily during year 2018-2019.

Place: A. C. Dhule
Date: / /2019

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EXERCISE NO. 1 AND 2
PREPARATION OF SATURATION PASTE EXTRACT

Principal :

Composition of solutes in soil solution at field water content is desirable. Ideally, this measurement should be done at field capacity but it is difficult to obtain extract at field capacity. Hence the extract is obtained at next higher water content i.e. at saturation of soil. The saturation extract is related in a predictable manner to field soil water contents. The crop tolerance to salinity is often related to EC of the saturation extract.

Procedure :

1. Weigh 250 g of air dry soil (2 mm) and place in the plastic container.
2. Take distilled water in 250 ml measuring cylinder and add to the soil with steering with a steel spatula until is nearly, saturated. Record the volume of distill water used.
3. At saturation, the paste glistens as it reflects light, flows slightly when the container is tipped and the paste slides freely and cleanly off the spatula for all soils except those with high clay content.
4. Allow the paste to stand for an hour and recheck the criteria for saturation. Free water should not stagnet on soil surface nor the paste stiffen markedly. If the paste dose stiffen or loose its glister, remix with more water.
5. Record the pH of the saturation paste. Using glass electrode assembly.
6. Transfer the paste to the Buckner funnel fitted with watman No.50 filter paper.
7. Apply Vacuum and collect the filtrate in the test tube suspended to the spout of the funnel in the vacuum flask.
8. Preserve the extract for ECe and soluble cations estimation by adding a drop of toluene or 0.1% calgon (Sodium hexametphosphate)
9. Record the ECe with the help of a conductivity meter.

Observations :

1) Weight of soil taken - 250 g
2) Volume of water added -

Reference Book :

USDA (1954) Hand Book No.60 pp. 84-88.
Page *et al*. (1989) Soil Chemical analysis part 2 pp.168-173.

EXERCISE NO. 3
DETERMINATION OF pHe AND ECe

Determination of Soil pH_e

One of the most enlightening attributes of soil is its pH. Whether a soil is acidic, or basic has much to do with the solubility of various components, the relative bonding of ions on exchange sites, and activity of various micro organisms. The plant nutrient availability is influenced by soil pH. The ideal pH range for availability of nutrients is 6.5 to 7.5. Thomas (1957) noted that the three soil pH ranges are particularly informative : a pH less than 4 indicates the presence of free acids generally from association of sulphides; a pH below 5.5 suggests the likely occurrence of exchangeable Al and a pH from 7.8 to 8.2 indicates presence of $CaCO_3$.

Equipments for soil pH_e

pH meter. It consists of two electrodes

(A) Glass electrode, and

(B) Calomel electrode (Reference electrode).

A. Glass electrode

1. The glass electrode consists of thin-walled bulb of pH sensitive glass, sealed to a stem of high resistance glass. It is better to choose a lower resistance electrode (pH range 0 to 12) with more rapid response, and to tolerate the possibility of small errors caused by the reaction between the electrode surface and the film of soil suspension in contact with it.

2. New electrodes should be checked in at least three standard buffers, say near pH 4, 7 and 9 for linearity of response.

3. The useful life of glass electrode is extended if it is kept moist when not in use. Combined glass and reference electrode should also be stored in a buffer solution, but separate reference electrodes should have their liquid junctions immersed in nearly saturated KCl solution protected from evaporation.

4. With continued use, the performance of glass electrode gradually worsens. Electrode with poor performance should be replaced

5. Erratic off scale readings indicate very high electrical impedance in the electrical circuit.

6. Air bubbles interrupt the path between the glass bulb and the internal reference electrode. These bubbles are usually dislodged by gentle tapping and shaking.

B. Calomel electrode / Reference electrode

1. These electrodes are usually the calomel type with saturated KCl electrolyte. But Ag-AgCl electrodes give quite satisfactory service and have an advantage in being easily repaired or even constructed in a laboratory.

2. Calomel electrodes must not be heated above 70 ^{0}C. They should be closely inspected regularly to see that no air gaps have developed.

3. The liquid junction between the reference electrode and the test liquid usually made with KCl solution, which is also the reference electrolyte. The liquid junction potential with soil suspensions is not the same with other electrolytes. The KCl solution used should not be saturated at any temperature above the minimum to which the electrode will be subjected. For example, solution of 32 g KCl in 100 mL water is just unsaturated at 15^{0}C.

4. The KCl solution should flow through the liquid junction at a very low but detectable rate.

5. The liquid junction of reference electrode should just enter the surface of the soil suspension in order to be in a zone of minimum clay concentration. This makes the junction potential as small as possible and closest to that in the standardizing buffer solution. The difference in the junction potential in buffer and suspension is included in the pH shown by the meter.

Reagents

1. **Standard buffer solution, pH 4.00 :** Prepare stock solution of 0.3 *M* potassium hydrogen phthalate by dissolving 15.3 g of the analytical grade salt in about 225 mL of hot water, cooling the solution, and diluting it 250 mL. Add a drop of toluene to discourage growth of microorganisms. For the standard buffer pH 4.0, mix 100 mL of the stock solution with 500 mL water. Prepare the fresh solution every week.

2. **Standard buffer solution, pH 9.2 :** Dissolve 3.81 g sodium tetraborate (AR) in water and dilute to 1000 mL.

3. **1.0 *N* potassium chloride solution (AR) :** Dissolve 74.56 g of KCl in water and make up the volume to 1000 mL.

Apparatus

Electrometric pH meter with glass and calomel electrodes.

Procedure

1. Weigh 250 g of air dry soil (2 mm) and place in the plastic container.
2. Take distilled water in 250 ml measuring cylinder and add to the soil with steering with a steel spatula until is nearly, saturated. Record the volume of distill water used. At saturation, the paste glistens as it reflects light, flows slightly when the container is tipped and the paste slides freely and cleanly off the spatula for all soils except those with high clay content.
3. Allow the paste to stand for an hour and recheck the criteria for saturation. Free water should not stagnet on soil surface nor the paste stiffen markedly. If the paste dose stiffen or loose its glister, remix with more water.
4. In the mean time turn the pH meter on, allow it to warm up, and standardize the glass electrode using both the standard buffers. Remember to adjust the temperature compensation knob to the temperature of the solution. Measure the pH of the sample suspension, stirring the suspension well just before introducing the electrodes.
5. Rinse the electrodes after each determination with water carefully but do not blot them dry with filter paper before the next determination.
6. Record the pH of the saturation paste. Using glass electrode assembly.

Determination of EC_e

The electrical conductivity of water extract of soil gives a measure soluble salt content of the soil. Pure water is a very poor conductor of electric current, whereas, water containing dissolved salts ordinarily found in soil conducts current approximately in proportion to the amount of salts present. Based on this fact, the measurement of electrical conductivity of an extract gives a satisfactory indication of total concentration of ionized constituents.

Equipment : Electrical conductivity meter

Reagent: Potassium chloride: KCl 0.01*N* :

Dissolve 0.7456g of KCl in distilled water, and add water and make up the volume

to one liter at 25^0C. This is a standard reference solution . At 25^0 C it has an electrical conductivity of 1.412 $mScm^{-1}$ or dSm^{-1}.

Procedure :

1. Weigh 250 g of air dry soil (2 mm) and place in the plastic container.
2. Take distilled water in 250 ml measuring cylinder and add to the soil with steering with a steel spatula until is nearly, saturated. Record the volume of distill water used. At saturation, the paste glistens as it reflects light, flows slightly when the container is tipped and the paste slides freely and cleanly off the spatula for all soils except those with high clay content.
3. Allow the paste to stand for an hour and recheck the criteria for saturation. Free water should not stagnet on soil surface nor the paste stiffen markedly. If the paste dose stiffen or loose its glister, remix with more water.
4. Transfer the paste to the Buckner funnel fitted with watman No.50 filter paper.
5. Apply Vacuum and collect the filtrate in the test tube suspended to the spout of the funnel in the vacuum flask.
6. Record the ECe of the extract with the help of a conductivity meter.
7. To determine the cell constant, determine the conductivity of the 0.01 *N* KCl solution ,and measure the temperature of the solution.
8. The cell constant, K is given by

$$\text{K, cell constant} = \frac{\text{Known conductivity of 0.01}N\text{ KCl}}{\text{Conductivity of 0.01 }N\text{ KCl measured}}$$

$$\text{ECe at } 25^0\text{C} = EC_T \times K \times ft$$

Where

ECe at 25^0C is conductivity of the extract at 25^0C
EC_T is the apparent conductivity of the extract as measured at temperature.
K is the cell constant and
ft is the temperature correction factor.
(Now a days the temperature correction is provided in the instrument itself).

Observations :

1) pH of saturation paste -
2) EC of saturation extract - $dS\ m^{-1}$

Reference Book :

USDA (1954) Hand Book No.60 pp. 84-88.
Page *et al*. (1989) Soil Chemical analysis part 2 pp.168-173.

EXERCISE NO. 4 AND 5
DETERMINATION OF CATIONS (Ca, Mg, Na AND K) AND COMPUTATION OF SAR

Determination of exchangeable calcium and magnesium

Principle:

Exchangeable Ca^{++} and Mg^{++} can be determined in ammonium acetate extracts of soils by titration with EDTA (versenate). The ammonium acetate and dispersed organic matter must be almost entirely removed from the soil prior to titration with EDTA (Versenate).

Evaporation of an aliquot of the soil extract to dryness followed by treatment with aqua regia (3 parts con. HCl + 1 part con. HNO_3) and a second evaporation to dryness usually suffices for the removal of ammonium acetate and organic matter. Very dark coloured soil extracts may require additional treatment with aqua regia. After treatment, dissolve the residue in a quantity of distilled water equal to the original volume of the aliquot taken for treatment.

Reagents:

1. **Ammonium chloride - ammonium hydroxide** buffer solution: Dissolve 67.5 g of ammonium chloride in 570 ml. of conc. ammonium hydroxide and make to 1 liter.
2. **4 *N* sodium hydroxide:** Dissolve 160 g of NaOH in 1 liter of water,
3. **Standard calcium chloride solution (0.01 *N*):** Dissolve 0.500 g of pure calcium carbonate in 10 ml of approximately 3 *N* (1 + 3) HCl and dilute to a volume of exactly 1 liter.
4. **Eriochrome black-T indicator:** Dissolve 0.5 g of Eriochrome black T and 4.5 g of hydroxylamine hydrochloride in 100 ml of 95% ethanol.
5. **Ammonium purpurate indicator:** Thoroughly mix 0.5 g of ammonium purpurate with 100 g of powdered potassium sulphate.
6. **Ethylene diamine tetra acetic acid (Versenate) solution (0.01 *N*):** Dissolve 2 g of disodium dihydrogen ethylene diamine tetra acetate (EDTA) and 0.05 g of magnesium chloride hexahydrate in water and dilute to a volume of 1 liter. Standardize the solution against standard $CaCl_2$ using the titration procedure given below. The solution should be standardized using each of the indicators.
7. Acetic acid (0.1 *N*)
8. Prepare ammonium acetate extract as described in exchangeable Na.
9. HCl
10. HNO_3

Method:

1. Place 10 g of soil in 500 ml beaker.
2. Saturate the soil sample with *N* NH_4OAC, pH 7.0.
3. Percolate NH_4OAC solution in stages in buckner funnel under suction.
4. Add NH_4OAC solution only after the previous one has completely filtered through. Make up the volume to 500 ml with distilled water and it use for analysis of Ca^{2+} and Mg^{2+}.

Pretreatment of Soil Extract:

1. Transfer ammonium acetate extract to a 250 ml beaker and evaporate to dryness on a hot plate or steam bath.
2. Wash down the walls of the beaker with a small quantity of water and again evaporate to dryness.
3. Add 1 ml of nitric acid and 3 ml of hydrochloric acid and again evaporate.
4. Dissolve the residue after evaporation in 20 ml of 0:1 N acetic acid,
5. Filter through whatman filter paper (low ash content filler paper) into a 50 ml volumetric flask using water to wash the beaker and filter paper. Dilute upto volume.
6. Prepare soil water saturation paste extract and make up the volume 100 ml and used for determination of Ca^{2+} + Mg^{2+} and calculation and water soluble Ca^{2+} + Mg^{2+} .

Calcium:

1. Pipette a 5 to 25 ml aliquot (obtained after step 5) into a 150 ml Erlenmeyer conical flask. Dilute to volume of approximately 25 ml.
2. Add 0.25 ml (5 drops) of 4 N sodium hydroxide and approximately 50 mg of ammonium purpurate indicator.
3. Titrate with 0.01 *N* EDTA using 10 ml micro burette. The colour change is from orange red to lavender or purple. When close to the end point. EDTA should be added at the rate of about a drop every 5-10 seconds as the colour change is not instantaneous.

Calcium + Magnesium

1. Pipette a 5 to 25 ml aliquot(obtained in after step 5) into a 125 ml. Erlenmeyer flask.Dilute to a volume of approximately 25 ml.
2. Add 0.5 ml (10 drops) of ammonium chloride - ammonium hydroxide buffer and 3 or 4 drops of Eriochrorme black T indicator.

3. Titrate with 0.01 *N* EDTA using 10 ml micro burette. The colour change is from wine red to blue or green. No tinge of the wine red colour should remain at the end point.

Observations for Ammo-acetate extraction Ca^{2+}+ Mg^{2+}

1. Weight of soil …….. =
2. Final volume of extract prepared soil saturation extract .. =
3. Volume of extract taken for Ca^{2+}estimation ……. =
4. Volume of extract taken for Ca^{2+}+ Mg^{2+}estimation ……...=
5. Indicator used for Ca^{2+} estimation ……..=
6. Indicator used for Ca^{2+} + Mg^{2+} estimation ……..=
7. Colour change in Ca^{2+} estimation ……..=
8. Colour change in Ca^{2+} + Mg^{2+} estimation ……..=
9. No of EDTA Solution ……=

Observations for water soluble Ca^{2+} or Mg^{2+}

1. Vol. of EDTA required for Ca^{2+} estimation
2. Vol. of EDTA required for Ca^{2+}+ Mg^{2+}estimation.

Sr. No.	Volume of aliquot taken (ml.)	Butter reading (ml.)		Volume of EDTA used (ml.)
		Initial	Final	
1.	Ca^{2+} or Mg^{2+} estimation	----	----	-----
2.	Ca^{2+} + Mg^{2+} estimation	----	----	-----

Calculations:

$$Ca^{2+} \text{ or } Ca^{2+} + Mg^{2+} \text{ in me/L} = \frac{\text{ml of EDTA used X Normality of EDTA}}{\text{ml of aliquot}} \times 1000$$

$$\text{Ammonium acetate extractable Ca or Ca + Mg in me/100g soil} = \frac{\text{Ca or (Ca + Mg) Conc. of Extract in me/L X 100}}{\text{Wt. of soil in gram}} \times \frac{\text{Vol. of extract (ml)}}{1000}$$

$$= \frac{Ca^{++} \text{ or } (Ca^{2+} + Mg^{2+}) \text{ Conc. of Extract in me/L X 10}}{\text{Wt. of Soil in gram}}$$

Here volume of ammonium acetate extract taken (obtained after centrifugation or filtration) is 100 ml.

Exchangeable Ca^{2+} or $Ca^{2+} + Mg^{2+}$ =
(Ammo acetate extractable Ca^{++} or $Ca^{++} + Mg^{++}$ in me/100 g) - (Water soluble Ca^{++} or $Ca^{2+} + Mg^{2+}$ in me / 100 g)

Water soluble Ca or Ca + Mg in me/100 g =
(Ca or Ca + Mg of saturation extract in me/l) x (saturation percentage)/ 1000

Determination of exchangeable Sodium

Reagents :

Standard Sodium chloride, NaCI solution

Weigh and dissolve 5.845 g of sodium chloride (AR) in water and make upto 1 litre mark. This gives 100 meq L^{-1} stock solution of sodium.

$$5.845 \text{ g} = 5845 \text{ mg NaCl}, \quad \frac{\text{mg } 5845}{\text{equivalent wt. NaCl}} = \frac{5845}{58.45} = 100 \text{ meq NaCl}$$

Standard curve for sodium

For preparing stock solution of 100 meq, weigh and dissolve 5.845 g of sodium chloride (AR) in water and make upto one litre mark. From this stock solutions, 0, 1, 2. 3, 4 and 5 mL solution is diluted to 1000 mL with a mixture of alcoholic ammonium chloride. This solution would contain 0.1, 0.2, 0.3, 0.4 and 0.5 meq Na L^{-1} which means 0.0, 2.3, 4.6, 6.9, 9.2 and 11.5 µg Na mL^{-1}, respectively. A curve is drawn by plotting flame photometer reading on 'y' axis against concentration of Na on 'x' axis. If graph is not in a straight line reduce the range of concentration of working standard and again draw the above relationship. Now atomise the unknown samples into the flame and record the readings. Dilute the sample and record the sodium concentration from the graph and multiply by dilution factor, if any, to get the final value. Dilution is done with a mixture of alcoholic ammonium chloride (80 : 15 : 5 proportion of 1 M NH_4Cl : NH_4Cl : 4 M HCl).

Determination of exchangeable potassium

Reagent

1. **Standard KCl solution, 1000 µg mL^{-1} :** Dissolve 1.906 g of AR grade KCl in distilled water. Make up the volume upto one litre mark. This gives 1000 mg K L^{-1} solution. Dilute this solution. Take 10 mL and dilute to 100 mL with a mixture of

alcoholic ammonium chloride. This forms 100 mg K L^{-1} or 100 ppm K or 100 µg K mL^{-1}.

2. **Standard curve of K :** From the 100 mg L^{-1} K solution, prepare working standard solutions of 0, 2, 4, 6, 8 and 10 mg K L^{-1}. A curve is drawn by plotting flame photometer reading on 'y' axis against the concentration of K on 'x' axis. Now atomise the unknown samples into the flame and record the reading. Dilute the sample and read the K concentration from graph and multiply by dilution factor, if any, to get the final value with a mixture of alcoholic ammonium chloride. The proportion of mixture is as 80:15:5 with alcoholic 1 *M* Cl : $\frac{M}{20}NH_4Cl$: 4 *M* HCl respectively.

$$\text{K meq } L^{-1} = \frac{\text{K mg } L^{-1} \text{ (from standard curve)}}{\text{39.1 (eq.wt. of K)}}$$

Calculations

$$\text{Calculations K meq per 100 g} = (\text{meq K in sample} - \text{meq K in blank}) \times \frac{100 \text{ g}}{\text{weight of soil sample g}}$$

Similarly, Ca, Mg and Na can be calculated

Sodium Adsorption Ratio (SAR)

It is calculated to indicate the sodicity or alkalinity hazard.

$$\mathbf{SAR} = \frac{\mathbf{Na^{+}}}{\sqrt{\frac{\mathbf{Ca^{2+}} + \mathbf{Mg^{2+}}}{\mathbf{2}}}}$$

Where concentration of cations is in meq per litre. Based on the values of SAR, extract can be rated into different categories of sodicity as under (Richards, 1954).

Suitability class	SAR rating	Remarks
S_1. Safe	Less than 10	Little or No hazard
S_2. Moderately safe	10 - 18	Appreciable hazard, but can be used appropriate management
S_3. Moderately unsafe	18 - 26	Unsatisfactory for most of crops
S_4. Unsafe	More than 26	Unsatisfactory for all crops

EXERCISE NO. 6 AND 7
DETERMINATION OF EXCHANGEABLE SODIUM PERCENTAGE (ESP) OF SOILS

Principle

Exchangeable Na^+ is determined in ammonium acetate extract of soil through flame photometer. Analysis by flame photometer is based on the measurement of intensity of characteristics line emission given by the element to be determined. When a solution of a salt is sprayed into a flame the salt gets separated into its component atoms because of the high temperature. The energy provided by flame excites the atoms to higher energy levels. When the electrons returns back to the ground state, they emit radiation of characteristics wavelength. The intensity of these radiations is proportional to the concentration of particular element in solution which is measured through a photocell in flame photometer.

Equipments and reagents

1. Flame photometer with Na filter
2. Centrifuge with centrifuge tubes
3. Volumetric flaks (100 ml)
4. **Ammonium acetate solution (1.0 *N* of pH 7)** : Dissolve 154 g ammonium acetate in distilled water and dilute to 1.8 lit. adjust pH to 7.0 with dilute ammonium hydroxide or acetic acid whichever is required and make to 2 lit. Alternatively to 700 ml of distilled water, add 57 ml 99.5% glacial acetic acid and then 69 ml of conc. Ammonium hydroxide. Dilute to a vol. of 900 ml and adjust pH to 7.0 by addition of more of NH_4OH or CH_3COOH and make up to 1 lit. Store in pyrex or polypropylene bottle.
5. **Std. Solution of NaCl** : Dissolve 5.845 g of A.R. grade NaCl in 1.0 *N* neutral ammonium acetate solution and made to 1 lit. It will give 100 me/L of sodium. This solution is treated as stock solution.

From this solution take 0.1, 2.5, 5.0, 7.5 and 10 ml in volumetric flask of 100 ml capacity and make the volume by further adding neutral ammonium acetate solution. This will give a series of std. solutions having 0.1, 2.5, 5.0, 7.5 and 10 me/L of Na.

Procedure

I) Extraction:

The ammonium acetate extract of soil is obtained by shaking followed by filtration or centrifugation.

a) Shaking and filtration

1. Place 5 g air dried in a 150 ml Erlenmeyer flask and pour in 25 ml of neutral normal ammonium acetate.
2. Shake on reciprocating shaker for 10 min. and immediately filter through filter paper Whatman No. 1. First few mL of filtrate may be discarded. (Make up this filtrate to 1000 ml by adding ammonium acetate solution).

OR

b) Shaking and centrifugation

1. Place 5 g air dried soil in 50 mL centrifuge tube.
2. Add 25 ml of neutral normal ammonium acetate solution, stopper and shake the tube for 10 min.
3. Centrifuge the tube at 200 rpm for 10 min. until the supernatant liquid is clear.
4. Decants the supernatant liquid in to 100 ml volumetric flask.
5. Make three additional extractions in the same manner. Dilute the combine extracts to 100 ml with ammonium acetate and mix.

c) Obtain the water extract of saturated soil in the similar way of ammonium acetate extract.

II) Determination:

Determine Na in the extract prepared by either of the above methods (a) of (b) with the help of flame photometer using Na filter after necessary setting and calibration of instrument as follows:

1. Read the operation manual of flame photometer. Set the Na filter. Start compressor and light the burner of flame photometer. Keep air pressure at 5 lbs and adjust the gas feeder so as to have a blue sharp flame cones.
2. Feed std. Na solution of the highest value in the std. series and adjust the flame photometer to read the full value of emission in the scale i.e. 100 reading. Adjust 0 reading of the meter by feeding extract solution ($CH3COONH_4$).
3. Now feed different std. Na solution one by one and record the emission value for each. Plot a std. curve between conc. And reading of std. Na solution.
4. Take extract of sample and feed in flame photometer. Note the reading for sample.

Observations

Reading of known solutions (Std. solution): Record the reading of known Na solution in following manner:

Sr. No.	Concentration of Na in known solution (me/L)	Reading of flame photometer
1.	1.0	X1
2.	2.5	X2
3.	5.0	X3
4.	7.5	X4
5.	10.0	X5

Reading of unknown solution of ammonium acetate extract = y_2

Weight of soil taken = g

Reading of unknown solution of soil saturated extract = y_1

Calculations

STD. curve for sodium

A curve is drawn by plotting flame photometer reading on Y axis against concentration of Na on X axis. The concentration of Na in the unknown sample is read from curve.

Ammonium acetate extractable Na in me/100 g is calculated as follows.

$$\text{Ammonium acetate extractable Na in me/100 g} = \frac{\text{Na Conc. of extraction me/L x 100}}{\text{Wt. of soil in g}} \times \frac{\text{Volume of extract (mL)}}{1000}$$

$$= \frac{Y2 \times 10}{5}$$

Where volume of extract = 100 mL weight of soil in 5 g

$$\text{Water soluble Na (me/100g)} = \frac{\text{No. of saturated extract (me/lit) x Saturation \%}}{1000}$$

Exchangeable Na = Total Na – Soluble Na

Exchangeable Na = me/l00 g of soil i.e. ESP (Ammo. Acetate extractable Na me/100g) - (Water soluble Na me/100g)

Relation between SAR (Sodium adsorption ratio) and exchangeable sodium percentage (ESP)

ESP = 0.0673 + 0.035 SAR

$$SAR = \frac{ESP-0.0673}{0.035}$$

Soils having SAR > 13 are considered as alkali or sodic soil.

Explanation of formula

Since Na concentration me/Lit = Na concentration in me/1000ml.

$$\text{Na Conc. in 1 ml} = \frac{\text{Na conc. in me}}{1000} \times \frac{1}{1}$$

$$\text{Na Conc. me 100 ml} = \frac{\text{Na conc. in me}}{1000} \times 100$$

(Here 100 ml is the volume of extract whose reading is taken)

Since Na Conc. in 100 ml extract = Na conc. in 5 g soil

(Soil taken for extraction = 5 g)

$$\text{Na Conc. (me) /5 g} = \frac{\text{Na conc. in me}}{1000} \times 100$$

$$\text{Na Conc. (me)/1 g} = \frac{\text{Na conc. in me}}{1000} \times \frac{100}{5}$$

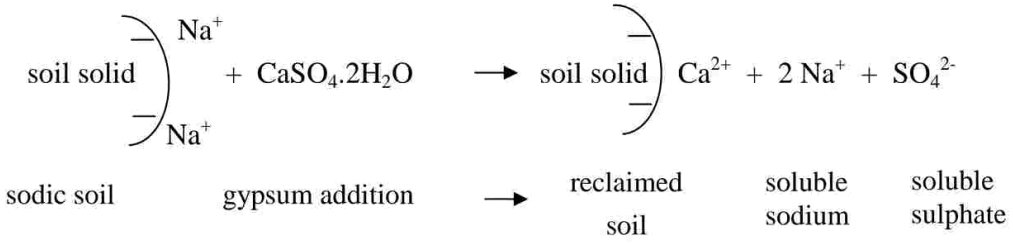
$$\text{Na Conc. (me)/ 100 g soil} = \frac{\text{Na conc. in me x volume of extract x 100}}{\text{1000 x wt. of soil taken}}$$

EXERCISE NO. 8
DETERMINATION OF GYPSUM REQUIREMENT OF SODIC SOIL

Sodicity is the major factor limiting the crop growth in most salt affected soils. The adsorption of Na molecules on clay surface enlarges the thickness of the diffuse double layer existing around the clay particles, thus increasing the repulsive force between adjacent particles of alike charge. A consequence is dispersion of clay particles and deterioration of soil structure. With increasing exchangeable sodium percentage (ESP) beyond about 15, Na enters interlayer positions between the parallel platelets of specific clay particles and bring about the swelling (Shainberg and Letey, 1984). The divalent cations are strongly adsorbed on the soil solids compared on that of sodium. Gypsum requirement does not distinguish between exchangeable K or any other exchangeable cations like Mg. If the soil is high in exchangeable K and Mg and sodium carbonate then gypsum requirement is spuriously of high value. The amount of calcium adsorbed on soil exchange complex is a measure of the gypsum requirement of soil.

Principle

A sample of sodic soil, with Na on soil complex is treated with Ca^{2+}. The difference in the Ca concentration, in the saturated gypsum solution before the addition to the soil and after addition to the soil is the Ca or gypsum requirement of soil. The Ca unutilized by the soil for exchange reaction is back titrated by EDTA complexiметry or by atomic absorption spectrophotometer. The exchange reaction is given below.



Exchangeable cations like Mg, Na and K are also displaced by calcium cations. The Ca unreacted with soil is quantitatively determined.

Reagents

1. **Saturated solution of gypsum :** Add 5 g of $CaSO_4.2H_20$ to one litre water. Shake for 1 hour and filter. Determine the Ca concentration with standard EDTA.
2. **Sodium hydroxide, 10%** : Add 10 g NaOH to 90 mL distilled water.
3. **Calcon indicator** : Dissolve 0.2 g calcon in 50 mL methanol.
4. **EDTA 0.01 *N* :** Dissolve 2 g of disodium salt of EDTA in one litre of distilled water. Determine the exact strength of EDTA with standard 0.01 *N* Ca solution.
5. **Ca solution** : 0.01 *N* : Weigh 0.5 g pure $CaCO_3$ and dissolve in 10 mL 1:1 dilute HCl and volume made to one litre.
6. **Hydroxylamine hydrochioride, $NH_2OH.HCl$:** Dissolve 5 g in 100 mL distilled water.
7. **Potassium Ferrocyanide, $K_4Fe(CN)_6$** : Dissolve 4 g in 100 mL distilled water.
8. **Triethanolamine**, reagent grade.

Procedure

1. Take 5 g soil in 250-mL conical flask.
2. Add exactly 100 mL saturated gypsum solution with pipette.
3. Shake at intervals for 10 minutes.
4. Filter through the filter paper, reject first few millilitres of filtrate.
5. Take 5 mL of filtrate in a 250-mL conical flask.
6. Add 25 mL distilled water.
7. Add 10 drops each of $NH_2OH.HCl$, $K_4Fe(CN)_6$ and triethanolamine.
8. Add 1 mL 10 % NaOH solution or enough to raise pH to 12 or more.
9. Add 5 drops of calcon indicator.
10. Titrate with standard EDTA solution. Colour changes from red to blue.
11. Run a blank using all the reagents except soil.

Observations

1. Soil sample used for treatment with gypsum solution……5 g
2. mL 0.01 *N* EDTA required for soil + saturated gypsum solution extract of 5 mL volume ……. A mL
3. mL 0.01 *N* EDTA required for blank sample ……..... B mL
4. mL saturated solution added to 5 g of soil …….. 100 mL
5. mL of aliquot of saturated gypsum solution used for titration ……5 mL
6. mL of soil + saturated gypsum solution used from 100 mL soil extract ..5 mL
7. meq of calcium to be worked out ……. ‘y’ meq

Calculation

$$\text{Y meq Ca kg}^{-1}\text{ soil} = [\text{Blank} - \text{Sample reading}] \times \text{normality of EDTA} \times \frac{\text{extract volume of 100 mL}}{\text{aliquot used 5 mL}} \times \frac{\text{1 kg 1000 g soil}}{\text{soil sample used g}}$$

$$\text{Y meq Ca kg}^{-1}\text{ soil} = [B - A] \times 0.01 \times \frac{100}{5} \times \frac{1000}{5}$$

$$\text{Y meq} = \text{Y meq Ca} = \text{Y meq } CaSO_4.2H_2O$$

$$\text{mg gypsum kg}^{-1}\text{ soil} = \text{Y meq } CaSO_4.2H_2O\text{ kg}^{-1}\text{ soil} \times \text{Equivalent weight of gypsum}$$

$$\text{mg gypsum} = \text{meq gypsum} \times 86 \text{ (Equivalent weight of gypsum)}$$

$$\text{Metric ton of gypsum ha}^{-1} = \frac{\text{mg of gypsum kg}^{-1}\text{ (Y x 86)} \times \text{soil wt in kg ha}^{-1}\text{ (2.24 x10}^6\text{)}}{\text{1000 to convert mg to g} \times \text{1000 to convert g to kg} \times \text{1000 to convert kg into M.Ton}}$$

EXERCISE NO. 9

DETERMINATION OF CALCIUM CARBONATE FROM SOIL

Carbonates occur in soils, particularly of sub - humid regions, as calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), magnesite ($MgCO_3$), and siderate ($FeCO_3$) when present in large amounts as fine earth carbonates can modify soil texture. They constitute a potential source of calcium for the replacement of exchangeable sodium during reclamation and can affect the choice of the chemical amendment to be applied to a sodic soil. Soil carbonate is usually quantified by acid dissolution as given :

$$(CaCO_3) + 2\ H^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$$

$$Ca\ Mg\ (CO_3)_2 + 4\ H^+ \longrightarrow Ca^{2+} + Mg^{2+} + CO_2 + 2H_2O$$

Basis for carbonate determination could be either acid consumption or CO_2 production or Ca and Mg production.

Neutralization Method

Reagents

1. Hydrochloric acid, 0.5 *N* standardized.
2. Sodium hydroxide, 0.25 *N*.
3. Phenolphthalein, 1 per cent in 60 per cent ethanol.

Procedure

1. Place 5 to 25 g of soil in a 150-mL beaker.
2. Add 50 mL of reagent 0.5 *N* HCl by means of a pipette.
3. Cover with a watch glass, and boil gently for 5 minutes cool, filter and wash all the acid from the soil with water.
4. Determine the amount of unused acid by adding 2 drops of phenolphthalein and titrating with standard 0.25 *N* sodium hydroxide.
5. Run the blank simultaneously.

Observations

1. Wt of soil used - 5 g
2. Hydrocloric acid 0.5 *N* added to soil - 50 mL
3. mL of extract taken for titration - mL
4. NaOH 0.25 *N* used for back titration of sample (A) - mL
5. NaOH 0.25 *N* used for back titration of blank (B) - mL

Calculations

$$\%\ CaCO_3 = (B - A)\ X\ N \text{ of NaOH } X\ \frac{\text{mL of extract prepared}}{\text{mL of extract taken}}\ X\ \frac{100}{\text{Wt. of soil}}\ X\ 0.05$$

EXERCISE NO. 10
DETERMINATION OF LIME REQUIREMENT OF ACIDIC SOIL

Principle :

A buffer solution is a mixture of weak acid and salt of the same weak acid which neutralizes both acids and bases and thus resists marked changes in pH of the system. The SMP buffer method is based on relationship between buffer indicated and $CaCO_3$ incubation measured lime requirement (LR) of group of soils. The pH of the soil buffer suspension is determined and the L.R. determined from standard L.R. Tables of Shoemaker et al.(1961).

Reagents and equipments

1. pH meter.
2. Standard buffers
3. Stirrer
4. **Buffer solution** : Dissolve following reagent grade chemicals in 800 mL distilled water. Adjust the pH to 7.5 with NaOH /HCl solution and make up volume to 1 litre.

   i. Calcium acetate - 2.0 g
   ii. Calcium chloride - 40 g
   iii. Potassium chromate - 3.0 g
   iv. p-nitrophenol - 1.8 g
   v. Triethnolamine - 2.5 mL

Procedure :

1. Take 10 g air dry soil in 100 ml beaker
2. Add 20 ml buffer solution.
3. Stir continuously for 10 min. or intermittently for 20 min.
4. Determine the pH of the suspension.
5. Read the L.R. value for the pH recorded from table below.

Observation : pH of soil buffer suspension

Table: Calibration to determine lime requirement of the surface soil using the SMP single buffer method

Soil-Buffer pH	Desired pH of soils		
	7.0	**6.5**	**6.0**
	Ag. limestone required (metric tons/ha) to reach desired pH		
6.8	3.2	2.7	2.3
6.7	5.3	4.7	3.8
6.6	7.6	6.5	5.3
6.5	10.1	8.5	7.0
6.4	12.3	10.5	8.5
6.3	14.6	12.3	10.1
6.2	16.8	14.3	11.6
6.1	19.2	16.1	13.2
6.0	21.5	18.1	14.8
5.9	23.8	201	16.3
5.8	26.2	21.9	17.9
5.7	28.5	23.9	19.5
5.6	30.6	26.0	21.0
5.5	33.2	28.0	22.8
5.4	35.4	30.0	24.4
5.3	37.8	31.8	26.0
5.2	40.1	33.8	27.6
5.1	42.5	35.8	29.1
5.0	44.8	37.8	30.6
4.9	47.2	39.9	32.3
4.8	49.5	41.6	33.8

EXERCISE NO. 11

COLLECTION OF IRRIGATION WATER AND SEWAGE WATER

Irrigation to crops is an essential input attaining high yield but quality of irrigation water affects production. For deciding the suitability of given water sample for irrigation purposes, it needs to be analysed for:

1. pH
2. Total soluble salts as EC (dS/m)
3. Cations: Calcium, magnesium, sodium and potassium
4. Anions: Carbonates, bicarbonates, chlorides and sulphates.

Collection of irrigation water sample

1. As far as possible glass or plastic bottles should be used for collection of water sample. Avoid using metal containers.
2. The container must be thoroughly cleaned before the use and should be rinsed 3 to 4 times with the water from which the sample is to be drawn.
3. While collecting the samples from tube well and hand pump, care should be taken to collect the sample only after continuous discharge of the source for 10 to 20 minutes.
4. If the source of irrigation water is a tank, canal or river, the sample should be drawn either from a spot, away from the sides or from the midstream. This can be easily managed with the help of small bucket tied at long pole.
5. About half a litre of the sample is quite sufficient.
6. The water sample after proper labelling must be sent to the laboratory immediately for testing in order to avoid any change or deterioration in its quality due to the chemical or microbial activity.
7. If delay is inevitable then 2 to 3 drops of pure toluene may be added to prevent the bacterial activity.
8. Filter the water sample through whatman no. 1 if sediments are present.
9. Storage of sample at low temperature (4^0C) is the best way to preserve most samples to prevent any microbial growth.

EXERCISE NO. 12

DETERMINATION pH AND EC FROM IRRIGATION WATER

Determination of pH

The pH value is the negative normal logarithm of the hydrogen ion activity (mol L^{-1}). As a result of the presence of strong bases and weak acids e.g. Na_2CO_3 increases the pH values, salts of weak bases and strong acids (*e.g.* $CaCl_2$) cause decreases.

The pH values of neutral water usually lie between 6.5 and 7.5 and lower values are a result of free CO_2. Biogenic decalcification in surface waters can cause the pH value to reach 9.5.

Apparatus

pH meter with glass-calomel electrode assembly

Reagents : Buffer solution pH 4, pH 7 and pH 9.2.

1. **pH 4 Buffer solution :** Dissolve 1.012 g anhydrous potassium hydrogen phthalate ($KHC_8H_4O_4$) in distilled water and make up to 100 mL in a volumetric flask.
2. **pH 7 Buffer solution :** Dissolve 1.361 g anhydrous potassium dihydrogen phosphate (KH_2P0_4) and 1.420 g anhydrous disodium hydrogen phosphate (Na_2HPO_4) (both dried at 100 ^{0}C to 130 ^{0}C for two hours) in distilled water and make up to 1000 mL in a volumetric flask.
3. **pH 9 Buffer solution :** Dissolve 3.81 g of sodium borate decahydrate (borax) $Na_2B_4O_7.10H_20$ in distilled water and make up to 1000 mL.
4. Ready made commercial buffer solutions, tablets and powders are also available in the market. These are to be dissolved in water and made up to the standard volume with distilled water as per the instructions of the manufacturer.

Procedure

1. Before measurement of pH of the sample, standardize the pH meter, using standard buffer solutions of pH near that of the sample to be tested, check the electrode response occasionally by measuring the pH of another standard buffer solution with a different pH.
2. Take 50 ml of water sample in 100 ml beaker
3. Insert the glass electrode assembly in the sample and record the pH reading using pH meter.

Observations

1. pH of irrigation water sample =

Determination of electrical conductivity

Electrical conductivity of water sample is determined directly by conductivity bridge meter and values corrected for temperature and cell constant. Electrical conductivity is commonly used for indicating the total electrolyte concentration of the ionized constituents of natural water. The EC is directly proportional to the amount of salts.

Procedure

1. Take 50 mL water samples in 100 ml beaker.
2. Insert the electrode of conductivity bridge and reading is noted after balancing the bridge.
3. Correct the reading for temperature and multiply by cell constant.
4. To determine the cell constant, determine the conductivity of the 0.01 *N* KCl solution, and measure the temperature of the solution.
5. The cell constant, K is given by

$$\text{K, cell constant} = \frac{\text{Known conductivity of 0.01}N\text{ KCl}}{\text{Conductivity of 0.01 }N\text{ KCl measured}}$$

$$\text{ECe at } 25^0\text{C} = EC_T \text{ x K x ft}$$

Where

ECe at 25^0C is conductivity of the extract at 25^0C

EC_T is the apparent conductivity of the extract as measured at temperature.

K is the cell constant and

ft is the temperature correction factor.

(Now a days the temperature correction is provided in the instrument itself).

6. The EC is expressed in dS/m = mmhos/cm (1 mhos = 1 Sieman)

Observations

1. The EC of irrigation water sample = ……. dS/m

EXERCISE NO. 13 AND 14

DETERMINATION OF CATIONS (Ca, Mg, Na AND K) FROM IRRIGATION WATER

Determination of calcium

The main cations present in irrigation water are calcium, magnesium, sodium and potassium. In this section, methods for Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} are described.

The most common and reliable method of calcium and magnesium determination in irrigation water is by complexiметric titration using disodium salt of ethylenediamine tetra acetic acid (sodium salt of EDTA).

Principle

When disodium salt of EDTA is added to water containing both Ca^{2+} and Mg^{2+}, calcium is determined separately with calcon indicator with 10% NaOH solution giving pH of 12. As sodium-EDTA forms a stronger complex with Ca^{2+}, the solution changes from pink to blue colour. Record the volume of standard EDTA for calculating Ca^{2+} in water.

Reagents

1. **Standard Ca solution, 0.01 *N* :** Weigh 0.5 g pure dried $CaC0_3$ and dissolve in 10 mL of 2 *N* HCl. Heat till the solution boils and CO_2 is completely driven off Cool and make the volume accurately to 1 litre. This solution is used for standardizing EDTA
2. **EDTA solution, 0.01 *N* :** Weigh 2 g versenate (disodium-di-hydrogen ethylene diamine tetra acetic acid), dissolve it in distilled water and make the volume to 1 litre. Standardize against 0.01 *N* Ca solution.
3. **Sodium hydroxide** : 10 % solution: 10 g NaOH + 90 mL distilled water.
4. **Calcon indicator** : Dissolve 20 mg of calcon in 50 mL of methanol.
5. **Potassium ferrocyanide, K_4FeCN_6** : Dissolve 4 g of potassium ferrocyanide in 100 mL of distilled water.
6. **Hydroxylamine hydrochloride, $NH_2OH.HCl$** : Dissolve 5 g of $NH_2OH.HCl$ in 100 mL of distilled water.
7. **Triethanolamine, TEA** reagent grade.

Procedure

1. Take a known volume (10 mL) of water sample in clean 100 mL conical flask and dilute it by adding about 25 mL of distilled water.
2. Add 10 drops each of $NH_2OH.HCl$, $K_4Fe(CN)_6$ and Triethanolamine.

3. Add approximately 5 mL, or enough of 10% NaOH solution to raise pH to 12 or higher and 5 drops of calcon indicator prepared freshly. Shake the content well.
4. Titrate with standard EDTA solution till the pink colour changes into blue.
5. Record the volume mL of EDTA used.

Calculations

$$Ca^{2+} \text{ meq } L^{-1} = \frac{\text{mL of EDTA x normality of EDTA x 1000 mL}}{\text{water sample mL}}$$

Determination of calcium and magnesium

Calcium and magnesium in water sample are determined by titrating them against standard EDTA solution using Erichrome black T (EBT) as indicator and $NH_4Cl + NH_4OH$ as buffer to give pH of about 10. The colour changes from wine red to blue or bluish green.

Principle

Sodium–EDTA forms complex a stronger complex with Ca and Mg in the alkaline buffer medium of pH 10 using Erichrome black T as indicator. At the end of reaction, the colour of indicator changes from wine red to blue or bluish green.

Reagents

1. **Buffer solution :** Add 67.5 g of pure ammonium chloride in 570 mL of concentrated ammonium hydroxide and make to one litre with distilled water.
2. **Erichrome black T, EBT indicator :** Weigh 0.5 g of EBT dye and 4.5 g of hydroxylamine hydrochloride and dissolve both in 100 mL of ethyl alcohol (95%).
3. **EDTA solution, 0.01 N :** Weigh 2 g of disodium salt of EDTA and dissolve in water and volume to 1 litre and standardize against 0.01 *N* calcium solution.
4. **Potassium ferrocyanide, $K_4Fe(CN)_6$:** Dissolve 4 g in 100 mL of distilled water.
5. **Triethanolamine, TEA** reagent grade.
6. **Calcium solution, 0.01 *N*** : Dissolve 0.5 g of pure $CaCO_3$ in 10 mL of 2 *N* HCl and dilute to 1000 mL volume.

Procedure

1. Take a known volume (10 mL) water sample in 100 mL of clean conical flask and dilute the content by adding about 25 mL distilled water.
2. Add 1 mL or enough of $NH_4Cl + NH_4OH$ buffer to raise pH to 10. Add 10 drops each of $NH_2OH.HCl$, $K_4Fe(CN)_6$ and triethanolamine and 4 drops of EBT indicator. It will give wine red colour to the solution.

3. Titrate against standard EDTA (0.01 *N)* till colour changes from wine red to blue. At the end point, no tinge of red colour should remain in titrated sample.
4. Note the volume, mL of EDTA used.

Calculations

$$Ca^{2+} + Mg^{2+} \text{ meq } L^{-1} = \frac{\text{mL of EDTA x normality of EDTA x 1000 mL}}{\text{water sample, mL}}$$

$$\text{Hence, } Mg^{2+} \text{ meq } L^{-1} = \text{meq } (Ca^{2+} + Mg^{2+})\ L^{-1} - \text{meq } Ca^{2+}\ L^{-1}$$

Determination of Sodium

Reagents :

Standard Sodium chloride, NaCI solution

Weigh and dissolve 5.845 g of sodium chloride (AR) in water and make upto 1 litre mark. This gives 100 meq L^{-1} stock solution of sodium.

$$5.845 \text{ g} = 5845 \text{ mg NaCl}, \quad \frac{\text{mg } 5845}{\text{equivalent wt. NaCl}} = \frac{5845}{58.45} = 100 \text{ meq NaCl}$$

Standard curve for sodium

For preparing stock solution of 100 meq, weigh and dissolve 5.845 g of sodium chloride (AR) in water and make upto one litre mark. From this stock solutions, 0, 1, 2. 3, 4 and 5 mL solution is diluted to 1000 mL with a mixture of alcoholic ammonium chloride. This solution would contain 0.1, 0.2, 0.3, 0.4 and 0.5 meq Na L^{-1} which means 0.0, 2.3, 4.6, 6.9, 9.2 and 11.5 µg Na mL^{-1}, respectively. A curve is drawn by plotting flame photometer reading on 'y' axis against concentration of Na on 'x' axis. If graph is not in a straight line reduce the range of concentration of working standard and again draw the above relationship. Now atomise the unknown samples into the flame and record the readings. Dilute the sample and record the sodium concentration from the graph and multiply by dilution factor, if any, to get the final value. Dilution is done with a mixture of alcoholic ammonium chloride (80 : 15 : 5 proportion of 1 *M* NH_4Cl : $\frac{M}{20}$ NH_4Cl : 4 *M* HCl).

Calculations

Na me/Litre in water extract = Na me/ litre as obtained form curve X dilution factor

$$= y \times \frac{100}{10}$$

Here, volume of made by dilution= 100 ml, water taken = 10ml

Determination of potassium

Reagent

1. **Standard KCl solution, 1000 µg mL^{-1} :** Dissolve 1.906 g of AR grade KCl in distilled water. Make up the volume upto one litre mark. This gives 1000 mg K L^{-1} solution. Dilute this solution. Take 10 mL and dilute to 100 mL with a mixture of alcoholic ammonium chloride. This forms 100 mg K L^{-1} or 100 ppm K or 100 µg K mL^{-1}.
2. **Standard curve of K :** From the 100 mg L^{-1} K solution, prepare working standard solutions of 0, 2, 4, 6, 8 and 10 mg K L^{-1}. A curve is drawn by plotting flame photometer reading on 'y' axis against the concentration of K on 'x' axis. Now atomise the unknown samples into the flame and record the reading. Dilute the sample and read the K concentration from graph and multiply by dilution factor, if any, to get the final value with a mixture of alcoholic ammonium chloride. The proportion of mixture is as 80:15:5 with alcoholic 1 *M* Cl : $\frac{M}{20}NH_4Cl$: 4 *M* HCl respectively.

Calculations

K ppm in water extract = K ppm as obtained form curve X dilution factor

$$= y \times \frac{100}{10}$$

$$K \text{ meq } L^{-1} = \frac{K \text{ mg } L^{-1} \text{ (from standard curve)}}{39.1 \text{ (eq.wt. of K)}}$$

EXERCISE NO. 15 AND 16

DETERMINATION OF ANIONS (CO_3, HCO_3, Cl and SO_4) FROM IRRIGATION WATER AND RSC AND SAR

Determination of carbonates and bicarbonates

Sum of the carbonate and bicarbonate ions constitutes to be total alkalinity of water as temporary and raises its pH to more than 7.5. This alkalinity also causes corrosion in the boilers and other metallic pipes, hence, their determination is also important for agricultural as well as industrial purposes.

Principle

The carbonate and bicarbonate ions in the sample can be determined by titrating it against standard sulphuric acid (H_2SO_4) using phenolphthalein and methyl orange as indicators, respectively. Addition of phenolphthalein (pH 8.3) gives pink red colour in the presence of carbonates and titration with H_2S0_4 converts these CO_3 into HCO_3 and decolorises the pink red coloured solution.

$$H_2SO_4 + 2CO_3^{2-} \longrightarrow 2HCO_3^{-} + SO_4^{2-}$$

In colourless solution methyl orange is added which gives yellow colour to the solution. Further titration against H_2SO_4 neutralises all HCO_3 (original + converted from CO_3) into H_2O and CO_2 and colour of solution changes from yellow to rosy red. The reaction is as given:

$$2HCO_3^{-} + H_2S0_4 \longrightarrow 2H_2O + CO_2 + SO_4^{2-}$$

Reagents

1. **Standard sulphuric acid, 0.01 *N* :** Take 0.28 mL of H_2SO_4 (36 *N)* with automatic pipette and dilute to one litre with distilled water and standardise against primary standard, Na_2CO_3.
2. **Phenolphthalein, 0.25% :** Dissolve 0.25 g pure phenolphthalein powder in 100 mL of 60 % ethyl alcohol (Ethanol).
3. **Methyl orange, 0.5% :** Dissolve 0.5 g dry methyl orange powder in 100 mL of 95% ethanol.

Procedure

1. Take a known volume (10 mL) of water sample in 100-mL conical flask and dilute it by 25 mL distilled water.
2. Add 3 drops of phenolphthalein. If pink red colour appears, it means CO_3 are present, titrate them against standard H_2SO_4 till pink colour disappears. The burette reading (volume used) is designated as 'y' mL. Here carbonates are converted into bicarbonates.
3. To this colourless solution add 3 drops of methyl orange or in original sample (if pink red colour was not noticed).
4. Again titrate with standard H_2SO_4 till colour changes from yellow to orange or rosy red. Record the volume of H_2S0_4 as 'z' mL. This volume corresponds to bicarbonates changed from carbonates plus initial bicarbonates present in irrigation waters. Here all bicarbonates are destroyed.

Calculations

1. Carbonates meq L^{-1} = $$\frac{2\text{ y x normality of } H_2SO_4 \text{ x } 1000\text{ mL}}{\text{water sample, mL}}$$

The reason for using 2y in the calculation is that mere 'y' mL H_2S0_4 reacts with CO^{2-}_3 for converting CO^{2-}_3 into HCO^{-}_3. Another y mL would be needed to act with these HCO^{-}_3 for their complete neutralization.

2. Bicarbonates meq L^{-1} = $$\frac{(z\text{-}2y) \text{ x Normality of } H_2SO_4 \text{ x } 1000\text{ mL}}{\text{water sample mL}}$$

Here, 'y' is the burette reading (mL of H_2SO_4) after phenoiphthalen is added and 'z' is the final burette reading (total volume of H_2SO_4) after addition of methyl orange.

Determination of chlorides

Chlorides are invariably present in small amounts in almost all natural waters and their content goes up appreciably with increasing salinity. Concentration of chlorides generally increases with increase in EC of irrigation water.

Principle

Mohr's titration method (argentomeric) is most commonly used for Cl determination. It depends upon the formation of sparingly soluble brick red silver chromate (Ag_2CrO_4) precipitate at the end point, when the sample is titrated against the standard silver nitrate ($AgNO_3$) solution in presence of potassium chromate (K_2Cr0_4) as colour indicator. The reactions involved are as under

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{White ppt}}{AgCl} + NO_3^-$$

$$K_2CrO_4 + 2AgNO_3 \longrightarrow \underset{\text{brick red ppt}}{Ag_2CrO_4} + 2KNO_3$$

Initially the Cl ions are precipitated as AgCl and then dark brick red precipitate of Ag_2CrO_4 starts just after the precipitation of AgCl is over.

Reagents

(**Note :** Use chloride free distilled water for the preparation of all the reagents)

1. **Potassium chromate, K_2CrO_4 indicator (5 %) solution:** Dissolve 5 g of K_2CrO_4 in about 75 mL distilled water and add a saturated solution of $AgNO_3$ dropwise until a slight permanent red precipitate is formed. Filter and dilute to 100 mL.
2. **Standard silver nitrate, 0.02 *N* :** 3.40 g of silver nitrate are dissolved in double distilled water and made up to one litre. It is to be standardised against standard NaCl solution and stored in amber coloured bottle away from light.
3. **Standard sodium chloride, 0.02 *N* :** 1.17 g NaCl (AR grade, dried at 80 ^{0}C for 1 hour), is dissolved in double distilled water and volume made to one litre.

Procedure

1. Take a known volume of water sample, say 10 mL and dilute to 25 mL or the same sample used for CO_3 and HCO_3 analysis may be utilized for chloride determination.
2. Add 5 drops of K_2CrO_4 indicator making it dark yellow and titrate with standard $AgNO_3$ (0.02 *N)* solution with continuous stirring till the first brick red colour appears. Note the volume of $AgNO_3$ required (V mL).

Calculations

$$\text{Chloride meq } L^{-1} = \frac{\text{volume of } AgNO_3 \text{ mL x normality of } AgNO_3 \text{ x 1000 mL}}{\text{water sample, mL}}$$

$$\text{Chloride meq } L^{-1} = \frac{\mu \text{ x 0.02 x 1000 mL}}{\text{10 mL}}$$

Determination of sulphate

Turbidimetric method : While traces of sulphate occur in all natural waters, its content can be appreciable in most saline waters showing EC values more than 1 mS cm^{-1} at 25 ^{0}C.

Principle

Sulphate ions are precipitated as barium sulphate crystals of uniform size in acid medium. Light absorbed by the precipitate is measured at 420 nm by using a spectrophotometer.

Reagents

1. **Barium chloride,** $BaCl_2.2H_20$ crystals of 20 - 30 mesh.
2. **Conditioning reagent :** Dissolve 75 g of sodium chloride in 300 mL distilled water and add 30 mL of concentrated HCl and 100 mL 95 % ethyl alcohol (or isopropyl alcohol). Add 50 mL of glycerol and mix well and make up to volume 500 mL with distilled water.

3. **Standard sulphate solution :** Dissolve 0.1479 g of anhydrous sodium sulphate in distilled water and make up to 1000 mL. This gives 100 µg mL^{-1} solution of sulphate.

Procedure

1. Take a known volume (100 mL) of water sample into 250 mL conical flask with pipette.
2. Add 5.0 mL of conditioning reagent and mix well using the magnetic stirrer. The speed of stirring should be the same for both sample and standards.
3. While stirring add about 0.5 g barium chloride crystals, all at once and continue to stir exactly one minute.
4. Immediately after one minute pour some of the solution into absorption cell of photometer and measure the optical density at 30-second interval for 4 minutes taking the maximum absorbance which will be normally after a period of 2 minutes after completion of the stirring at 340 nm.
5. Carry out a blank determination on the reagents used.
6. Pipette 0, 10, 20, 30, 40 and 50 mL standard sulphate solution of 100 µg mL^{-1} separately in 250-mL conical flask. Add the balance of distilled water 100, 90, 80, 70, 60 and 50 mL to make 100 mL proceed as above step '2' step to '4' for each flask and use the readings for plotting standard curve. From the standard curve, read sulphate concentration of a given sample.

Calculations

$$\text{mg } SO_4^{2-}\ L^{-1} = \frac{\text{mg } SO_4^{2-} \text{ from standard curve X } 1000}{\text{sample mL}}$$

$$\text{meq } SO_4^{2-}\ L^{-1} = \frac{\text{mg } SO_4^{2-}\ L^{-1}}{\text{Equi. wt. of } SO_4^{2-}}$$

$$= \frac{\text{mg } SO_4^{2-}\ L^{-1}}{48}$$

Water quality indices

Sodium Adsorption Ratio (SAR)

It is calculated to indicate the sodicity or alkalinity hazard.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

Where concentration of cations is in meq per litre. Based on the values of SAR, waters can be rated into different categories of sodicity as under (Richards, 1954).

Suitability class	SAR rating	Remarks
S_1. Safe	Less than 10	Little or No hazard
S_2. Moderately safe	10 - 18	Appreciable hazard, but can be used appropriate management
S_3. Moderately unsafe	18 - 26	Unsatisfactory for most of crops
S_4. Unsafe	More than 26	Unsatisfactory for all crops

Residual sodium carbonate (RSC)

This index is important for carbonate and bicarbonate rich irrigation waters. It indicates their tendency to precipitate Ca^{2+} as $CaCO_3$.

$$\textbf{RSC meq } L^{-1} = \textbf{meq } (CO_3^{2-} + HCO_3^{-}) - \textbf{meq } (Ca^{2+} + Mg^{2+})$$

Where concentration of both cations and anions is in meq L^{-1}. Sodicity hazard in terms of RSC is categorized as under (Eaton, 1950).

Suitability class	RSC Rating	Remarks
Safe	Less than 1.25 meq L^{-1}	Little or No hazard
Moderate	1.25 - 2.50 meq L^{-1}	Appreciable hazard, but can be used appropriate management
Unsafe	More than 2.5 meq L^{-1}	Unsatisfactory for most of crops

EXERCISE NO. 17

DETERMINATION OF BOD AND COD

Biochemical oxygen demand (BOD)

BOD is evaluated by measuring oxygen concentration in sample, idometrically before and after incubation in the dark at 20° C for 5days. Preliminary dilution and aeration of sample (with the help of dilution water) are usually necessary to ensure that not all the oxygen is consumed during incubation. Excess dissolved oxygen must be present during the whole incubation. Samples absorbing more than 6 mg/L of oxygen should therefore be diluted with a synthetic dilution water made from BOD free (distilled) water (reagent 4) to which the major constituents are added me concentration as in the sample. Sometimes a culture of bacteria (seed material) is added so that more of the organic matter will be used up during incubation. Generally, sewage is used as a standard seed material.

Materials and Reagents

1. BOD incubator, BOD bottles
2. All reagents used in determination of dissolved oxygen as discussed in foregoing pages.
3. BOD-free water: Pass the deionized glass distilled water through a column of activated carbon and redistill it.
4. Phosphate buffer solution: Dissolve 42.5 g potassium dihydrogen phosphate in 700 mL BOD free water and add 8.8 g NaOH. Adjust the pH 7.2. Add 2 g ammonium sulphate and dilute to 1 Litre with BOD free water.
5. Magnesium sulphate solution: Dissolve 82.5 g of magnesium sulphate in BOD-free distilled water to prepare 1 L of solution.
6. Calcium chloride solution: Dissolve 27.5 g of anhydrous calcium chloride in BOD-free distilled water to prepare 1 L of solution.
7. Ferric chloride solution: Dissolve 0.25 g of ferric chloride in 1 L of BOD-free distilled water.
8. Sulphuric acid (1 *N*): Add 2.8 mL of concentrated sulphuric acid to 100 mL of BOD-free distilled water.
9. Sodium hydroxide solution (1 *N*): Add 4 g of sodium hydroxide in BOD free distilled water and make the volume 100 mL.
10. Allylthiourea solution: Dissolve 500 mg of allylthiourea in distilled water and make the volume 1 L.

Method : Preparation of Dilution Water

1. To prepare synthetic dilution water, aerate the required volume of BOD free distilled water in a glass container by bubbling compressed air for 1 to 2 days to attain dissolved oxygen saturation. After saturation it is kept at 20 °C for atleast one day. Add per Litre of this water 1 mL each of phosphate buffer solution, magnesium sulphate solution, calcium chloride solution and ferric chloride solution. If required, add requisite amount of seed (sewage) also.
2. Dilution of sample: Adjust the pH of sample to neutrality (around 7.0) using 1 N sulphuric acid or 1 N sodium hydroxide solution as the case may be. To ensure that not all the oxygen of sample is exhausted during incubation, dilute the sample with appropriate amount of dilution water (see Table 1) according to the expected BOD content of the sample.
3. Fill two sets of BOD bottles of either 125, 250, or 300 mL capacity with this diluted water (sample) and add 1 mL of allylthiourea solution to each bottle. As far as possible avoid entraping air bubbles in BOD bottles.
4. Stopper the bottle immediately.
5. Determine the dissolved oxygen content (Do) in one set immediately following the Winkler's method of oxygen estimation as described earlier. Incubate the other set in BOD incubator. Take out the bottles after 5 days and determine immediately their dissolved oxygen content (D5).

Table1: Dilution of sample required for various ranges of expected BOD

	Volume of sample (mL)/L of mixture*	Dilution factor
0-6	1000	1
4-12	500	2
10-30	200	5
20-60	100	10
40-120	50	20
100-300	20	50
200-600	10	100
400-1200	5	200
1000-3000	2	500
2000-6000	1	1000
>6000	0.5	2000

* mixture denotes the diluted water sample. Calculations

BOD5 (mg/L) = (D0 - D5) x Dilution factor

Where, D0 = initial dissolved oxygen in the sample (mg/L); and D5 = dissolved oxygen left out in the sample after 5 days incubation (mg/L).

Note: In tropical and subtropical regions where rate of metabolism is an incubation for 3 days at 27 °C (instead of 5 days at 27 °C) is in practice and BOD so determine is expressed as BOD3 mg/L.

Chemical oxygen demand (COD)

Principle :

Most of the organic matter decomposed and produces carbon dioxide and water when boiled with a mixture of potassium dichromate sulphuric acid. A sample is refluxed with a known amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate (FAS). The amount of dichromate consumed is proportional to the oxygen required to oxidize the organic matter.

Materials and Reagents :

1. COD reflux unit consisting of flat bottom flask with ground glass mouth (250 mL) and Leibig (straight tube, single surface) condenser (30 cm).
2. Hot water bath or heating mantle,
3. Potassium dichromate solution (0.25 N): Dissolve 12.259 g of AR grade potassium dichromate, previously dried at 103°C in distilled water. Add about 120 mg sulphamic acid to this and dilute to 1 L.
4. Dry powder of silver sulphate
5. Dry powder mercuric sulphate
6. Concentrated sulphuric acid.
7. Ferroin indicator solution: Dissolve 0.695 g of ferrous sulphate and 1.485 g of 1, 10-phenonthroline in distilled water to make 100 mL of indicator solution.
8. Standard ferrous ammonium sulphate solution (0.25 N): Dissolve 98 g of ferrous ammonium sulphate in distilled water, add 20 mL of sulphuric acid, cool and dilute to 1 L by further adding distilled water. To standardize this solution, dilute 25 mL of potassium dichromate solution to about 250 mL with distilled water, add 20 mL of sulphuric acid, and cool it. Add 5-6 drops of ferroin indicator solution and titrate against ferrous ammonium sulphate solution. The colour changes from blue green to a reddish blue at end point. The exact normality of FAS is calculated as:

$$\text{Normality of FAS} = \frac{\text{Volume of } K_2Cr_2O_7 \times 1000 \times 0.25}{\text{Volume of FAS}}$$

Method :

1. Take 20 mL of sample in the flask of reflux unit and add 10 mL of potassium dichromate solution, a pinch of each silver sulphate and mercuric sulphate, and 30 mL of sulphuric acid.
2. Attach Liebig condenser to the mouth of flask and heat the flask on a hot water bath or heating mantle for at least 2 hours to reflux the contents.
3. Cool the flask, detach from unit and dilute its contents to about 150 mL by adding distilled water.
4. Add 2-3 drops of ferroin indicator solution and titrate against ferrous ammonium sulphate solution. At the end point blue green colour of contents changes to reddish blue. Run simultaneously a distilled water blank in similar manner.
5. Calculations

$$\text{COD (mg/L)} = \frac{\text{(B-T) x N x 1000 x 8}}{\text{Volume of Sample (mL)}}$$

Where, T = volume of titrant (FAS) used against sample (mL); B = volume of titrant (FAS) used against blank (mL);. N = normality of titrant (FAS) (0.25), equivalent weight of oxygen is 8.

Question :

1. What is the meaning of BOD ? What it indicates? What is its significance?
2. Write in brief the procedure for BOD determination.
3. What is the meaning of COD ? What it indicates? What is its significance?
4. Write in brief the procedure for COD determination.

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EXERCISE NO. 18

SATELLITE IMAGE ANALYSIS BY VISUAL METHOD

Remote Sensing is the science and art of obtaining information about an object/phenomena or area through the analysis of data acquired by a device that is not in contact with the object under investigation. This technology first emerged in 1840 and pictures were taken by balloon. Subsequently, Cameras were mounted in airplane for military survey in the first world war for reconnaissance survey.

This technology includes both satellite and aerial remote sensing. The basis source for this technology is electromagnetic radiation and this energy from the sun reaches the earth surface and again reflected or transmitted or absorbed by the objects which is collected by the satellite sensors or recorded in the photographic film. The product from the aerial camera is called photograph and the term image is used for any pictorial representation of image data. The reflectance/ remittance/ absorption of energy by an object forms the base for the brightness or darkness in an image or photographs. This is further interpreted for the identification of the features. The earlier stage aerial and satellite data were in black & white and subsequent advancement in sensor development and colour film leads the generation of colour photographs and images. The significant advance in sensor technology stemmed from subdividing spectral ranges of electromagnetic radiation into several bands allowing sensors in several bands to form multispectral images In general there are three different types of data products namely black and white photograph or panchromatic image (single band), normal colour and false colour composite (Multispectral). Single band image displays as a gray scale but combination of three bands at a time generates colour composite images.

Interpretation

Interpretation is the processes of detection, identification, description and assessment of significant of an object and pattern imaged. The method of interpretation may be either visual or digital or combination of both. Both the interpretation techniques have merits and demerits and even after the digital analysis the output are also visually analysed. The ability of human to identify an object through the data content in an image/photo by combining several elements of interpretation.

There are two types of extraction of information from the images/ photographs namely; Interpretation of data by visual analysis, Semi automatic processing by computer followed by visual analysis like generation of vector layer from raster image through onscreen digitisation and DTM/DEM generation. Similarly interpretation of aerial photographs through 3D generation through visual studies. In general analog format in remote sensing data is being used in visual interpretation. This involves the systematic examination of data, studying existing maps, collection of field information and works at various levels of complexity. The analysis depends upon the individual perception, and experience of the interpreter, nature of the object, quality of the data, scale, combination of special bands etc.

The entire process of visual interpretation can be divided into following few steps namely detection of an object, interpretation, recognition and identification, analysis, classification, deduction and idealisation and based on this identifying an object conclusion. Hence interpretation is the combined result of identification of feature through photo recognition elements, field verification and preparation of final thematic maps. It also requires the process of observation coupled with imagination and great deal of patience.

Basic elements of interpretation

The interpretation of satellite imagery and aerial photographs involves the study of various basic characters of an object with reference to spectral bands which is useful in visual analysis. The basic elements are shape, size, pattern, tone, texture, shadows, location, association and resolution.

Shape : Image showing that shape can be a very distinctive clue for interpretation. Shape refers to the general form, structure, or outline of individual objects. Shape can be a very distinctive clue for interpretation. Straight edge shapes typically represent urban or agricultural (field) targets, while natural features, such as forest edges, are generally more irregular in shape, except where man has created a road or clear cuts. Farm or crop land irrigated by rotating sprinkler systems would appear as circular shapes.

Size : Size of objects in an image is a function of scale. Size of objects in an image is a function of scale. It is important to assess the size of a target relative to other objects in a scene, as well as the absolute size, to aid in the interpretation of that target. A quick approximation of target size can direct interpretation to an appropriate result more quickly. For example, if an interpreter had to distinguish zones of land use, and had identified an area with a number of buildings in it, large buildings such as factories or warehouses would suggest commercial property, whereas small buildings would indicate residential use.

Pattern : refers to the spatial arrangement of visibly discernible objects. Typically an orderly repetition of similar tones and textures will produce a distinctive and ultimately recognizable pattern. Orchards with evenly spaced trees, and urban streets with regularly spaced houses are good examples of pattern.

Texture : refers to the arrangement and frequency of tonal variation in particular areas of an image. Rough textures would consist of a mottled tone where the grey levels change abruptly in a small area, whereas smooth textures would have very little tonal variation. Smooth textures are most often the result of uniform, even surfaces, such as fields, asphalt, or grasslands. A target with a rough surface and irregular structure, such as a forest canopy, results in a rough textured appearance. Texture is one of the most important elements for distinguishing features in radar imagery.

Shadow : it is also helpful in interpretation as it may provide an idea of the profile and relative height of a target or targets which may make identification easier. However, shadows can also reduce or eliminate interpretation in their area of influence, since targets within shadows are much less (or not at all)

discernible from their surroundings. Shadow is also useful for enhancing or identifying topography and landforms, particularly in radar imagery.

Tone: Refers to the colour or relative brightness of an object. The tonal variation is due to the reflection, emittance, transmission or absorption character of an objects. This may vary from one object to another and also changes with reference to different bands. In General smooth surface tends to have high reflectance, rougher surface less reflectance. This phenomenon can be easily explained through Infrared and Radar imagery .

Infrared imagery: Healthy vegetation reflects Infrared radiation much more stronger than green energy and appears very bright in the image. A simple example is the appearance of light tone by vegetation species and dark tone by water. Particularly in thermal infrared images the brightness tone represents warmest temperature and darkness represent coolest temperature. The image (Fig2) illustrates daytime and night time thermal data. The changes in kinetic water temperature cause for the tonal changes. Hence time is also to be taken consideration before interpretation

Radar Imagery : Smooth surfaces reflect highly and area blocked from radar signal and appear dark. Bridges and cities show very bright tone, on the contrary calm water, pavement and dry lake beds appears very dark tone.

Location Site : The relationship of feature to the surrounding features provides clues to words its identity. Example: certain tree species words associated with high altitude areas

Resolution: It depends upon the photographic/imaging device namely cameras or sensors. This includes of spectral and spatial resolutions. The spectral resolution helps in identifying the feature in specific spectral bands. The high spatial resolutions imagery/photographs is useful in identifying small objects.

Association : it takes into account the relationship between other recognizable objects or features in proximity to the target of interest. The identification of features that one would expect to associate with other features may provide information to facilitate identification. In the example given above, commercial properties may be associated with proximity to major transportation routes, whereas residential areas would be associated with schools, playgrounds, and sports fields. In our example, a lake is associated with boats, a marina, and adjacent recreational land.

Hence, careful examination has to be done to identify the features in the imagery combined with field information.

Issues in interpretation :

- Unfamiliar scale and resolutions.
- Lack of understanding of physics of remote sensing.
- Understanding proper spectral character of each object
- visually interpret 3 layers of information at a time.

Success of interpretation :

- Training and experience of the interpreter
- Quality of photo/images
- Local knowledge of the study area.

Advantages in visual Interpretation :

- Simple method
- Inexpensive equipment
- Uses brightness and spatial content of the image
- Subjective and qualitative
- Concrete

Advantages of digital image processing :

- Cost-effective for large geographic areas
- Cost-effective for repetitive interpretations
- Cost-effective for standard image formats
- Consistent results
- Simultaneous interpretations of several channels
- Complex interpretation algorithms possible
- Speed may be an advantage
- Explore alternatives
- Compatible with other digital data

Disadvantages in digital processing :

- Expensive for small areas
- Expensive for one-time interpretations
- Start-up costs may be high
- Requires elaborate, single-purpose equipment
- Accuracy may be difficult to evaluate
- Requires standard image formats
- Data may be expensive, or not available
- Preprocessing may be required
- May require large support staff
- High resolution images

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