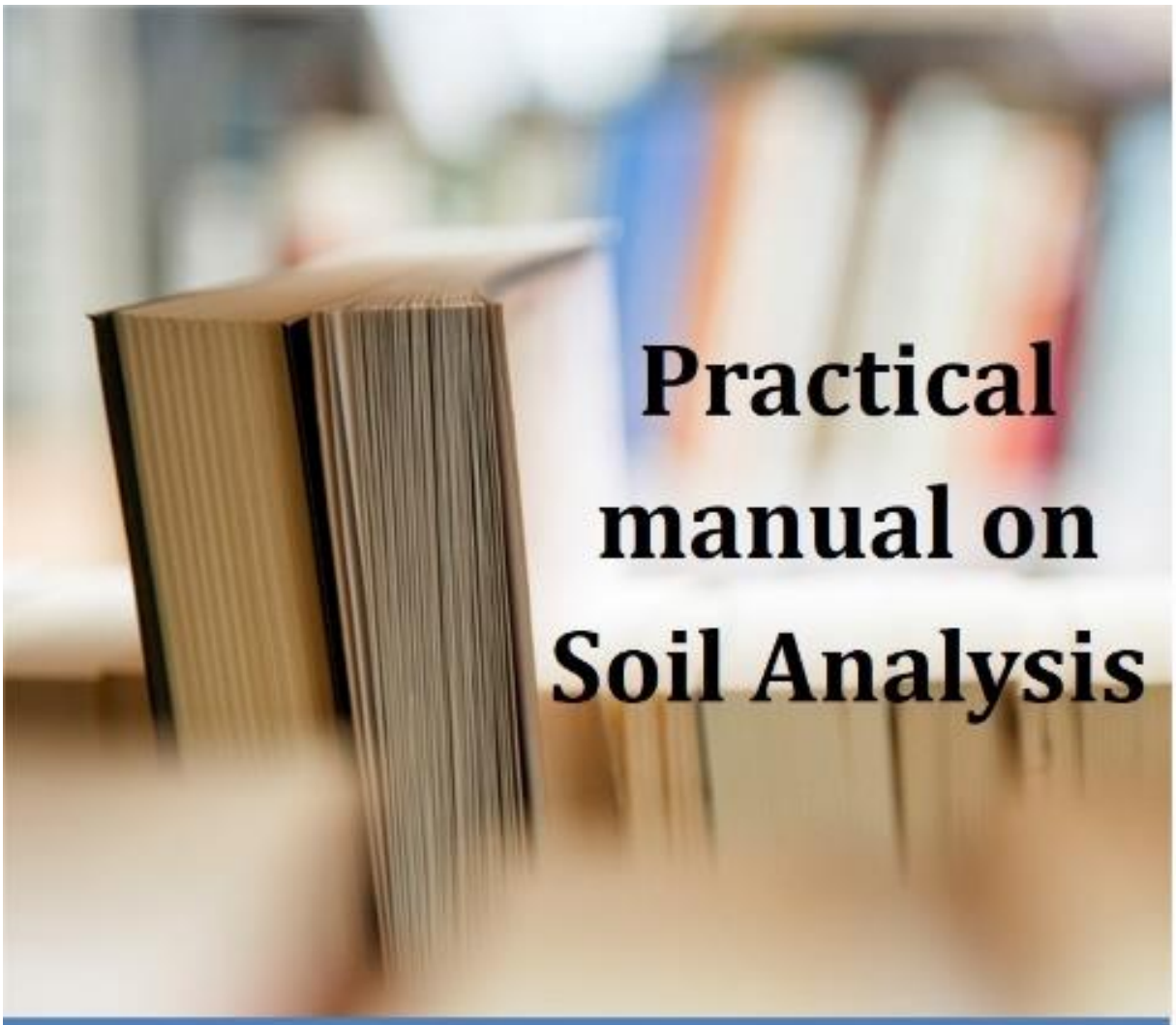

Practical manual on Soil Analysis

भाकृअनुप–केन्द्रीय शुष्क क्षेत्र अनुसंधान संस्थान
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1. Collection and Preparation of Soil Sample for Analysis

Soil testing is an acceptably accurate and rapid soil chemical analysis for assessing available nutrient status for making fertilizer recommendations. The major steps in practical soil testing are:

1. Soil sampling
2. Processing of soil sample
3. Chemical analysis
4. Interpretation of soil analysis data

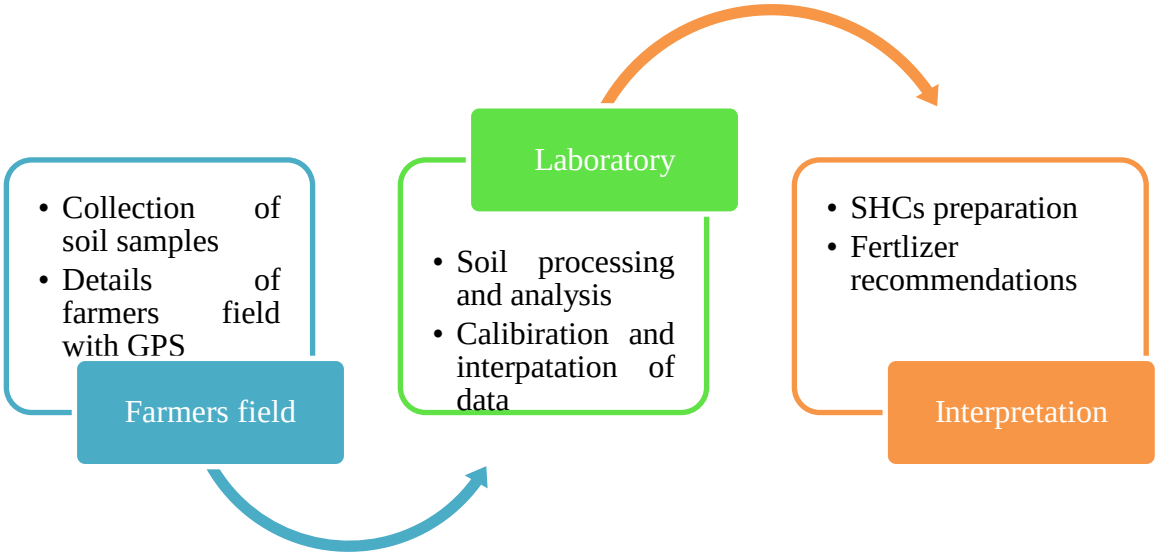


Fig. 1.1 An overview of soil testing process from farmer field to laboratory and vice-versa

1. Soil sampling

The soil sampling is perhaps the most vital step for any analysis. A useful soil testing service starts with the collection of representative soil samples. A fertilizer recommendation made after analyzing of soils. The importance of taking a representative composite soil sample is, therefore, self-evident. One field can be treated as a single sampling unit only if it is relatively uniform and does not exceed ~ 0.5 ha area. Variations

in slope, colour, texture, management, and cropping pattern should be taken into account and separate composite soil sample adequately representing the field, small portions of surface soil should be collected ~ 15 cm soil depth from at least ten well-distributed spots in the field, mixed well, and ~ 500 g of representative sample sent to laboratory. Proper sampling tools are essential for collection of good soil samples. Spade or *Khurpi* is an appropriate tool for sampling of soft and moist soil. However, a screw type auger is more suitable on hard and dry soil although post hole auger is useful in the excessively wet area.

Soil sample collection from field

Numbers of equipments are required for soil sampling (*i.e.* spade/khurpi/auger; polythene bucket; scale; marker/ball pen/lead pencil; a sheet of thick paper; polythene sheet; sampling bag etc.)

Fig. 1.2 Different equipment useful for the collection of soil samples

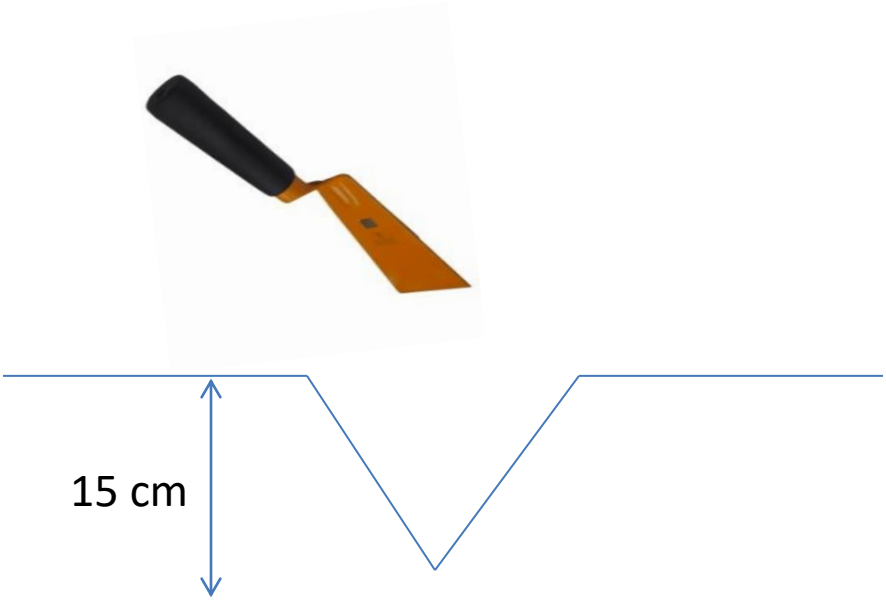


Fig. 1.3 Draw samples from field in “V” shaped cut

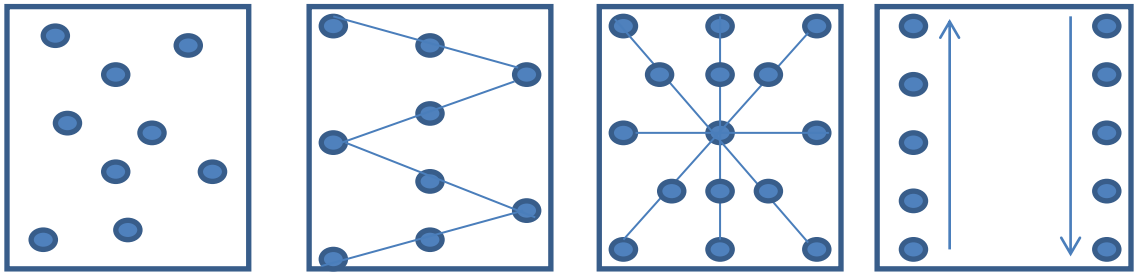


Fig. 1.4 Several ways of taking samples: (a) network (b) Z-scheme (c) diagonally in (d) permanent crops or standing crops

Procedure of soil sampling

1. Decide the soil unit (or plot) and make a traverse over the soil unit (or plot).
2. Clean the site (with spade) from where soil sample is to be collected.
3. Standing on opposite side, a lump of soil is removed
4. A pit of vee (V) shape is formed. Its depth should be 0-15 or 0-30 cm. (*i.e.*, depth of tillage).
5. Take out the soil-slice (like bread-slice) of half inch thick from both the exposed surface of the pit from top to bottom. This slice is also termed furrow-slice. To collect the soil-slice spade may be used.

6. Collect furrow-slices from 8-10 or sometimes 20-30 sites. Select the sites at random in a zig-zag (or criss-cross) manner. Distribute the sites throughout the entire soil unit (plot). Do not take the prohibited samples and local problem soils.
7. Reduce the collected bulk soil up to 250-500 g by **quartering process** (Fig 1.5)
8. Furnish the following information in two sheets of thick paper with the sample. One sheet is folded and kept inside the bag. Another sheet is folded and attached with the bag.
9. For making composite sample, collect small portions of soil up to the desired depth (0-20 cm or more) by means of suitable sampling tools from 15 to 20 well-distributed spots, moving in a zig-zag manner from each individual sampling site after scrapping off the surface litter, if any, without removing soil and store in a clean basket

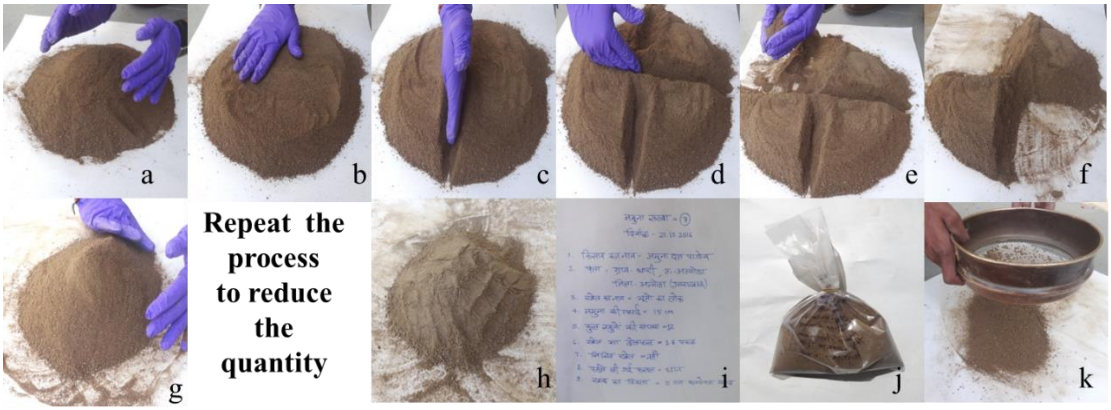


Fig. 1.5 Collecting of soil sample and mix thoroughly (b) Spread soil sample on wooden floor like a thick layer (c, d, e, f, g) the quartering process (make four quarters, discard the opposite ones) (h) remixing the remaining two quarters and repeat the process to reduce the quantity to about 250-500 g. (i, j, k) attach one label inside or outside the bag indicating above mention information and transfer the remaining (250-500 g) soil in bag and send to soil testing laboratory for processing.

2. Processing of soil samples

After the sample reaches the laboratory room it is to be dried, ground and sieved before undertaking the analysis work. Preserve the fresh sieved samples before drying for

specific analysis like enzymes, ammonium and nitrate nitrogen etc.

Drying: Samples are generally air-dried (25-35^{o}C; relative humidity 20-60%) and/or oven dried below 8% soil moisture before further process for analysis. The analyzed results of soil samples are generally expressed on oven dry basis.

Sieving: Field moist samples prior to drying can be made to pass through a 6 mm sieve (about 4 mesh per inch) by rubbing with fingers. This practice seems of much advantage in case of heavy soils. Soils in the right moisture condition can even be passed through a 2 mm sieve (about 10 meshes per inch). For certain type of analysis (*e.g.* organic carbon), grind the soil further so as to pass it through 0.2 to 0.5 mm sieves.

Grinding: A roller, rubber pestle in an agate mortar, or a motorized grinder is commonly employed. Crushing of the gravel and primary sand particles should be avoided. For heavy soil, it is better to pass these through a 2 mm sieve before allowing them to get completely air dried.

Mixing: Sample should be thoroughly mixed by rolling procedure. Place the dried, ground and sieved sample on a piece of a cloth. Grasp the opposite corners and then holding one corner down pull the other corner across the sample. The process should be repeated back in the reverse direction.

Storing: Store the processed soil samples in suitable containers keeping in view the contamination prospects of the storing material. Label the samples properly with all possible details including location, date, soil depth, cultivation history etc. giving cultivators or experimenters name, plot number, date of sampling and initials.

Precautions in collections and storage of samples

Special care in collection and handling of the soil samples is required in order to prevent contamination. The following precautions should be taken to minimize error:

- The sample should be avoided contact with chemicals, fertilizers or manures.
- Use stainless steel and wooden augers instead of rusted iron khurpi or kassi for collectingsample for micronutrient analysis.
- Fertilizers, salt or other chemicals bags or boxes should not be used for storing of

sample.

- Store soil sample in clean, preferably new, cloth or polythene bags.
- Use porcelain, glass or polythene jar for long duration storage.

Labeling of samples

Samples should be labeled properly for identification. A label of thick paper having marked identity and other details should be put inside the sample bag and another one carrying same details tied/pasted outside the bag. If the soil sample is wet, the label should be written with lead pencil or apermanent ink marker, before air drying.

Information sheet

- Name, address and phone no. of the farmer (or farm owner)
- GPS coordinates
- Plot number or any other number that identifies the plot (or Soil unit)
- Soil texture (sandy/clay/loam)
- Availability of irrigation facilities and drainage system
- Upland/Medium land/Lowland
- Depth of soil sample (0-15/15-30/30-45 cm)
- Information of the previous crop- Name and variety of the crop,
- Dose of organic manure and dose of fertilizers, if applied and yield
- Information's of the crop that will be grown-Name and variety of the crop, Season (pre Kharif/Kharif/rabi)
- Problem, if any
- Date of sample collection
- Signature of the farmer (or farm owner)

3. Soil analysis

Soil analysis is a set of various chemical processes that not only determine the amount of available plant nutrients in the soil, but also the chemical, physical and biological soil properties important for soil health as well as nutrition of plants. . Various analytical procedures for physico-chemical properties like soil reaction (pH), soil salinity (EC), total $CaCO_3$, lime requirement, gypsum requirement, organic matter, and the content of

plant nutrients; nitrogen (N), phosphorus (P), potassium (K), humus content, total sulphur (S), trace elements, and other physical characteristics like water holding capacity, permeability, bulk density, soil texture etc. are being described in the manual.

4. Interpretation

The soil results obtained will be categorized based on critical limits i.e., low, medium and high and developing nutrient indexes. The results may also be used for other academic and research purposes.

Benefits of soil testing

Soil test reports will generally provide appropriate fertilizer application recommendations for nitrogen, phosphorous, potassium, gypsum and limestone. Soil testing also allows the determination of the micronutrient requirements of crop. Application of too little fertilizer will result in lower, your crop yields and returns. Too much fertilizer will waste time and money and risk environmental damage due to nutrient runoff. Consequently, soil testing provides a farm management tool with a potential benefit to the farmer of increased yields, reduced operating costs and superior environmental risk management. Additional benefits include; improved crop maturity and quality, higher tolerance to disease and pest damage, and increased growth. It gives farmers a service leading to better and more economic use of fertilizers and better soil management practices for increasing agricultural production

Summary

Soil testing is an important for better fertilizer recommendation. From this soil test report, farmers know the actual amount of nutrient present in soil and accordingly plan his future cropping patterns carefully without indiscriminate uses of chemical fertilizers with better crop growth. With the help of soil testing, soil health card is also issued to every farmer every three years for efficient utilization of nutrient.

2.
Determination of Soil Moisture

Estimation of soil moisture is required for almost all types of soil studies. It is mainly utilized to:

(i) It is important to assess the availability of soil water to plants

(ii) To work out available water storage capacity of soils and optimum soil water regimes, depletion patterns and consumptive use of water in various crops.

(iii) To find out the suitable time for irrigation and calculate the amount of irrigation water needed to bring the soil to a specified water content.

(iv) To study the soil water movement.

(v) To predict the strength and mechanical behavior of soil.

Multiple methods including direct and indirect methods are being used for estimation of soil moisture in the soil systems.

1. DIRECT METHOD

1.1 Gravimetric Method

Principle

The dry mass of the soil is recorded after drying the soil at a temperature of 105°C for 24 hours or till the weight becomes constant. At this temperature all the soil water, except the chemically-bound is expected to be driven out. The difference in wet and dry weights of soil sample is expressed as soil water content on dry-weight basis of soil.

Equipment

I. Auger or sampling tube
II. Moisture box (Aluminum)
III. Precision balance

IV. Hot air oven

Procedure

1. Weigh an empty aluminum moisture box and record the weight.
2. Put the soil in a moisture box and record the weight.
3. Place the moisture box containing wet soil sample into hot air oven and heat at 105℃ for 24 hrs. or until constant weight.
4. Cool the box in a desiccator.
5. Weigh the moisture box with dry soil sample at room temperature.

Calculation

Mass of moisture box + moist soil = Wbsm g

Mass of moisture box + dry soil = Wbsd g

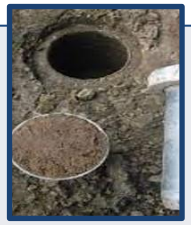
Mass of empty moisture box = Wb g

Per cent water content = $\frac{(Wbsm-Wbsd)}{(Wbsd-Wb)} \times 100$

2. INDIRECT METHOD

2.1 Moisture Meter (i.e., TDR-150)

2.2 Neutron Probe Method



3.
Determination of Soil Bulk Density

Soil bulk density (Db) is defined as the ratio of mass of oven-dry soil (Ms) to its bulk volume (Vb). This bulk volume includes the volume of soil particles as well the pore space. It is expressed in the units similar to that of particle density as Mg m^{-3}. The value of bulk density depends upon the mineral matter composition, organic matter content, soil structure and state of packing. It largely depends upon soil management practices. Ploughing a soil loosens its state of packing and bulk density decreases. Compacting the soil increases its bulk density. Higher organic matter tends to lower soil bulk density. The fineness of soil increases its pore space and decreases bulk density. The bulk density of soil generally increases with depth due to the low organic matter content in the lower layers and due to the compaction resulting from the overburden pressure of the upper layers of the soil. Roots have some critical bulk densities which if exceeded restrict their penetration into the soil. Thus, the management practices should be so chosen and conducted which do not raise the bulk density of any layer above the critical level. The critical bulk density varies with soil type and the crop grown. The bulk density of soils generally varies from 1.0 to 1.8 Mg m^3. It, however, may be lower or exceed this range depending upon the extent of soil packing. The bulk density of soil is used to convert water content by mass to volume water content, for calculating total soil porosity and void ratio when particle density of soil is known; and for estimating the mass of a volume of a soil too large to weigh conveniently, such as mass of furrow slice.

Methods of Determination

Clod saturation method:

The bulk volume (Vb) of an oven-dried clod weighing. Ws, can be expressed as:

$$Vb = Vs + Vp \quad (1)$$

Where Vs and Vp are the volumes of the soil solids and pore space, respectively. Vs may be calculated as:

$Vs = Ms / Dp$ (2)

The particle density, Dp may either be determined separately by taking soil contiguous to the dry clod or an average value of 2.65Mg m^{-1} may be used when the determination is not possible. Students may make use of this value determined in Exercise I. From equations (1) and (2)

$Vb = Ms / Dp + Vp$ (3)

When the oven-dried clod is saturated, all the pores are filled with water and the volume of water absorbed (Vwa) by the soil upon saturation gives its total pore space.

Substituting for Vp:

$Vb = Ms/Dp + Vwa$ (4)

since b

ulk density (Db) is mass per unit bulk volume of the soil

$Db = Ms/Vb$ Mg m^{-3}

This method is not suited to the soils which swell on saturation.

Apparatus:

1. Soil moisture gauge or Pycnometer with all the accessories to determine Dp
2. A balance
3. Sand column to saturate the clods
4. Watch glass
5. Filter paper

Procedure

1. Take an oven-dried clod weighing about 50-70 g.

2. In case the clod is not oven-dried, remove 25 g of soil from it and determine its moisture content.

3. Weigh the clod.

4. Prepare sand column by filling coarse sand in metallic sieve or any other container with perforated bottom.

5. Cover the sand column with filter paper and put it in a tray filled with water to about 2 mm below the upper surface of column.

6. Put small filter-paper disc on the filter paper covering the sand column. - Place the

clod gently on the filter paper disc.

7. Place the clod gently on the filter paper disc.
8. Let clod saturate completely by capillarity. This can be judged form the appearance of clod surface. In case of fine-textured soil, the clod may be left overnight on the sand column for saturation
9. After it is completely saturated, transfer the clod along with the filter paper disc on to a watch - Push the ring using a spatula.
10. Immediately weigh the clod along with filter paper and watch glass. Find out weight of water absorbed by the filter paper disc taking the dry and wet weights of 3-4 discs of similar size and shape subtract from this mass, the mass of watch glass and weight of water absorbed by filter paper disc.

Observations and calculations

Mass of dry clod	= Ms g	
Particle density of soil	= Dp g cm^{-3}	
Volume of solid phase of clod Vs	= Ms/Dp cm^3	(1)
Mass of the saturated clod	= Msm g	
Mass of water absorbed during saturation	= (Msm-Ms) g	
Volume of water absorbed, Vwa	= (Msm –Ms)/Dw cm^3	(2)
Total volume of the clod, Vb	= (1) + (2) cm^3	

$$\text{Bulk density } \left(\frac{\text{Mg}}{\text{m}^3}\right) = \frac{\text{Ms}}{\text{Vb}}$$

2. CORE METHOD:

The undisturbed soil cores are taken out at a given soil depth with the help of cylindrical iron rings and dried in an oven at 105°C for 24 h or till the weight of soil becomes constant. The ratio of dry soil mass of core and the internal volume of the cylindrical ring (equivalent to bulk soil volume) is expressed as bulk density of soil in Mg m^{-3}.

Apparatus

1. Cylindrical iron rings of 5-7.5 cm internal diameter and 5 cm length with one end sharpened so as to penetrate the soil.

2. Concentric rings about 2 cm length and of diameter similar to that of the cylindrical rings (collar).
3. Spade
4. Moisture box
5. A hot-air oven
6. Precision balance

Procedure

1. Dig out a pit about 50 cm wide and 30-180 cm deep depending on the depth of bulk density
2. Clean the soil surface at one end of the pit of any vegetation or litter Place the iron ring on the soil surface and place the collar ring on it
3. Push the ring into the soil with the help of a hammer till the ring is embedded completely into the soil and the collar remains on the surface
4. Push the spade underneath the ring and take out the iron ring along with collar.
5. Scrap the two ends of soil core with a sharp blade so as to remove the soil which is in excess to the dimensions of the iron rings and weigh the soil core along with the iron ring.
6. Keep the soil core in an oven at 105°C for 24 h so as to dry the soil completely.
7. If it is not possible to transport the whole of the soil core to the laboratory for drying, place as of soil from the core in the moisture box and put on the lid to determine its moisture co gravimetrically.
8. Record the internal diameter of the core with the help of a Vernier Calipers and note down length.
9. Calculate its internal volume of the core which is equivalent to the bulk volume of the soil.
10. The dry weight of the soil core when divided by its bulk volume gives bulk density of the soil using the foot scale, the bulk density of the next desired layer can be determined by taking out a soil core at that depth as described above.

Calculations

I. Bulk volume of the soil

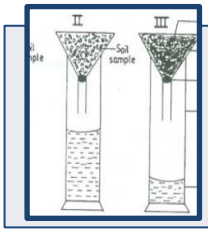
Length of the core	= L cm
Inner diameter of the core	= D cm
Volume of the soil core	= π (D^2/4) L, cm^3

II. Dry mass of the soil core

Mass of the iron core	=Mc g
Mass of iron ring + dry soil	= Mcds g
Mass of dry soil core	=(Mcds - Mt) g
Bulk density of the soil	=(Mcds - Mc)/[(D^2/4) L] g cm^3

Precautions

1. The iron ring should be pushed into the soil uniformly.
2. The depth of soil to be sampled for bulk density should be measured accurately with the foot scale.
3. The excess soil at the two ends of the iron ring should be removed carefully with the help of a fine blade.



4.

Dertemination of the Maximum Water Holding Capacity of Soil

A soil is said to be saturated when all its pore space is filled with water and air is completely excluded. The amount of water present in a saturated soil is called saturation percentage. This implies that the saturation percentage numerically equals the total volume of the soil pores. This assumption is not always correct, because some entrapped air always remains in the soil in spite of the best precautions. Error is also introduced when the salts present in the soil dissolve in water or the soils swell on moistening. Despite these errors, it is reasonable to base saturation percentage on the porosity of soil.

The saturation percentage gives good information regarding the total porosity and the water holding characteristics of the soil. The analysis of the saturation extract is commonly employed to study the physical and chemical properties of the soil. This value is reproducible and is the closest approach to moisture conditions in the soil. Most often the field soils are not saturated, their water content can be expressed as degree of saturation. It is defined as the ratio of water content on volume basis and total porosity of the soil.

Saturation Percentage from the volume of water added to the soil

The method is based on the principal of removing the entrapped air by stirring the sample with a spatula. In case of undisturbed soil sample, the entrapped air causes a serious error. In that case, the sample is saturated under vacuum for 24-36 hours. When a disturbed soil sample is stirred with a spatula along with the addition of water, stage is reached when the paste, so formed, flows freely and the mass, as a whole glistens and reflects light. At this stage, all the pores are thought to be filled with water making the soil saturated.

Apparatus

1. A burette of 50 mL capacity
2. A steel spatula
3. A beaker of 500-mL capacity.

Procedure

1. Take 200 g of an oven-dried soil sample in a 500-mL beaker. (If the soil is not oven-dried, place a sample of it in the oven for moisture determination on the dry-weight basis.)
2. Start adding water to the sample from the burette and continue adding water in successive but small lots without stirring the soil until water just wets the entire soil mass.
3. Add a few more drops slowly till the surface glistens.
4. Mix the soil with spatula.
5. Add more drops of water if needed, so that the paste slides freely down the spatula, reflects light and glistens.
6. See if the soil paste just flows together to close a hole left by the spatula drawn through it at this stage, the soil is at the saturation percentage.
7. Cover the beaker with a watch-glass and leave the saturated paste for an hour to attain equilibrium.
8. Check it again for the end point.
9. If the paste stiffens or loses its shine, remix it after adding more water.
10. Note that total amount of extra water, if added.

Precautions

Very fine textured soils should be stirred to the minimum, especially during the earlier stages wetting otherwise, no definite end-point will be arrived at and the results will not be repeatable. Coarse textured soils, on the hand, should be stirred vigorously.

Observations and calculations

Weight of soil taken = 200g
Initial Reading = X ml
Final Reading = Yml
Volume of water added = (Y-X) mL
Saturation Percentage = (Y-X) × 100/200

Maximum Retentive Capacity from the weight of water absorbed by the soil

With the capillary rise of water, the soil immediately above a water-table gets saturated. The height up to which the soil is saturated depends upon the texture and the structure of

soil.

Apparatus

1. Keen's Box: This is a cylindrical dish with its internal diameter 5.6 cm and height 1.6 cm. The bottom of the box is perforated with holes, 0.75 mm in diameter and 4 mm apart. Each box is supplied with a slit brass wire ring which serves to hold a filter-paper in position over the perforated bottom
2. Filter-paper discs of a diameter corresponding to the inner diameter of the Keen's box
3. A watch-glass
4. A Physical balance
5. A soaking-tray
6. A spatula

Procedure

1. Place a Whatman No.1 or No. 44 filter-paper disc at the bottom of Keen's box. - Record the weight of the filter-paper and the box.
2. Add soil to the box in 5-6 g lots at a time and tap the box 20-30 times gently and then add subsequent lots with continual tapping until it is nearly full.
3. Add more soil to fill the box and level off the surface with the spatula.
4. Carefully tap the upper edge of the box several times with soil as before (avoid the loss of coarse particles which tend to come to the surface on tapping).
5. Place the box in the soaking-tray in such a way that the water level is about 1/2 cm above the base of the box. - After some time, when whole of the soil mass is moistened through the capillary rise of water, add water to restore the initial depth.
6. Leave the sample overnight. (If the soil expands on wetting, crumbs of soil may fall from the top, but this will not affect the water-holding capacity).
7. On next day, remove the Keen's box from the soaking tray.
8. Observe a continuous and shining film of water at the soil surface.
9. Carefully wipe the box dry from outside.
10. Transfer the box on to a watch-glass and weigh it immediately
11. Place the box in an oven at 105°C for 24 hours, or until constant weight is

obtained.

12. Cool the box in a desiccator and weigh it again.
13. Determine the amount of water absorbed by the filter-paper disc by weighing four water-saturated and four dry filter paper discs of the same size as placed originally in the box.
14. Calculate the average weight of disc under dry and saturated conditions. The difference in weight gives the amount of water absorbed by one disc.

Observation and calculations

Weight of Keen's box + filter paper = Wk g

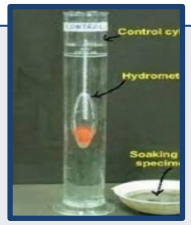
Weight of watch glass + keen's box + filter paper + saturated soil = Wsw g

Weight of watch glass + keen's box + filter paper + oven-dry soil = Wsd g

Weight of watch glass = Wg g

Weight of water absorbed by filter paper = Wf g

$$\text{Maximum water holding capacity } (\%) = \frac{\text{Wsw} - \text{Wsd} - \text{Wf}}{\text{Wsd} - \text{Wk} - \text{Wg}} \times 100$$



5.
Determination of Particle Size Distribution in soil

Particle size distribution is a fundamental and stable property governing the specific surface area of the soil particles which affected different physical and chemical properties of the soils. It also helps to understand the weathering and profile development, soil structure, permeability and water retention, plasticity, aeration, cation exchange capacity, workability, erodibility of the soils etc. Factors like soil organic matter, colloidal substances, oxides of iron and aluminum, calcium carbonate content, hydration of clay particles etc. affected the aggregate stability of the soil particles. Therefore, these binding agents need to be removed to disperse the soil particle for analysis of particle size distribution in the soil system. According to size of the particles, there are three major size groups namely sand, silt and clay. These groups are called soil separates and can be further subdivided into smaller size classes. The International Society of Soil Science (ISSS) has grouped the soil particles into following size classes (Table 19.1).

Table 5.1 Relative diameter of different soil particle fractions as per ISSS.

Soil fraction	Diameter of the particles (mm)
Coarse sand	0.2 to 2.0
Fine sand	0.02 to 0.2
Silt	0.002 to 0.02
Clay	<0.002

The determination of relative proportion of sand, silt and clay particles in the soil systems is called particle size analysis which is further grouped in to different textural classes as defined in the triangle texture diagram (Fig. 19.1). Though, soils also contain variable shape particles not only of different sizes but shape also. The size of an individual soil particle in terms of diameter is defined by one of the following criteria:

(a) the diameter of a sphere whose volume is equal to that of the particle; (b) the diameter of a round on square opening through which a particle can pass,

(c) the diameter of a sphere, the settling velocity and specific gravity of which are same as those of the particles.

Even though ideally suited for spherical particles, these criteria are also applied to soil particles for want of other reliable measures.

Methods

A. International Pipette method

B. Hydrometer method

These methods make use of Stokes' law for the fractionation of finer particles, but differ in the mode of recording Pipette method is laborious and time consuming whereas hydrometer method is simple rapid. Nevertheless, the former method is considered to be the most accurate method.

A. International Pipette Method (Piper, 1966)

The soil particles usually exist as floccules which may be cemented together. In order to determine the particle size distribution, it becomes necessary to completely disperse soil particles. The of soils is achieved by inactivation or removal of cementing and flocculating agents as described belong:

1. Dispersion

(i) Removal of cementing agents

(a) Organic matter - It is removed by treating the soil with hydrogen peroxide. This chemical oxidizes the organic matter to carbon dioxide and water.

(b) Oxides of iron and aluminum - The removal of iron and aluminum is very important in lateritic soils. The oxides are reduced to soluble forms, using reducing agents like nascent hydrogen of sodium dithionate in sodium citrate. Cementation due to the oxides of iron and aluminum is not common in the Punjab soils so this step is not followed.

(c) Clay to clay cementation - Clay particles, when dehydrated, are strongly bonded with one another Clays must be hydrated to break these bonds. The physical methods that are adapted to aid rehydration are shaking, stirring, vibration and rubbing the soil in water.

(d) Calcium carbonate - Cementation due to calcium carbonate is removed by treating the soil with dilute HCI.

(ii) Removal of flocculating agents –

The flocculating agents present in soils are soluble salts and ions in order to deflocculated the soil particles the soil is repeatedly washed with distilled water till it is free from soluble salts. The HCl treatment renders the exchange complex H saturated. The H on the soil exchange complex is replaced by a peptizing cation like Na. Sodium hydroxide is used for this purpose. Other dispersion (peptising) reagents that can be used are sodium oxalate ($Na_2C_2\ O_4$), sodium phosphate $(NaHPO_3)_6$ and sodium metaphosphate ($NaPO_3$), sodium pyro-phosphate ($Na_4HP_2O_7$) and sodium hexametaphosphate $(NaPO_3)_6$ or different mixtures of these in dilute concentrations. As sodium ions replace other cations on the clay, a strong electrical repulsion force develops between soil particles. These forces keep the clay particles dispersed. In the Pipette method, use of sodium hydroxide is recommended. The final separation and hydration of the particles is accomplished by vigorous stirring of the soil water suspension.

2. Fractionation

Coarse sand particles are separated by sieving the dispersed soil suspension. Fine sand particles are separated by decantation Fractionation of the fine size fractions is based on differential velocity of sedimentation of particles of different sizes. The principle of the technique is as follows: A rigid particle falling freely through a liquid of a lower density will attain a constant velocity where the force opposing movement is equal and opposite to the force of gravity acting on the particle. The frictional force acting vertically upward on a spherical particle is calculated from the Stokes' law. The net gravitational force acting down wards is equal to the weight of the submerged particle. At equilibrium, these expressions can be combined to give an equation for terminal settling velocity. V, as

$$V = 2/9\ gr^2\ (Dp-Dw)/\eta = h/t \qquad (1)$$

Where g is acceleration due to gravity (cm sec^{-2}); r is the radius of soil particle (cm), ŋ is the viscosity of viscosity of the liquid (water), g cm sec^{-1} and Dp and Dw are the densities

of the soil particles and the dispersion medium, respectively. Thus, in a time t' all particles having settling velocities greater than hit would be located below depth 'h' and the particles having settling velocities lesser than h/t would be retained above this depth. After a lapse of 50 seconds, all particles coarser than 50 had passed the 10 cm mark in the cylinder. A small aliquot taken by a pipette at a 10 cm depth at 50 seconds will, therefore, furnish a fraction of suspension in which all particles finer than this size are in the same proportion as before.

Application of Stokes' law is subject to the conditions that (i) soil particles are solid spheres; (ii) the size of the particles is so small that they do not cause turbulence during fall and (iii) the temperature fluctuations do not set up convection currents in the suspension. Despite these assumptions, this law is fairly accurate in determining particle size distribution in soils. The times of sedimentation calculated from the settling velocity equation, assuming particle density of 2.60 Mg m^{-3}

The soil sample is dispersed by removing the binding force in soil particles. The settling rate of dispersed particles in water is measured. Large particles are known to settle out of suspension more rapidly than do small particles. This is because larger particles have less specific area and hence have lesser buoyancy than smaller particles. Stoke’s law (1851) is used to express the relationship. The law stipulates that the resistance offered by the liquid to the fall of the particle varies with the radius of the sphere and not with the surface. Accordingly, the formula was given as below:

Apparatus

1. A hot water bath or a hot plate.
2. Whatman No. 50 filter paper
3. An electric stirrer
4. Thermometer
5. 1 L mark sedimentation cylinder.

Reagents

1. Hydrogen peroxide (30%)

2. 2*N* HCI 2*N*

3. *N*/10 $AgNO_3$

4. 5-6% Sodium hexa-metaphosphate ($NaPO_3)_6$: Dissolve 50-60g of sodium hexa-metaphosphate in distilled water and make the to 1 L volume. Filter through Whatman No.1 filter paper.

5. Phenolphthalein indicator

Procedure

1. Take 50 g oven-dry soil (ground and sieved through a 2 mm sieve) in a 600-mL beaker.
2. Add 20 mL H_2O_2 and swirl the contents well.
3. Let the reaction proceed for 5-10 minutes.
4. Place the beaker over a hot water bath, or a hot plate.
5. Continue digestion, stirring the contents all the time with a glass rod to minimize frothing, till the reaction completely subsides (in case of severe frothing and prolonged reaction a second lot of H_2O_2 should be added). The Rajasthan soils do not contain high amount of organic matter and a single treatment with H_2O_2 is usually sufficient.
6. Cool the beaker and its contents.
7. Wash the soil particles from the inner sides of the beaker by rubbing with a policeman and with a jet of distilled water.
8. Add 25 mL 2*N* HCl (**if more than 2% $CaCO_3$, is present**) should be added at the rate of 2.5 mL for each percent of $CaCO_3$).
9. Make the volume 400-500 mL with distilled water. Add a few drops of the **phenolphthalein indicator**.
10. Add 25 mL Sodium hexametaphosphate (5-6%) till the whole suspension shows a pink colour (indicating its alkaline reaction). Stir the contents of the beaker with an electric stirrer for 10 minutes.
11. Make up the volume of the suspension in the cylinder to one-litre by adding more distilled water.
12. Place the cylinder in a temperature control chamber to ensure minimum variation of temperature between the two samplings.

13. Next day early in the morning note down the temperature of the suspension.

14. Find out the required time for sampling against the temperature for silt + clay (1^{st} reading) and clay (2^{nd} reading) from Table.

15. Stir the contents with the plunger by moving it up and down 20-25 times in one minute, so that no settled soil remains at the bottom of the cylinder.

16. Remove the plunger gently and note down time at which the plunger is taken out. **This is the starting time for settling.**

17. Insert the sampling pipette gently into the suspension and dip it to 10 cm depth from the surface of suspension about 20 seconds before the sampling time.

18. Pipette out **25 mL** of the suspension at each requisite time at a moderate speed.

19. Transfer the sample collected to a weighed 50-100-mL beaker dry it at 105°C in the oven to a constant weight.

20. Record this weight in your data sheet.

21. After taking two reading for silt + clay (1^{st} reading) and clay (2^{nd} reading)

22. Weigh the beakers with silt + clay and clay samples up to milligram level.

23. Decant the remaining suspension using 0.25 mm sieve by washing repeatedly with distilled water.

24. Remove any particles left in the cylinder with a jet of distilled water into a weighed 100-mL beaker.

25. Dry the contents of beaker in an oven and weigh these.

26. The weight of the soil particles in the beaker is the amount of fine sand in the total sample.

27. Compare the per cent fine sand, thus obtained with that obtained by the difference method.

Calculations

Mass of soil taken = 50 g

Mass of soil taken = W_1

Mass of beaker + coarse sand = W_2 g

Per cent coarse sand, Pes =$((W_2-W_1)/50 \times 100$

Temperature of the suspension = ℃

Time at which plunger is taken out of the cylinder = To, Time at which sample for silt + clay is to be collected To+Tsic (hr.min.sec), Time at which sample for clay is to be collected To+Tc (hr.min.sec.)

At To+Tsic

Mass of beaker = W_3 g

Mass of silt+ clay+ beaker = W_4 g

Mass of (silt + clay) = $(W_4 – W_3)$ g

Per cent silt +clay, Psic = $[\{(W_4-W_3)/50) \text{ x } 1000/25] \times 100$

At To+Tc

Mass of beaker = W_5 g

Mass of beaker + clay = W_6 g

Mass of clay = $(W_6 – W_5)$ g

Per cent clay, Pc = $[\{(W_6-W_5)/50) \text{ x } 1000/25] \times 100$

Percent fine sand (by subtraction) = 100- (Psic + Pcs)

Interpretation

The texture of soil is determined from the relative proportions of sand, silt and clay that it contain Triangular classifications suggested by USDA and ISSS are in common use. Both make use of a is lateral triangle whose area is divided into 12 compartments each representing a texture. The differences between the two are primarily due to differences in size ranges of sand and silt fractions. The triangle based on ISSS size fractions is given in for the determination of the texture of a s locate the clay and the silt percentages on the respective sides of the triangle. Draw a line in-way parallel to the sand axis in the former case and the parallel to the clay axis from the later point. The compartment in which the two lines intersect is the texture of the soil. The drawback in this presentation 120- is that it does not account for the organic matter of the soil. However, the method is good determining the textural class of the soil.

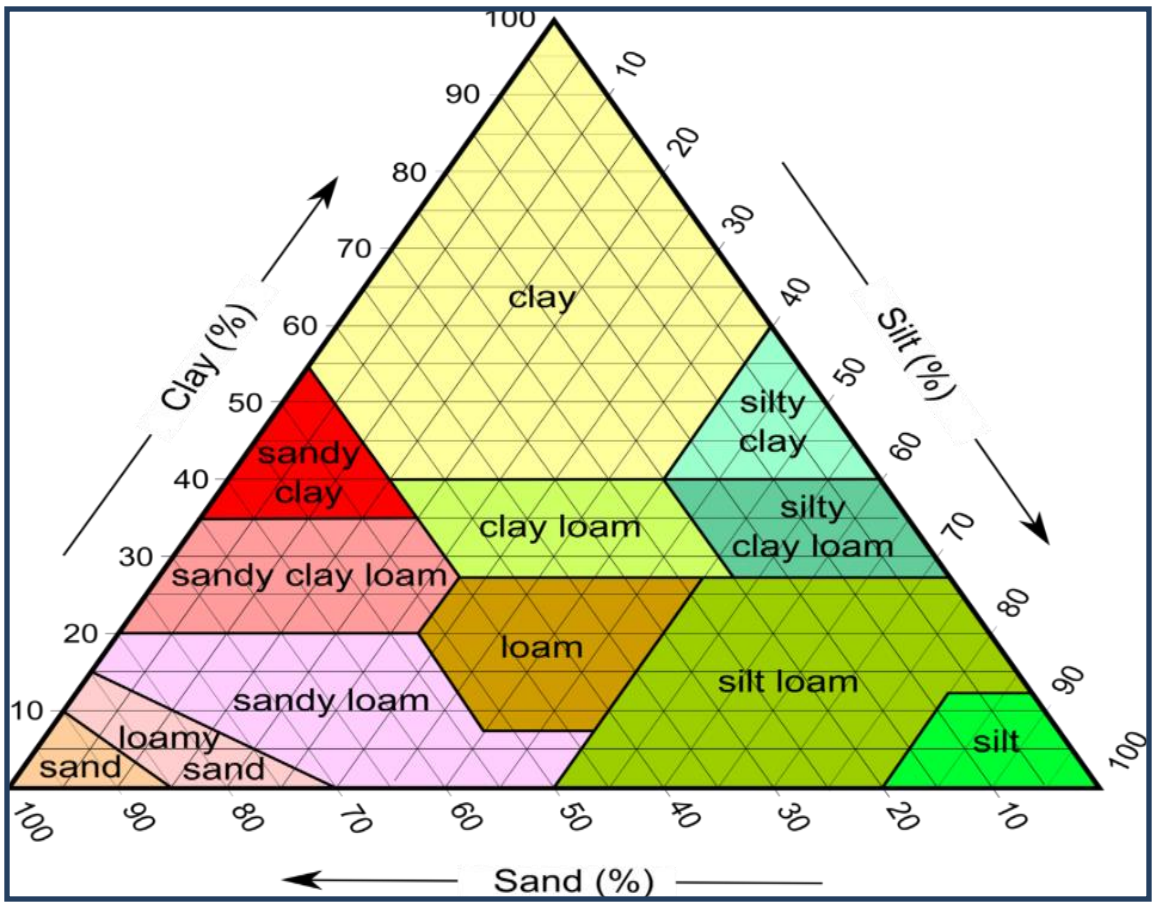


Fig. 5.1 Triangular texture diagram based on international fractions

Precautions

1. H_2O_2 is an oxidizing agent and should be handled carefully.

2. Do not add excess alkali (NaOH) than required, otherwise it will initiate flocculation instead dispersion.

Table 5.2 Sedimentation times for particles of silt and clay in water for the 10 cm depth

Temperature °C	Settling time			
	Silt + clay (1st Sampling)		Clay (2nd Sampling)	
	Minutes	Seconds	Hours	Minutes
10	6	20	10	25
11	6	10	10	10
12	6	0	9	60
13	5	50	9	35
14	5	40	9	20

15	5	30	9	5
16	5	20	8	50
17	5	10	8	35
18	5	0	8	25
19	4	50	8	10
20	4	45	8	0
21	4	40	7	50
22	4	35	7	35
23	4	30	7	25
24	4	20	7	15
25	4	15	7	0
26	4	10	6	55
27	4	5	6	45
28	4	0	6	40
29	3	55	6	30
30	3	50	6	20
31	3	45	6	15
32	3	40	6	0
33	3	35	5	55

6.
Determination of Soil pH

Soils differ considerably in H^+ ion concentration, expressed in terms of pH, a term first coined and used by S.P.L. Sorensen in 1909. Soil pH may be defined as negative logarithm of the hydrogen ion activity.

$$pH = -\log(H^+) = \log 1/[H^+]$$

Where, H^+ is the hydrogen ion activity in moles per litre. The pH is a measure of hydrogen or hydroxyl ion activity of the soil-water system. It indicates whether the soil is acidic, neutral or alkaline in reaction. Since crop growth suffers under both very low (strongly acidic) as well as very high pH (alkaline) conditions, appropriate reclamation measure become essential. The presence of neutral soluble salts as in saline soils is not normally reflected in its pH, but when their content is excessively high, they tend to reduce H^+ activity. The value of soil pH is affected by several factors, such as (i) soil: water ration employed, (ii) partial pressure of CO_2, (iii) salt content, and (iv) Drying of soil sample.

Soil pH is mostly determined in soil: water suspension. The amount of water added varies from that enough to bring the saturation to ten times the weight of soil. Schofield and Taylor (1955) have shown that a much reliable measurement of soil pH can be made in a 0.01*M* $CaCl_2$ solution.

Reagents

Standard buffer solutions: Specified buffer solutions of pH 4.0, 7.0 and 9.2 are to be used as standard buffers for calibration of pH meter. In case of buffer tablets, one buffer tablet of the respective pH is dissolved in 100mL de-ionized water. Store the buffer solutions below 25^0C temperature, may also refrigerated to avoid the microbial growth for some time but it should be used only after the solution temperature reached to 25^0C for instrument calibration purpose. Avoid using the microbial contaminated pH buffers and preparing a fresh buffer solution as these solutions can't be kept for a longer period.

Instrument

Fig. 6.1 pH Meter

Measurements of Soil pH

pH in saturated soil paste

1. Take 100 g of soil sample in 500 mL beaker for making a saturated soil paste.
   Add small amount of distilled water at 1–2 minute intervals to the soil, while working with aspatula.
2. The beaker is allowed with a cover on it to stand for about an hour. At saturation, the soil pasteglistens, flows slightly when the container is tilted and slides freely and cleanly off the spatula. A perfect paste will neither show collections of free water on the soil surface nor loseits glistening characteristic on standing.
3. Adjust pH meter knob for the temperature. Calibrate with two buffers, one in the acidic range(4.0) and the other in the alkaline (9.2) or at neutral (7.0) pH.
4. Insert the glass and calomel or combined electrodes in the paste carefully and measure the pH
5. Move the electrodes a little to ensure removal of water film around them and take the pH reading again when constant.

b) pH in soil-water suspension

The pH may be determined in soil-water suspension of varying ratios but the results should be expressed along with the ratio adopted. Conveniently, the suspension is prepared in 1:2 or1:2.5ratios.

Procedure

1. Take 20 g of soil sample in 100 mL beaker.
2. Add 40 mL of distilled water, stir well for about 5 minutes and keep for half an hour.
3. Again stir just before immersing the electrodes and take the pH reading.

c) pH in 0.01*M* $CaCl_2$ Solution

1. Take 20 g of soil sample in a 100 mL beaker.
2. Add 40 mL of 0.01*M* $CaCl_2$ aqueous solution (1.470 g of AR grade $CaCl_2.2H_2O$ per liter)
3. Stir the suspension well for 30 minutes and record the pH.

In acid soil, the pH with this method normally ranges from 4 to 5 and in calcareous one from 6.9 to 7.2.The pH of near neutral soil in $CaCl_2$ solution is usually around 6.0.

Note: Before each determination, the electrodes must be washed with a jet of distilled water and dried with the help of a piece of filter paper or tissue paper.

Selection of method for pH Measurement

For identifying specific soil problems like acidity or alkalinity and salinity saturated paste method is used. Fertilizer recommendations are made by 1:2 soil-water suspension methods. The pH in $CaCl_2$ solution is measured to mask the variability in salt content of the soil. The results areindependent of dilution over a wide range of soil: solution ratio and more reproducible than thoseobtained in water. For a more rapid, though not accurate pH tests, the universal indicator can be used. In this care, 10 mL portion of the supernatant solution from the soil water suspension is taken for pH estimation. To this 0.2 mL of universal indicator (commercially available) is added and the pH in noted on the basis of colour matching with standard colour strips given on the indicator bottle.

Interpretation

S. No.	Soil acidity	pH range	Recommendation
1	Acidic	< 6.5	Requires liming for reclamation
2	Neutral	6.5-7.5	Optimum for most of the crops
3	Alkaline	7.5-8.5	Require application of organic manure
5	Alkali (Sodic)	> 8.5	Requires gypsum for amelioration

7.
Determination of Electrical Conductivity of Soil

Soils contain varying amounts of different soluble salts derived from parent rocks, minerals, fertilizers, irrigation water and decomposition of organic residues. When a soil contains an excess of salts, it is termed as saline soil. Sometimes it is called a "white alkali" soil because of white saline crust that appears on drying. Excessive accumulation of these soluble salts in the soil restricts the plant growth by decreasing the entry of water into the plant roots and hence absorption of nutrients. In arid and semi-arid regions, the excessive salts may accumulate due to poor salt water balance under impeded drainage and high-water table conditions. It is, therefore, essential that the amount of these soluble salts is determined to assess the salinity problem of soils and to decide as to which crops can be successfully grown therein as crops differ considerably to salt tolerance.

Soluble salts in soils are determined by measuring the electrical conductivity of soil solution at any particular temperature. Higher the salt content, more is the flow of electric current through the solution. Electrical conductivity (EC) or specific conductivity is defined as the reciprocal of the resistance of a conductor 1 cm long and 1 cm^2 in cross sectional area and is expressed as mhos per cm. Since, the values of EC are very small for soil solution, it is expressed as millimhos/cm (EC × 10^3) or deci Siemens/m (dS/m). The soil salinity in relation to plant growth is generally measured in terms of conductivity of the saturated extracts of the soils. The percentage of soluble salts can be computed from the following relationship.

Percentage of soluble salts in soil = 0.064 × EC × SP/100

Whereas, SP is the saturation percentage of soil and EC is in dS/m.

Apparatus

Conductivity meter and a conductivity cell with known cell constant, vacuum pump,

spatula,China dish, beakers and glass rod, etc.

Instrument

Fig. 7.1 EC Meter

Reagents:

i. Saturated solution of calcium sulphate (Reagent quality)

ii. 0.01 *N* KCI solutions: Dissolve 0.7456 g of potassium chloride in distilled water and dilute to1 L.

a) EC in saturated soil paste

Use soil saturation paste as described in methodology for pH.

b) EC in soil-water suspension

The EC may be determined in soil-water suspension of varying ratios but the results should beexpressed along with the ratio adopted. Conveniently, the suspension is prepared in 1:2 ratios as described in pH methodology Take the reading using EC meter as described above.

Calculation:

The measured EC values at various temperatures need to be reported as corresponding to a standard temperature because EC is dependent on temperature. An arbitrary constant is commonly used for temperature compensation assuming that EC-temperature relation is

linear (for example 2% increase of EC per 1 degrees C).

$$\text{EC} = \text{Reading} \times \frac{12.89}{0.1\ N\ \text{KCl reading}}$$

mS/cm = dS/m = S/m × 10 or mScm × 0.1= S/m

Total cations/anions (m mols/L) = EC (mS/cm) × 10

TDS (mg/L) = EC (mS/cm) × 640 TDS

Interpretation

S. No.	Soil type	EC (dS/m)	Recommendation
1	Normal	< 0.8	Optimum for most of the crops
2	Saline soil	> 0.8	Require some management

Table 7.1 Classification of salt-affected soils

Classification	ECe (dS m^{-1})	pHs	ESP (%)	Physical condition
Saline	>4	<8.5	<15	Normal
Sodic	<4	>8.5	>15	Poor
Saline-sodic	<4	<8.5	>15	Normal

8.
Determination of Cation Exchange Capacity of Soil

The Cation exchange reaction is the second most important in nature, surpassed in fundamental importance only by the photosynthetic process of green plants. Cation exchange in soils has long been of interest to soil chemists. Cation exchange determination for soils includes the measurement of the cation exchange capacity (CEC) of soils and soil colloids. Soils with high CEC typically have a high clay and organic matter content. These soils are considered to be more fertile, as they can hold more plant nutrients. Sandy soils typically have a lower CEC and require more frequent fertilizer applications. Typically, cation exchange capacities of soil components and soil types as given below in table 1.

Table 1: Typical cation exchange capacities of soil components and soil types

Material	CEC (me/100g)
Clays minerals	
Illite	15-40
Montmorillonite	80-100
Organic Matter	200-400
Kaolinite	3-15
Soil texture	
Sand	1-5
Loamy Sand to Sandy Loam	5-10
Loam	5-15
Clay Loam	15-30
Clay	> 30

The CEC determination involves measuring the total quantity of negative charge per unit weight of the material. The amounts of CEC measured vary somewhat according to nature of the cation employed, concentration of salt and equilibrium

pH. It gives an indication of the potential of the soil to hold plant nutrients, by estimating the capacity of the soil to retain cations, which are positively-charged substance. The procedure of CEC is described below:

Instruments

1. Flame photometer
2. Centrifuge & centrifuge tube
3. pH meter

Reagents

1. Sodium acetate solution, 1.0 *N*: Dissolve 136 gm of sodium acetate trihydrate in water and dilute to volume of one litre. The pH value of the solution should be approx. 8.2.
2. Ethanol 95%
3. Ammonium acetate solution (neutral normal ammonium acetate): Dissolve 77.08 g of ammonium acetate in about 500 ml of distilled water and make the volume to one litre. Adjust the pH to 7.0 with acetic acid or ammonia solution.
   Or
   This is for one litre: 800 ml H_2O + 57 ml of concentrate glacial acetic acid + 68 ml of ammonia solution (sp. Gr. 0.91) and dilute to volume of one litre and adjust the pH of 7.0.
4. Standard Solution (100 me Na L^{-1}): Dissolve 5.845 g of AR grade dried NaCl in distilled water and make the volume to one litre
5. Working standards (WS) solution of Na: Dilute 5, 10, 15, 20, 30, 40 and 50 ml portions of stock solution (containing 100me Na L^{-1}) to 100 ml in volumetric flasks to get WS of 5, 10 15, 20, 30, 40 and 50 me Na L^{-1} concentrations.

Procedure

1. Take 5 g soil in centrifuge tube.
2. Add 30 ml of reagent 1, shake for 5 minutes and centrifuge it 10,000 RPM for 5

minutes. Discard the supernatant. This should be repeated four times.

3. Add 30 ml of reagent 2 in the tube shake for 5 minutes and centrifuge it for 5 minutes. Discard the supernatant. This should be done at least three times.
4. After 3rd washing with solution 2, measure electrical conductivity and it should be less than 40 micromhos/cm.
5. Add 33 ml of reagent 3, shake for 5 minutes and centrifuge for 5 minutes and centrifuge 5 minutes. Collect the supernatant in 100 ml volumetric flask. Make the volume up to 100 ml. Read the sodium concentration of the extract on flame photometer.

Calculation

$$\boldsymbol{Na\ conc.of\ extract\ (in\frac{me}{L})\times 10=\frac{Na\ conc.of\ extract\ (in\frac{me}{L})\times 10}{Weight\ of\ sample\ (g)}}$$

9.
Determination of Soil Organic Carbon

Soil organic matter (SOM) is not only store house of nutrients but also an important parameter for soil health determination. Mainly two methods as being used for measurement of SOC namely the titration method described by (Walkley and Black 1934) and the colorimetric method as described by (Datta et al., 1962). In both the methods, organic matter is oxidized with chromic acid ($K_2Cr_2O_7 + H_2SO_4$). In the titration method, the unconsumed potassium dichromate is back- titrated against ferrous sulphate or ferrous ammonium sulphate (redox titration). Carbon in the sample is oxidized as follows:

$$2H_2Cr_2O_7 + 3C + 6H_2SO_4 = 3Cr_2(SO_4)_3 + 3CO_2 + 8H_2O$$

Thus, $2H_2Cr_2O_7$ or $2K_2Cr_2O_7 = 3C$

or 588 g of $K_2Cr_2O_7$ = 36 g of C or

12 liters f 1 *N* $K_2Cr_2O_7$ = 36 g of Cor

1 mL of 1*N* $K_2Cr_2O_7$ = 0.003 g of C

In the colorimetric method, the intensity of the green colour of chromic acid obtained due to its reduction is measured calorimetrically. The intensity is directly proportional to the amount of organic carbon present in the soil.

Reagents

1. 1 *N* Potassium dichromate: Dissolve 49.04 g of AR grade potassium dichromate ($K_2Cr_2O_7$) inabout 500 mL of distilled water and make the volume to 1 L.
2. Concentrated sulphuric acid
3. 0.5 *N* Ferrous ammonium sulphate (FAS): Dissolve 196 g of ferrous ammonium sulphate indistilled water, add 20 mL of conc. H_2SO_4 and make volume to 1 L. The ferrous ammonium sulphate should be from a fresh lot and light green in colour. Yellowing of the saltindicates its oxidation
4. Diphenylamine indicator: Dissolve 0.5 g of the dye in a mixture of 20 mL of distilled waterand 100 mL of conc. H_2SO_4
5. Ortho-phosphoric acid (85%) or sodium fluoride (NaF)

Procedure

1. Weigh 1 g weight of sieved soil sample into 500 mL dry conical flask of borosilicate glass.
2. Add 10 mL of 1 *N* $K_2Cr_2O_7$ and 20 mL of concentrated H_2SO_4.
3. Swirl a little and keep on an asbestos sheet for 30 minutes.
4. Add slowly 200 mL of distilled water and 10 mL of ortho-phosphoric acid.
5. Add 1 mL of diphenylamine indicator.
6. Take 0.5 *N* ferrous ammonium sulphate (FAS) solutions in 50 mL burette.
7. Titrate the contents until green colour starts appearing.
8. Carry out a blank titration (without soil) in a similar manner.
9. If the titre value is <6, repeat taking 0.2 to 0.5 g of soil sample.

Fig. 9.1 Determination of soil organic carbon

Note:

1. Use of NaF along with H_3PO_4 gives a sharper end point.
2. High chloride content, as in case of saline soils, interferon in the

estimation. It can beprevented by adding Ag_2SO_4 @ 1.25 per cent to the conc. sulphuric acid.

Calculation:

$$\text{Organic carbon (\%)} = \frac{10(B - S)}{B} \times 0.003 \times \frac{100}{\text{Wt. of soil taken (g)}}$$

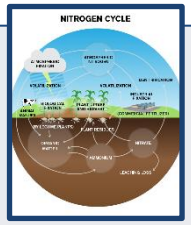
Where, B and S stand for the net titer value in mL of blank and samples, respectively.

Organic Matter (%) = Organic carbon (%) x 1.724

(1.724 is Van Bemmelen Factor) because organic matter

Interpretation:

Organic carbon (%)	Rating
< 0.5%	Low
0.5-0.75%	Medium
< 0.75%	High



10.
Determination of Available Nitrogen in Soil

More than 90 per cent of soil nitrogen (N) exists as a constituent of complex organic compounds like proteins, amino acids and amino sugars, etc. which can't be directly used by the plants. It becomes available to plants after its mineralization. Only a small fraction, usually about 2 per cent, gets mineralized due to microbial activity in a growing season. Very little amount of N is also present in the inorganic or ionic forms (NH_4^+, NO_3^- and NO^-). NH_4-N and NO_3-N are important indices of N availability in arable soils having both aerobic and anaerobic conditions. The estimation of CO_2 evolved during decomposition of organic matter in N free environment is also an important indicator for availability of N in the soils.

Available (mineralizable) N in soil by alkaline permanganate method:

Principle

Available (mineralizable) N in soil is determined by alkaline permanganate method as described by Subbiah and Asija (1956). In this method, soil is distilled with alkaline potassium permanganate (0.32% $KMnO_4$) solution. The organic matter present in soil is oxidized by $KMnO_4$ in presence of sodium hydroxide (40% NaOH) and the liberated ammonia (NH_3) is absorbed in boric acid (2% H_3BO_3) containing mixed indicator (methyl red + bromocresol green). The ammonium borate ($NH_4H_2BO_3$) formed is then titrated with standard sulphuric acid (0.02 N H_2SO_4) and the amount of mineralizable N was calculated from the quantity of acid consumed.

The easily mineralizable N is estimated using alkaline $KMnO_4$, which oxidizes the organic matter present in the soil and hydrolyses the liberated ammonia which is condensed and absorbed in boric acid, and titrated against standard acid. The method has been widely adopted to get a reliable index of nitrogen availability in soil due to its rapidity and reproducibility. A progressive one and hence a uniform time and heating temperature should be allowed for best results. Use of glass beads checks bumping while liquid paraffin checks frothing during heating.

Fig. 10.1 Kjeldahl apparatus

Reagents

1. 0.32% $KMnO_4$ solution: Take 3.2 g potassium permanganate ($KMnO_4$) and dissolvein 1 L distilled water.
2. 2.5% NaOH solution: Take 25 g NaOH crystals and dissolve in about 800 mL distilled water, left for overnight and finally make up the volume to 1 L with distilled water.
3. 0.02 *N* H_2SO_4 solution: Take 200 mL of 0.1 *N* H_2SO_4 and dilute it in 1 L volumetric flask with distilled water.
4. Mixed indicator (methyl red + bromocresol green): Mixed indicator is prepared by dissolving 0.066 g methyl red and 0.099 g bromocresol green in 100 mL of 95% ethyl alcohol.
5. 2% Boric acid (H_3BO_3): Dissolve 20 g H_3BO_3 in approximately 900 mL hot distilled water in 1 L volumetric flask. Add 20 mL of mixed indicator to it; adjust the pH(4.5) by adding dilute NaOH and finally make up the volume to 1 L mark by adding distilled water.
6. Liquid paraffin: Extra pure grade
7. Glass beads

Procedure:

1. Take 20 g soil sample (2-mm sieved) in 800 mL macro-Kjeldahl distillation flask.
2. Add 10 mL of distilled water to moisten the soil.

3. Add 100 mL of 0.32% $KMnO_4$ solution followed by 100 mL of 2.5% NaOH solution to distillation flask.
4. Add 1 mL of liquid paraffin in order to prevent frothing.
5. Add few glass beads to prevent bumping during distillation.
6. Pipette out 20 mL of 2% boric acid containing mixed indicator in 250 mL conical flaskand place it in the macro-Kjeldahl distillation unit in such a way so that the outlet of the condenser is dipped inside the boric acid.
7. Run the distillation unit (for 1/2 hour) and collect the distillate (about 100 mL) by absorbing liberated NH_3 in 2% boric acid which will turn green.
8. Titrate the NH_3 absorbed against standard H_2SO_4 (0.02 *N*) solution till the green colour changes to pink (original colour of 2% boric acid).
9. Record the amount of standard H_2SO_4 consumed and calculates the mineralizable N content in soil as given below:
10. Run a blank without soil sample but add all other reagents.

Calculation:

$$\text{Available N}\left(\frac{\text{kg}}{\text{ha}}\right)\text{ in soil } = (\text{S} - \text{B}) \times \frac{0.00028}{\text{Wt (g)} = 20\text{g}} \times 2.24 \times 10^6 = (\text{S} - \text{B}) \times 31.36$$

Where,

S = volume of standard H_2SO_4 consumed for soil

B = volume of standard H_2SO_4 consumed for blank

W= weight of soil taken (g)

The factor 0.00028 is arrived at by considering the following simple equation:

$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$

Or 98 g of H_2SO_4 (or 1L of 2*N* H_2SO_4) = 28 g N

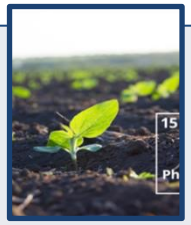
Or 1 mL of 0.02*N* H_2SO_4 = 0.00028 g N

kg/ha = mg/kg × 2.24;
(Taking 2.24 million kg ha^{-1} as the weight of 0-15 cm surface soil)

Interpretation

Available N (kg/ha) soil rating

Available N (kg/ha)	Rating
<280	Low
280-560	Medium
>560	High



11.
Determination of Available Phosphorus in Soil

Phosphorus (P) occurs in soils, both in organic and inorganic forms. Organic fraction is present in humus and other compounds like phytins and nucleic acids. Inorganic fraction occurs in combination with calcium, iron, aluminium and other elements. The content of inorganic-P (Ca, Fe and Al-phosphates) in soils is higher than that of organic-P except in organic soils. Plant absorb P from soil as $H_2PO_4^-$ and HPO_4^{2-} ions. For the estimation of available P, two methods are commonly used (i) Olsen's method (Olsen *et al.*, 1954) for alkaline and neutral soils and, (ii) Bray's method (Bray and Kurtz, 1945) for acid soils, which involves soil extraction with a solution consisting of 0.03*N* NH_4F and 0.025*N* HCl is widely used.

Olsen's Method (Olsen et al. 1954)

The soil is extracted with 0.5*M* Sodium bi-carbonate, pH 8.5 in the presence of Darco G-60(which adsorbs dispersed organic matter and helps in giving clear extract). Phosphorus in the extract is treated with ammonium molybdate, which results in the formation of heteropoly complexes (phosphomolybdate). The phosphomolybdate is reduced by the use of ascorbic acid (reducing agent). Due to this reduction, some of Mo^{6+} is converted to Mo^{3+} and/or Mo^{5+}, and the complex assumes the blue colour. The intensity of blue colour can be measured at an appropriate wavelength on a visible spectrophotometer.

In calcareous, alkaline or neutral soils, $NaHCO_3$ buffered to pH of 8.5 controls the ionic activity of Ca through precipitation of Ca as $CaCO_3$. As a result, the concentration of H_2PO_4 in solution increases. In acid soils, Al and Fe phosphates (H_2PO_4) concentration in the solution increases as pH rises by way of suppressing Al and Fe activities by adding NH_4F: secondary precipitation reactions are kept at minimum be the concentration of Al, Ca and Fe remains at a low level extractant.

Instrument

Fig. 11.1 Spectrophotometer

Reactions Extraction

$$Ca_3(PO_4)_2 + 6\,NaHCO_3 \longrightarrow 3\,CaCO_3 + 2H_3PO_4 + 3\,Na_2CO_3$$

Colour Development

$$(NH_4)_6\,Mo_7O_{24}.4H_2O + 6\,HC1 \longrightarrow 7H_2MoO_4 + 6\,NH_4Cl$$

(Ammonium molybdate) (Molybdenic acid)

$$H_3PO_4 + 12\,H_2M_oO_4 \longrightarrow H_3P(Mo_3O_{10})_4 + 12\,H_2O$$

(Phosphoric acid) (Phosphomolybdate)

$$\text{Phosphomolybdate} \xrightarrow[\text{Reduction}]{\text{Ascorbic acid}} \text{Phosphomolybdate}$$

(Light yellow) (Blue colour)

Bray's Method (Bray and Kurtz, 1945)

The combination of HCl and NH_4F is designed to remove easily acid-soluble P forms, largely calcium phosphates, and a portion of the so-called aluminum and iron phosphates. The NH_4F complexes, aluminum and iron in acid medium thereby protecting re-precipitation of the extracted phosphate ions.

Reactions

$3NH_4F + 3HF + AlPO_4 \longrightarrow H_3PO_4 + (NH_4)_3A1F_6$

$3\ NH_4F + 3HF + FePO_4 \longrightarrow H_3PO_4 + (NH_4)_3FeF_6$

$H_3PO_4 + 12H_2MoO_4 \longrightarrow H_3P(Mo_3O_{10})_4 + 12H_2O$

(Phosphate) (Molybdenic acid) (Phosphomolybdate)

Ascorbic acid

Phosphomolybdate $\longrightarrow$ Phosphomolybdate

(Light yellow) Reduction (Blue colour)

Ascorbic acid method for Phosphorus estimation

The major drawback with the blue colour development method (Dickman and Bray, 1940) is that the colour starts fading soon, and hence the intensity has to be measured quickly. A method based on the use of ascorbic acid (Watanabe and Olsen, 1965) as described below provides a more stable blue colour and is, therefore, preferred over the former.

Reagents:

i. **Extractant for Olsen's method:** (0.5 M Sodium bicarbonate): Take 42.0 g of $NaHCO_3$ in 900 mL of distilled water, adjust the pH to 8.5 with dilute NaOH or HCl and make up the volume to 1 L.

ii. **Extractant by Bray's method:** Dissolve 1.11 g of NH_4F in distilled water using 2 mLof concentrated HCl and make up the volume to 1 L.

iii. **Solution A:** Dissolve 12 g of AR grade ammonium molybdate in 250 mL of distilled water. In 100 mL of distilled water, dissolve 0.291 g of antimony-potassium tartrate separately. Mix both of the solutions and add 148 mL of conc. H_2SO_4 and make the final volume to 2 litre with distilled water.

iv. **Ascorbic acid solution (Solution B):** Dissolve 1.056 g of ascorbic acid in 200 mL of solution A. This should be prepared fresh as and when required.

v. **Standard solution of 200 mg L^{-1} P:** Dissolve 0.8782 g of KH_2PO_4 in 1 L of distilled

water. This is 200 mg P L^{-1} solution.

vi. **Diluted standard of 2.0 mg g^{-1} P:** Dilute 10.0 mL of the standard 200 mg L^{-1} P solution to 1 L.

vii. **p-nitrophenol (PNP) indicator (0.25%):** Dissolve 0.5 g of p-nitrophenol in 100 mL of distilled water.

viii. **5*N* H_2SO_4:** Carefully dilute 140 mL of conc. H_2SO_4 to 1 L with distilled water to get approx. 5*N* H_2SO_4.

Colour development from standard solution for preparing standard curve

1. Pipette out 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mL of 2 mg L^{-1} P solution in 25 mL volumetric flask.
2. Add 5 mL of the extractant (Bray's or Olsen's).
3. Add ammonium molybdate as for Bray's or Olsen's method and proceed to develop blue colour as described.
4. Measure blue colour intensity and draw a standard curve by plotting concentrations of p in µg against absorbance reading.
5. If a straight line is obtained, find out a factor for each reading.

Procedure

1. Transfer 5 mL of extract (extracted with $NaHCO_3$ or Bray's extractants) in a 25 mL volumetric flask and add 2-3 drops of p-nitrophenol as indicator.
2. Add 0.5 mL (required quantity) of 5 *N* H_2SO_4 to it and shake for a while till CO_2 evolution disappears.
3. Add 4 mL of ascorbic acid solution (solution B) to it and make the volume with distilled water.
4. Wait for 10 minutes and read the intensity of blue colour using spectrophotometer at 760 nm wavelength by using red filter.
5. Run a blank without soil in identical manner.

Calculations

Weight of soil taken = 2.5 g

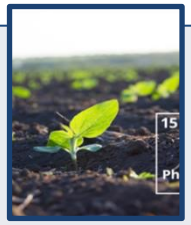
Volume of 0.5 *M* $NaHCO_3$ solution added	= 50 mL
First dilution	= 50/2.5 = 20 times
Volume of filtrate (extract) taken for color development	= 5 mL
Final volume made	= 25 mL
Second dilution	= 25/5 = 5 times
Total dilutions made	= 20 x 5 = 100 times
Conc. of P reading from the standard curve	= A ppm
Available P (ppm) in soil	= A x 100
Available P (kg/ha) in soil	= A x 100 x 2.24
Available P_2O_5 (kg/ha) in soil	= A x 100 x 2.24 x 2.29

Precautions

1. All glassware to be used for P determination should be cleaned with chromic acid, followed by thorough washing with distilled water to minimize contamination.
2. Add more Darco G-60, shake and filter again if filtrate is not clear.
3. If the intensity of the colour is too high redevelop the colour with smaller volume of aliquot.

Interpretation:

Available P (kg/ha)	Available P_2O_5 (kg/ha)	Soil rating
<10	< 25	low
10-25	25-50	Medium
>25	>50	High



12.
Determination of Available Potassium in Soil

About 90-98% of the total potassium (K) in soil is present in minerals, such as potash feldspars, muscovite and biotic micas. Potassium from these minerals is released slowly by weathering processes and usually is not of much significance to meet immediate crop requirements. However, cumulative contribution of this form over a period of time is of considerable importance. One to 10% of total K is also found in secondary clay minerals like illites, vermiculites and chlorites. Potassium in these expanding type minerals forms an integral part of the crystal lattice and cannot be replaced by ordinary exchange methods. It is, therefore, referred to as non-exchangeable K. Although this is not readily available to plants, it acts as an extremely important reservoir of slowly available K and is in equilibrium with readily available K. The readily available K constituents about 1-2% of the total K in mineral soils. It consists of soil solution and exchangeable K adsorbed on soil colloidal surfaces. The neutral normal ammonium acetate solution which extracts both exchangeable and water-soluble K is most commonly used for determination of available K in soils. For all practical purpose the extraction and estimation of exchangeable K along with water soluble K is good enough. The ammonium ions are very close in size to K^+ and replace the latter efficiently. During the estimation, acetate burns cleanly and does not leave any residue on the burner of flame photometer.

Ammonium acetate method of Available K determination (Hanway and Heidel, 1952) Instruments

1. Flame photometer
2. Mechanical shaker

Instrument

Fig. 12.1 Flame photometer

Reagents

i. **1 *N* Ammonium acetate:** Take 77.08 g of ammonium acetate in about 500 mL of distilled water and make the volume to 1 L. Adjust the pH to 7.0 with glacial acetic acid or ammonia solution. This reagent may also be prepared by taking 800 mL of distilled water and adding to it 57 mL of glacial acetic acid and 68 mL of ammonia solution (sp. gr. 0.91), followed by dilutions to 1 L and adjusting pH at 7.0 after cooling.

ii. **Standard K solution:** Prepare 1000 ppm K solutions by dissolving 1.908 g of AR grade KCl salt (dried in oven at 70^{O}C for two hours) per L solution. Dilute suitable volumes of this solution to get 100 mL of working standards containing 5, 10, 15, 20, 25, 30 and 40 ppm. The working standards should be prepared in ammonium acetate.

Procedure:

1. Take 5 g of soil sample in 100 mL conical flask.
2. Add 25 mL of the neutral 1*N* ammonium acetate solution and shake for about 5 minutes.

3. Filter the suspension though Whatman No. 1 filter paper.
4. Measure K concentration in the filtrate using flame photometer.

Preparation of standard curve for K

Record the flame photometer readings for each of the working standards of K after adjusting blank. Record the flame photometer readings for each of the working standards of K after adjusting blank to zero. Draw a standard curve by plotting the reading against K concentrations.

Calculation:

Available K (kg/ha) = C x dilution (25/5) x 2.24 i.e., C x 11.2

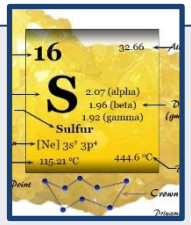
Where, C is concentration of available potassium in mg/L in the soil sample obtained on X axis against the standard potassium concentration.

Note:

1. The filtrate should be clear and transparent in order to avoid choking of capillary tube of theflame photometer, which occurs quite often.
2. During the operation of flame photometers a constant air pressure of and steady flow of gas (LPG) and air combination is absolutely necessary for precise estimation. An appropriatecombination is achieved by fixing the air pressure around 0.75 kg cm^{-2} and then adjusting the gas supply so as to get a non-luminous blue flame.
3. Fans and coolers should be switched-off so that flame is not affected.
4. Ammonia bottle should be stored in cool conditions.
5. Flame should not be uncontrolled.
6. Potassium standards should be prepared fresh after every 15 days.

Interpretation

Available K (kg/ha)	Soil rating
<120	Low
120 -280	Medium
>280	High



13.
Determination of Available Sulphur

Sulphur (S) is present in soils both in organic and inorganic forms. The amount depends upon parent materials, climate, soil organic matter status and soil texture etc. In humid region surface soils, most of the sulphur is in organic form, but in arid region soils, sulphates of Ca, Mg, Na and K are present in large quantities in the soil profile. Most of the sulphur available in mineral soils occurs mainly as adsorbed in sulphate (SO_4^{2-}) ions. A large number of extractants like water, monocalcium phosphate $Ca(H_2PO_4)_2$, calcium chloride ($CaCl_2$), potassium dihydrogen orthophosphate (KH_2PO_4), Morgan's reagent (CH_3COONa + CH_3COOH), ammonium acetate + acetic acid (CH_3COONH_4 + CH_3COOH) and NaCl have been used for extraction of available S. Among different extraction procedures used, 0.15% or 0.01*M* $CaCl_2$ extractable method suggested by Williams and Steinbergs, (1959) is most widely used.

Soil is shaken with 0.15% $CaCl_2$ solution. Chloride ion displace adsorbed sulphate during extraction. Calcium ions suppress the extraction of soil organic matter and hence eliminate the contamination caused by extractable organic S. The filtrate is analyzed for S by the turbidimetric method of Chesnin and Yien (1950) in which the turbidity produced due to precipitation of sulphate as barium sulphate is measured on a colorimeter at a 420 nm wavelength using a blue filter. Gum acacia solution is added to stabilize the turbidity so that the precipitates of barium sulphate do not settle down.

Instruments

i. Spectrophotometer or Colorimeter

ii. Mechanical shaker

Reagents

1. **0.15% or 0.01 *M* Calcium chloride solution**: Dilute the 105 g of calcium chloride dehydrate ($CaCl_2.2H_2O$) in 500 mL water and make the volume to 1 litre.

2. **Barium chloride crystals**: Grind $BaCl_2$ (AR grade) crystals to pass through a 30 mesh sieve and retain on 60 mesh sieve, and store in a clean bottle.

3. **Gum acacia solution**: Dissolve 0.25 g of gum acacia in distilled water and dilute to 100 mL

4. **Standard S Solution**: dissolve 0.5434 of oven-dried AR grade K_2SO_4 in distilled water and dilute to 1 litre. This contains 100 µg S mL

Preparation of standard curve

a) Take 0.25, 0.50, 1.0, 2.5 and 5.0 mL of standard S solution in 25 mL volumetric flasks, and add 10 mL of extracting solutions (*i.e.* 0.15% $CaCl_2$ solution) to each flask. For blank take 10 mL of extracting solution in a 25 mL volumetric flask.

b) Add 1 g of $BaCl_2$ crystals to each flask and swirl to dissolve the crystals.

c) Add 1 mL of 0.25% gum acacia solution, make up the volume with distilled water and shake well manually.

d) Within 5-30 minutes of development of turbidity (white colour), read to absorbance at 340 nm on a spectrophotometer, or on a colorimeter using blue filter.

e) Draw a curve taking S concentrations on X-axis and absorbance reading on Y-axis.

Procedure

1. Take 10 g of air-dry soil in a 150 mL conical flask and add 50 mL of 0.15% $CaCl_2$ solution.

2. Shake for 30 minutes on a rotary shaker and filter through Whatman No. 42 filter paper.

3. Take 10 mL of the clean filtrate in a 25 mL volumetric flask, follow the steps given for standard curve to develop the turbidity and record the absorbance.

Calculation:

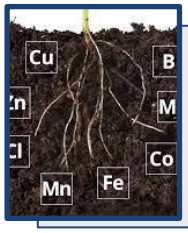
$$\text{Available S } \left(\frac{\text{mg}}{\text{kg}}\right) = \text{R} \times \frac{50}{10} \times \frac{1}{10}$$

Where, R stands for S content in µg as read on X-axis.

Note: In case the available S content of the soil is very low, a 20 mL aliquot (instead of 10 mL) should be taken to develop the turbidity.

Interpretation

Available S (mg/kg)	Soil rating
<10	Low
10 -20	Medium
>20	High



14.
Determination of Available Micronutrients in Soil

Few decades back the necessity of soil testing for micronutrient elements, namely Zn, Cu, Fe, Mn, B, Cl and Mo was given a little concern. By the use of high analysis inorganic fertilizers, the deficiency of few micronutrients (e.g., Zn, Fe, Mn B) has appeared in certain areas mainly because, not using organic manures and heavy removal by high yielding varieties. Generally colorimetric method has been widely used for majority of the micronutrients. Neutral ammonium acetate and chelating agents like EDTA, have been used as extractants for Fe, Zn and Mn, and the extracted amount determined colorimetrically. Zinc determination by dithizone method (Show and Dean, 1952) has been very popular until AAS became available. For those laboratories where the AAS is not yet available, the alternative (colorimetric) methods as described by Jackson (1967) are still employed. However, for a rapid and accurate analysis of Zn, Cu, Fe and Mn the DTPA method (Lindsay and Norvell, 1978) as given below is most widely used. Available soil B is generally extracted by hot water (Berger and Truog 1939) and Mo by ammonium oxalate (Grigg, 1960) method. The B from soil extracts is determined by azomethine-H and Mo by dithiol method.

Fig. 14.1 Atomic absorption spectroscopy (AAS)

DTPA-$CaCl_2$-TEA extraction method for Zn, Cu, Fe and Mn (Lindsay and Norvell, 1978)

Principle

Diethylene Tri-amine Penta Acetic acid (DTPA) is act as a chelating agent, combines with free metal ions in solution. During extraction, chelate reduces the activity of free metal ion in solution through the formation of soluble complex metal-chelate complex. In response to this depletion of metal ion in solution, more metal ion come from solid phases to replenish this depletion. Such depletion in the activity of metal solution due to plant uptake. This will closely mimic the reduction in activity of metal ion in solution due to plant uptake. Thus, quantity of micronutrients extracted by a chelate reflect in both the initial concentration under the soil solution (Intensity factor) and the ability of soil to maintain this concentration (Capacity factor). Thus, chelating agent simulates micronutrient cations removal by plant roots and subsequent replenishment from labile solid phases in the soil. DTPA offers the most favorable combination of stability constants for the simultaneous complexing of Zn, Cu, Fe and Mn. Since Fe and Zn deficiencies are frequently experienced in calcareous soils, the method is designed to avoid excessive dissolution of $CaCO_3$ with the release of occluded micronutrients, which are normally not available to plants. This is achieved by i) the inclusion of soluble Ca^{++}, and ii) buffering the reagent at pH 7.3 with triethanolamine (TEA) which burns cleanly during flame atomization. When the extractant is added to soil, additional Ca^{++} & some Mg^{++} enter the solution. This is largely because the protonated TEA exchanges with these ions from the exchanges sites which in turn helps in suppressing the dissolution of CaCO3. DTPA extractant has the ability to chelate Zn, Cu, Fe and Mn in competition with Ca^{++} & Mg^{++}, and unlike most other chelating agents, it applies a moderate stress to solubilize soil Fe at a pH, where $CaCO_3$ is not dissolved. Suitability of this method has been proved through excellent relationships between the test value and plant utilizable micro nutrients under pot and field studies conducted world over.

Instruments

i. Mechanical shaker

ii AAS (Atomic absorption spectrophotometer)

Reagents

i. **Dilute HCl:** Dil. HCl with double distilled water (DDW) by 5 times

ii. **DTPA solution extractant:** Take 1.967 g Diethylene-triamine-Penta acetic acid (DTPA) and 1.470 g of $CaCl_2.2H_2O$ in about 25 mL of double distilled water (DDW) by adding 13.3 mL of Tri-ethanolamine (TEA), followed by 100 mL more of DDW. Transfer the solution to 1 L volumetric flask giving 4 to 5 washings. Just before making up the volume, adjust pH to 7.3 with dilute HCl. This reagent has 0.005*M* DTPA, 0.1 *M* TEA and 0.01 *M* $CaCl_2.2H_2O$.

Determination of Available Zinc

Zinc present in the DTPA extract can be determined with the help of AAS. Prepare standard.

iii. **Standard stock solution 'A'** (1000 mg Zn L^{-1}): Take 1.0 g of pure Zn metal and dissolve it is minimum volume (about 10 mL) of dil. HCl (1:1) and make the volume to 1 L.

iv. **Standard solution 'B'**: Dilute 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mL portions of solution B to 50 mL to get working standards containing 0.5, 1.0, 1.5, 2.0, 2.5 and 5.0 mg Zn L^{-1}. The working standards should be prepared in the medium of the extracting solution after every few days as these cannot be preserved for long.

Procedure

1. Weigh 10 g of soil sample in 100 mL conical flask.
2. Add 20 mL of the DTPA extractant and shake for 2 hours on a mechanical shaker.
3. Filter through Whatman No. 42 filter paper, discarding first few drops. For quick filtration, Whatman No.1 filter paper can also be used if the filtrate is clear.
4. Use the filtrate for Zn measurement on AAS.
5. Feed the standard working solutions and prepare a standard curve by plotting AAS readings against Zn concentrations.

Calculation:

$$\text{Available (DTPA} - \text{extractable) Zn } \left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{A} \times 20}{10}$$

Where, A stands for the Zn concentration in aliquot as read from X-axis of

Determination of available Iron

Iron in the DTPA composition can also be determined with the help of AAS exactly in the same manner as Zn and Cu described above. However, the working standard solutions of Fe should be prepared for higher concentrations, as the DTPA- extractable Fe content of soil is generally more than both Zn and Cu. Thus, the Fe standard may be prepared as given below:

Prepare standard stock solution (solution 'A') by dissolving precise 1.0 g Fe metal in about 50 mL of 1:1 diluted HNO_3 and dilute the contents to 1 L with double distilled water. Prepare solution 'B' by diluting 50 mL of solution 'A' to 500 mL to get 100 mg Fe L^{-1}. Finally prepare working standard solutions containing 1.0, 2.0, 3.0, 5.0 and 10.0 mg Fe L^{-1} by diluting appropriate volume of solution 'B' with the medium of extraction (DTPA in this case) standard curve against the sample reading.

Determination of Available Copper:

Available copper can be determined in the DTPA extract similar to Zn, using AAS. For this, the standard stock solution can be prepared as given below:

Accurately weigh 1.0 g AR grade copper metal wire or turning and dissolve it in 50 mL of diluted HNO3 (1:1 with DDW) and finally make the volume to 1 L. This is solution 'A' containing 1000 mg Cu L^{-1}. Prepare solution 'B' containing 50 mg Cu $L^{-1}$by diluting appropriate volume of solution 'A'. Finally prepare working standards containing 0.25, 0.50, 1.0, 1.5, 2.0 and 2.5 mg Cu L^{-1} from solution 'B'

Determination of Available Manganese:

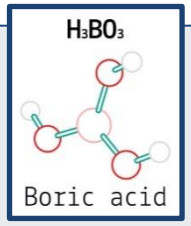
DTPA - extractable Mn is also determinate following the same technique as adopted for Zn, Cu and Fe. For this, prepare the standard solutions as Weigh 1.583 g of AR grade MnO_2 or 1.0 g of pure Mn metal and dissolve it in 50 mL of diluted HNO3 (AR grade). Make the volume to 1 litre with DDW to get solution 'A' having a Mn concentration of 1000 mg L^{-1}. From solution 'A' dilute 25 mL to 250 mL with DDW to get solution 'B' having 100 mg Mn L^{-1}. Finally prepare working solutions of 0.5, 1.0, 2.0, 2.5 and 5.0 mg Mn L^{-1}concentrations by diluting 0.5, 1.0, 2.0, 2.5 and 5.0 mL portions of solution 'B' to 100 mL

Interpretation

Nutrient	Critical level of micronutrient deficiency (mg/kg)	Soil rating: deficient
Zinc	0.6	< 0.6 mg/kg
Manganese	1.0	< 1.0 mg/kg
Iron	2.5-4.5	< 2.5-4.5 mg/kg
Copper	0.2	< 0.2 mg/kg

General recommended doses of micronutrient fertilizers

Micronutrient	Materials and doses for application	
	Soil application	Foliar spray
Zinc	Zinc Sulphate ($ZnSO_4$); 25 kg/ha	$ZnSO_4$ (0.5%) + Lime (0.25%)
Iron	Ferrous sulphate ($FeSO_4$); 50 kg/ha	$FeSO_4$ (1%) + Lime (0.5%)
Copper	Copper sulphate ($CuSO_4$); 10 kg/ha	$CuSO_4$ (0.1%) + Lime (0.05%)
Manganese	Manganese sulphate ($FeSO_4$); 10	$FeSO_4$ (1%) + Lime (0.25%)



15.
Determination of Available Boron in Soil

Boron exists in organic as well as in inorganic forms in soils and most of the B-compounds that have high availability are water-soluble. Boron deficiency is encountered in calcareous and acid soil, whereas toxicity occurs in salt-affected soils as well as in soils irrigated with high B water Among the methods proposed from time to time for B determination, the most widely used one was that of Berger and Truog (1939), which involved refluxing of soil with hot water. The method was, however, time consuming and also required special reflux apparatus Subsequently Gupta (1967) developed a rapid and easy method wherein the soil could be extracted by boiling with water directly on a hot plate. Use of azomethine-H (John et al, 1975) in place of carmine or curcumin has further simplified the determination of hot water soluble B. Azomethine- H forms a stable colored complex with H_3BO_3 at pH 5.1 in aqueous media, which retains proportional absorbance-concentration properties for several hours independent of the presence of variety of salts.

Hot-water Soluble Boron

Instruments:

1. Colorimeter or Spectrophotometer
2. Hot plate
3. Refrigerator

Reagents

1. **Buffer solution:** Dissolve 250 g of ammonium acetate and 15 g of EDTA (disodium salt) in 400 ml of distilled water, slowly add 125 ml of glacial acetic acid and mix thoroughly
2. **Azomethine-H reagent:** Dissolve 0.45 g of azomethine-H in 100 ml of 1% L ascorbic acid solution. Store in polypropylene bottle in a refrigerator. Prepare fresh solution every week.

3. **Boron standard solution:** Dissolve 0.114 g of AR grade boric acid (H_3BO_3) in distilled water and make the volume to 100 mL Each ml of this solution contains 20 µg of B. Dilute 0.5, 1, 2, 3, 4,5 10, 20, 30, 40 and 50 ml of this stock solution to 100 ml with distilled water to have solution concentrations of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0 and 10 ug B ml, respectively
4. **Activated charcoal**

Procedure

1. Weigh 20 g of a dry (20 mesh) soil sample in a 250 ml quartz or other boron-free conical flask and add 40 ml of distilled water.
2. Add 0.5 g of activated charcoal and boil for 5 minutes on a hot plate, filter immediately through Whatman No. 42 filter paper.
3. Cool the contents to room temperature and transfer 1 ml aliquot of blank (filtrate obtained after boiling of distilled water and activated charcoal), diluted B standard or sample filtrate into 10 or 15 mL polypropylene tubes.
4. Add 2 ml of buffer solution and mix.
5. Add 2 ml of azomethine H reagent mix and after 30 minutes read the absorbance at 420 nm on a spectrophotometer.
6. Prepare a standard curve plotting 1 concentration (0 to 10 µg B mL) on X axis and absorbance on Y axis.
7. Refer the absorbance readings of sample aliquots to the standard curve to obtain B content of aliquots.

Calculation:

$$\text{Available Boron } \left(\frac{\text{mg}}{\text{kg}}\right) = \text{A} \times 2$$

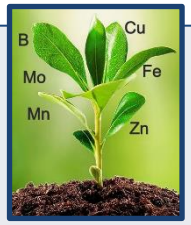
Where, A is the B content (g) obtained from standard curve

Interpretation

Nutrient	Critical level of micronutrient deficiency (mg/kg)	Soil rating: deficient
Boron	0.5	< 0.5 mg/kg

Precautions

1. As far as possible, avoid the use of borosilicate glass in determinations and storage of reagents
2. 2. Don't store azomethine-H reagent for long Prepare a fresh solution every week.
3. In order to eliminate interferences due to Al in high-Al acid sols, use tetra sodium salt of EDTA instead of di sodium salt for preparation of buffer solution.



16.
Determination of Available Molybdenum in Soil

Amongst the essential nutrients for plants, Mo is required in the smallest quantity. Molybdenum is the only heavy transition metal taken up by plant as molybdate ions (MoO_4^{-2}). Ammonium oxalate has been widely used for assessing available Mo in soil. (Grigg, 1960).The extractant is advantageous as it is easy to prepare, does not allow a signification change in pH during shaking due to bufferingaction and molybdenum forms stable complex with oxalic acid. The extraction is based on the replacement of MoO_4 ions from exchange sites, which is irreversible due to formation of strong Mo oxalic acid complexes.

Instruments:

1. Spectrophotometer
2. Hot plate
3. Refrigerator
4. Water bath

Reagents:

i. **50% KI (Potassium iodide) solution:** Dissolve 50 g of Kl in 100 mL of double distilledwater (DDW)

ii. **50% Ascorbic acid solution:** Dissolve 50 g of ascorbic acid in 100 mL of DDW

iii. **10% NaOH (Sodium hydroxide) solution:** Dissolve 10 g of NaOH in 100 mL of DDW.

iv. **10% Thiourea solution:** Dissolve 10 g thiourea in 100 mL of DDW and filter. Preparefresh solution before use.

v. **Toluene-3,4dithiol solution (commonly called dithiol):** Weigh 1.0 g of AR grade melted dithiol 51^{O}C) in a 250 mL glass beaker. Add 100 mL of the 10% NaOH solution and warm the contents up to 51^{O}C with frequent stirring for 15

minutes. Add 1.8 mL ofthioglycolic acid and store in a refrigerator.

vi. **10% Tartaric acid:** Dissolve 10 g in 100 mL of double distilled water.

vii. **Ethyl alcohol**

viii. **Iso-amyl acetate**

ix. **FAS (Ferrous ammonium sulphate) solution**: Dissolve 63 g of the salt in about 500 mLof DDW and then make the volume to 1 L.

x. **Extracting reagent:** Dissolve 24.9 g of AR grade ammonium oxalate and 12.6 g oxalicacid in water and make the volume to 1 L. Adjust the pH at 3.3 with dilute HCl/dil. ammonia solution.

xi. **Standard stock solution (100 µg Mo mL^{-1}):** Dissolve 0.150 g of AR grade MoO_3 in 100 mL of 0.1*N* NaOH, make slightly acidic with dil. HCl and make the volume to 1L.

xii. **Working standard solution (1 µg Mo mL^{-1}):** Dilute 10 mL of the stock solution of 1 L.

Procedure

1. Take 25 g of processed soil (air-dry soil sample) in 500 mL conical flask.
2. Add 250 mL of the extracting solution and shake for 10 hours.
3. Filter through Whatman No. 50 filter paper. Transfer 200 mL of the clear filtrate in a 250 mL glass beaker and evaporate to dryness on a water bath.
4. Heat the contents in the beaker at $500^{O}C$ in a furnace for 5 hours to destroy organic matterand oxalates. Keep overnight.
5. Digest the contents with 5 mL of HNO_3-$HClO_4$ mixture (4:1), then with 10 mL of 4 NH_2SO_4 and H_2O_2 each time bringing to dryness.
6. Add 10 mL of 0.1*N* HCl and filter. Wash the filter paper with additional 10 mL of 0.1*N* HCl and DDW until the volume of the filtrate becomes 100 mL
7. Run a blank side by side (without soil)
8. Take 50 m of filtrate in 250 mL separatory funnels and add 0.25 mL of the ferrousammonium sulphate solution and 20 mL of DDW and shake vigorously.

9. Add excess of Kl solution and clear the liberated iodine by adding ascorbic acid drop bydrop while shaking vigorously.
10. Add one mL of tartaric acid and 2 mL of Thiourea solution and shake vigorously.
11. Add 5 drops of dithiol solution and allow the mixture to stand for 30 minutes.
12. Add 10 mL of iso-amyl acetate and separate out the contents (green colour) in colorimeter tubes/cuvettes.
13. Read the colour intensity at 680 nm (red filter)

Preparation of Standard Curve for Mo estimation:

1. Take 0, 2, 5, 10, 15 and 20 mL of the working standard Mo solutions containing 1 µg Mo mL^{-1} in a series of 250 mL separator funnels.
2. Similar procedure will be follow for colour development as described above for soilsample aliquots.
3. Colour intensity will be read and prepare the standard curve by plotting molybdenumconcentration against reading.

Calculation:

$$\text{Available Mo } \left(\frac{\mu g}{g}\right) = A \times \frac{250}{200} \times \frac{100}{50} \times \frac{1}{25} = \frac{A}{10}$$

Where, A stands for Mo concentration in µg as obtained on x-axis against a sample reading.

Determining Available Molybdenum by AB-DTPA Method:

The Mo can also be estimated by AAS using graphite furnace. This method is especially useful for low Mo concentration in soil extract (<0.5 µg g^{-1} soil). Anion-resin method is also used for this purpose, but the ammonium bicarbonate-DTPA (AB-DTPA) method suggested by Soltanpour et al. (1982) and described below appears to be the better alternative (mainly for sodic soils) if ICP-AES/OES is available.

Principle

The NH_4HCO_3 reagent used in the method will work as an extractant but a buffer. During the extraction, the pH of soil reagent mixture increases to 8.5 dissolving the Ca, Al

and Fe molybdate. The HCO_3^- ions help in displacing MoO_4^{2-} ions from the colloidal surface. The extracted Mo can be measured using ICP.

Instruments

i. Mechanical shaker

ii. Inductively coupled plasma spectrophotometer

Reagents

AB-DTPA (Ammonium bicarbonate-diethylene tri amine Penta acetic acid) extracting solution: Take 1.97 g of AR grade DTPA to 800 mL of double distilled water. Add 2 mL of 1:1 diluted NH_4OH to aid dissolution and prevent effervescence. When maximum amount of the DTPA is dissolved, add 79.06 g of NH_4HCO_3 and stir gently to dissolve. Modify or adjust the pH to 7.6 with dil. HCl or dil. NH_4OH. Make the volume 1 L.

Standard Mo solution: Dilute 1 mL of standard Mo solution (containing 1 mg Mo L^{-1}) to 500 mL with AB-DTPA reagent. Because of linearity with ICP-AES/OES, a control and one standard are generally enough to prepare the standard curve.

Procedure

1. Take 10 g processed soil sample in 100 mL conical flask.
2. Add 20 mL of the AB-DTPA reagent and shake for 15 minutes on shaker.
3. Filter through Whatman No. 42 filter paper.
4. Add 0.25 mL conc. HNO_3 in a 10 mL beaker and then carefully add 2.5 mL of the extractto it.
5. Shake on a rotary shaker for 15 minutes and determine Mo using ICP-AES

Interpretation

Nutrient	Critical level of micronutrient deficiency (mg/kg)	Soil rating: deficient
Molybdenum	0.2	< 0.2 mg/kg

17.
Gypsum Requirement for Alkali Soil

Alkali and saline-alkaline soils are considered in the presence of Na^+ ions in large amount as high as15% or more, on their exchange complex. Due to this, the pH of soils increases higher then 8.5, which causes nutritional imbalances, elimination of organic matter, deterioration of soil physical properties and also affects the soil biota. The reclamation of alkali soil (pH= >8.5) requires gypsum treatment for replacement of Na^+ ions from the exchange complex. The sodium released has to be leached out by flooding. The gypsum requirement can be determined by adding a known excess of saturated solution of gypsum ($CaSO_4.2H_2O$) to soil and estimating its unreacted amount by Ethylene Di-amine Tetra Acetic acid (EDTA, Versenate) titration proposed by Schoonover (1952). Gypsum, being the cheapest and easily available, is most commonly used as reclaiming material. The quality of gypsum ($CaSO_4.2H_2O$) required to be applied to reclaim an alkali soil depend upon the factors like degree of soil deterioration, texture, degree of amendment desired, crops to be grown, leaching conditions, quality of irrigation water, etc.

$2NaX + CaSO_4$ Ca X + Na_2SO_4 Leachable)

Where, X express the soil exchange complex

Instruments:

Mechanical shaker, burette, pipette, conical flasks and filter papers etc.

Reagents

1. **Saturated gypsum solution ($CaSO_4.2H_2O$):** Take 5.0 g $CaSO_4.2H_2O$ to 1 L of distilled water and shake it for 10 minutes on a mechanical shaker, and filter it through filter paper Whatman No.1

2. **Ammonium chloride-ammonium hydroxide buffer solution (pH-10):** Dissolve 67.5

g ofammonium chloride in 570 mL of concentrated ammonium solution (Sp. gr. 0.88) and diluted to 1 L with distilled water and adjusted pH 10 using dilute NH_4OH **(Caution: liq. ammonia should be refrigerated before opening the bottle.**

3. **Eriochrome black T indicator:** 0.5 g of EBT (Eriochrome black) and 4.5 g of hydroxylamine hydrochloride (AR) dissolved in100 mL of 95% ethyl alcohol

4. **Standard EDTA (Versenate) solution 0.01*N*:** Dissolve 2.0 g of disodium di-hydrogen - EDTA and 0.05 g of $MgC1_2$ in water and dilute to 1 L. Standardize the solution againstthe standard $CaC1_2$ solution

5. **Standard calcium chloride solution 0.01*N*:** Dissolve 0.50 g calcium carbonate in about 10 mL of dilute HCl when it completely dissolved, transfer to 1 L volumetric flask and make the volume 1 L with distilled water. The $CaC1_2$ salt being highly hygroscopic should notbe used

Procedure:

1. Take 5 g of the processed soil in a 250 mL conical flask, and add 100 mL of the saturated $CaSO_4.2H_2O$ solution.
2. Shake for 5 minutes on a mechanical shaker and filter the content by Whatman No.1 paper.
3. Pipette out 5 mL of the soil extract into a 100 mL conical flask, and dilute to about 25 mL withdistilled water.
4. Add 0.5-1.0 mL of the NH_4CI- NH_4OH buffer solution and 2-3 drops of the EBT indicator.
5. Titrate with the standard EDTA solution until the colour changes from wine red to blue.
6. Run a blank using 5 ml of the saturated gypsum solution place of sample aliquot.

Calculations:

1. Weight of soil = 5 g
2. Vol. of saturated gypsum solution added = 100 g
3. Vol. of saturated gypsum solution taken for titration = 5 mL

4. Volume of EDTA used in titration for 5 mL of (As a blank) = X mL
5. Volume of EDTA used in titration for 5 mL of (aliquot/filtrate) = Y mL sample
6. Concentration of Ca in gypsum solution (meq/l) =X/5×0.01×1000 =S
7. Concentration of Ca+mg in filtrate (meq/l) = Y/5×0.01×1000=T
8. Gypsum requirement in meq/100g = 2(S-T) G
9. Gypsum requirement t/ha for a furrow slice = G × 1.924

Why a factor of 1.924 as used?

(Molecular weight of gypsum = 172/2=86)

The quantity of pure gypsum required to supply for

1 meq Ca/100 g soil = 86 mg gypsum

1 meq Ca/kg soil = 86 × 10 mg gypsum

Since weight of soil of the plough layer (0-15 cm) of 1 hectare field is 2.24×10^6 kg

$$\therefore \text{ Gypsum requirement } \left(\frac{\text{t}}{\text{ha}}\right) = \frac{86 \times 10 \times 2.24 \times 10^6}{1000 \times 1000 \times 1000} = \text{G} \times 1.924$$

Interpretation

The dose of gypsum to be decided on the basis of the extent of deterioration of the soil and the crop to be grown. Normally, it varies between 25 and 50 % of the total gypsum requirement estimated by this method.

18.
Lime Requirement for Acid Soil

In highly acidic soil having pH less than 6.0, nutrient availability is affected adversely. Reclamation of acid soils, by liming, is usually practiced for keeping the soil pH in the optimum range for making nutrients available in appropriate quantities. The amount of lime or liming material required depends on the nature of the soil. Through liming, the exchangeable H^+ is neutralized, and the $CaCO_3$ equivalence of the exchangeable H^+ of soil is called "lime requirement of soil". The value of lime requirement depends on the extent to which the exchangeable H^+ is to be neutralized, as different crops demand variable soil pH for optimum growth and response. On liming, Ca^{2+} and mg^{2+} replace both H^+ and Al^{3+} on the colloidal surface. The liming materials [CaO or $Ca(OH)_2$ or $CaCO_3$] react with CO_2 and water to form $Ca(HCO_3)_2$. By way of replacement of H^+ and Al^{3+} ions, the Ca^{2+} ions raise the percentage base saturation, which leads to a corresponding rise in soil pH. The widely followed method for determination of the lime requirement of soil (pH < 6.0) is that given by Shoemaker et al. (1961) which is described below.

Apparatus

pH meter

Reagents

ii. Extractant buffer solution: Dissolve 1.8 g of nitrophenol, 2.5 mL of triethanolamine, 3.0 of potassium chromate, 2.0 g of calcium acetate and 53.1 g of calcium chloride dihydrate in 1 L of distilled water and adjust the pH to 7.5 using dilute NaOH.

iii.pH buffer solution: Solutions of pH 4.0, 7.0 and 9.2, as described under pH determination.

Procedure:

1. Weigh air-dried soil g of dry soil in 50 mL beaker.
2. Add 5 mL of distilled water and 10 mL of the extractant buffer solution.
3. Stir continuously for 10 minutes or intermittently for 20 minutes with a glass rod.

4. Measure the pH of the soil-buffer suspension on a pH meter after standardizing with known pH buffer solutions
5. Against the measured pH, find out the amount of lime required to bring the soil pH to a desired level (e.g. 6.0, 6.4 or 6.8) as given in Table. Make necessary correction to get the value of agricultural lime based on purity percentage.

Table 17.1 Lime requirement for different pH targets

Measured pH of soil-buffer suspension	Lime requirement in tones/ha of pure CaCO3 for achieving different soil pH targets		
	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	5.56	7.53
6.3	6.56	7.78	8.99
6.2	7.53	8.99	10.21
6.1	8.50	10.21	11.66
6.0	9.48	11.42	13.12
5.9	10.69	12.64	14.58
5.8	11.66	13.85	15.79
5.7	12.64	15.07	17.25
5.6	13.61	16.28	18.71
5.5	14.58	17.50	20.17
5.4	15.79	18.71	21.63
5.3	16.77	19.93	22.84
5.2	17.98	20.90	24.30
5.1	18.95	22.11	25.76
5.0	19.93	23.33	27.22
4.9	20.99	24.54	28.67
4.8	22.11	25.76	30.13

19.
Determination of Calcium Carbonate in Soil

Calcite ($CaCO_3$) is the most abundant carbonate mineral in soils. It is also inherited from limestone, marl and chalk rocks, as well as from marble parent materials. Dolomite ($CaCO_3$. $MgCO_3$) is inherited in soil parent materials from dolomitic limestone and mantle rocks derived therefrom. A knowledge of the calcium carbonate content of the soil is most valuable guide for successful tree plantation and others agricultural crops. A qualitative rapid test for free calcium carbonate ($CaCO_3$) is made by adding about diluted HCl in soil on a watch glass and observing the intensity of effervescence which results from the evolution of CO_2. Based on the degree effervescence the amount of $CaCO_3$ present in the soil can be broadly categorized in to "traces or negligible" low, medium, high and very high. Soils having trace to low amounts of $CaCO_3$ do not pose any problem. But for those showing medium to very high degree of effervescence, a separate quantitative analysis should be carried out, using Puri's rapid titration method.

Rapid Titration Method (Puri, 1930)

The soil-water suspension is titrated against dilute H_2SO_4 in presence of bromothymol blue and bromocresol green indicators. In order to make the colour change distinct, $CaSO_4.2H_2O$ is added to the suspension. $AlCl_3$ added to the suspension lowers its pH to a point where the indicators show their yellow colour. Following reactions take place:

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

Reagents

1. **0.5 *N* Sulphuric acid**
2. **0.1*N* Aluminium chloride ($AlCl_3.6H_2O$):** Dissolve 8.05 $AlCl_3.6H_2O$ in distilled water and make the volume 1 L.
3. **Calcium sulphate powder ($CaSO_4.2H_2O$)**
4. **Bromothymol blue indicator:** Grind 1.0 g bromothymol blue in an agate pestle and mortar and dissolve it in 100 mL ethanol.

5. **Bromocresol green indicator:** Grind 1.0 g bromocresol green in an agate pestle and mortar and dissolve it in 100 mL ethanol.

Procedure

1. Weigh 10 gm soil passed through 2 mm sieve in 250-mL conical flask (soil amount may vary as per $CaCO_3$ content of soil with higher $CaCO_3$ content less amount of soil e.g. 5 g may be taken where's for soils with low $CaCO_3$ content, higher amount of soil e.g. 25 g soil needs to be taken.
2. Add 100 mL distilled water.
3. Add about 0.5 g $CaSO_4.2H_2O$ and 10 mL of $AlCl_3.6H_2O$ solution.
4. Shake the suspension thoroughly and add 10 drops of each of the indicators.
5. Heat the content using a hot plate to bring up to boiling and then remove the flasks allowing settling of the particles.
6. Appearance of green colour will indicate the presence of $CaCO_3$, and the golden yellow color the absence of $CaCO_3$.
7. If the supernatant is green in colored, titrate it against 0.5*N* H_2SO_4 until it turns yellow.
8. Bring the suspension to boil again and repeat the above step till a permanent golden yellow color is obtained that persists for a couple of minutes on boiling and allowing it to settle for a minute or two. This is the end point. Note the volume of acid used.

Calculation:

Wt of soil taken = 10 g

Volume of 0.5 *N* H_2SO_4 used = Y mL

1 mL of 0.5 *N* H_2SO_4 = 0.025 $CaCO_3$

(As 1000 mL of 1*N* H_2SO_4 = 50 gm $CaCO_3$

∴ 1 mL of 0.5 *N* H_2SO_4 = 0.025 $CaCO_3$

Percentage of $CaCO_3$ in soil = 0.025 × Y × 100/10= 0.25Y

Or

$$\text{CaCO3 (\%)} = \frac{0.025 \times \text{Volume of H2SO4 used}}{\text{Wt of soil sample}} \times 100$$

$$= 0.25 \times \text{Volume of H2SO4 used}$$

Interpretation

$CaCO_3$ (%) in soil	Suitability for crops
< 5	Suitable for growing citrus and others crops
< 10	Unsuitable for growing citrus but suitable for others crops

20.1 Multi-nutrient Extraction Procedure: MEHLICH 3 METHOD

(P, K, Ca, Mg, S, B, Zn, Fe, Cu, Mn)

Mehlich 3 is an acidic solution commonly used as an extractant for measuring plant-available nutrients in soils. It was developed as an improvement over previous extractants (Mehlich 1 and 2) by incorporating a higher concentration of strong acid to extract more nutrients and a chelating agent to improve the extraction of micronutrients. The resulting solution is used to determine the levels of essential nutrients, such as phosphorus, potassium, calcium, magnesium, zinc, and copper, in soil samples. Mehlich 3 extractant is widely used in soil testing laboratories and is recommended by various organizations and agencies, including the USDA and the Soil Science Society of America.

REAGENTS:

1. 0.2*N* CH_3COOH
2. 0.25*N* NH_4NO_3
3. 0.015*N* NH_4F
4. 0.013*N* HNO_3
5. 0.001*M* EDTA

PREPARATION OF EXTRACTING SOLUTION:

1. Weigh 20 g of NH_4NO_3 into a one litre volumetric flask containing 800 mL deionized water.
2. Add 0.5556 g NH_4F and dissolve it.
3. Add 0.2922 g EDTA and dissolve it.
4. Add 11.5 mL acetic acid and 0.82 mL nitric acid.
5. Dilute the volume with deionized water and mix well.
6. The Mehlich 3 extractant is now ready to use.

EXTRACTING PROCEDURE:

1. Take soil and extracting solution in the ratio of 1: 10 in a extraction bottle (2.5 cc soil and 25 mL solution in a extraction bottle).
2. Shake for 5 minutes on reciprocating shaker at high speed (250 oscillations per minute).
3. Filter using Whatman 1 filter paper.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analysed for all elements.
2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn and Cu.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.
5. Sulphur estimated by turbidometric method.
6. Ca & Mg can be analyzed by complexometric titration method.
7. Boron estimated by colorimetric method.

Note: Pyrex glassware cannot be used for extraction or storage of extractant because of Zn content.

20.2 Multi-nutrient Extraction Procedure: AB-DTPA (P, K, Zn, Fe, Cu, Mn)

AB-DTPA is a multi-nutrient extractant commonly used in soil testing and plant analysis. It is a chelating agent that can extract essential plant nutrients, including NO_3, P, K, Zn, Fe, Cu and Mn. AB-DTPA has been extensively used in research and practical applications to assess nutrient availability in soils and to diagnose nutrient deficiencies in plants. Its effectiveness and reliability have been well-established in various soil and plant types, making it a valuable tool in agriculture and environmental management.

REAGENTS:

1. 1 M NH_4HC0_3
2. 0.005 M DTPA,
3. NH_4OH

PREPARATION OF EXTRACTING SOLUTION:

1. Add 1.97 g DTPA to 800 mL water in a 1000 mL volumetric flask.
2. Approximately 2 mL of 1:1 NH_4OH is added to facilitate dissolution and to prevent effervescence when the bicarbonate is added.
3. When most of the DTPA is dissolved, 79.06 g NH_4HCO_3 is added and stirred gently until dissolved.
4. The pH is adjusted to 7.6 with ammonium hydroxide.
5. Make up the volume to 1000 mL.

EXTRACTING PROCEDURE:

1. Take soil and extractant in the ratio of 1: 2
2. Ten grams of soil are weighed into a 125 mL Erlenmeyer flask.

3. Two 2.5 mL scoops of Fisher G carbon black are added to each soil, followed by 20 mL extracting solution.
4. The soil mixture is then shaken on a reciprocating shaker for 15 minutes at 180 cycles/minute with flasks kept open.
5. The extracts are then filtered through Whatman 42 filter paper.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analysed for all elements.
2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn and Cu.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.

20.3 Multi-nutrient Extraction Procedure: MORGAN EXTRACTANT

(P, K, Ca, Mg, B, Zn, Fe, Cu, Mn)

The first universal soil extracting reagent was developed by Morgan, a 0.73M sodium acetate ($NaC_2H_3O_2$.) solution buffered at pH 4.8 in 1941. The Morgan extraction reagent was widely used in the 1950s and early 1960s, but it is in little use today.

REAGENTS:

1. 0.73 *M* Sodium acetate
2. Glacial Acetic acid
3. HCl

PREPARATION OF EXTRACTING SOLUTION:

1. Add 100 g of sodium acetate to 500 mL of distilled water. After dissolving add 30 mL of glacial acetic acid and make up to one liter. Adjust the pH at 4.8 with HCl.

EXTRACTING PROCEDURE:

1. Take soil and extractant in the ratio of 1: 5.
2. 5 g of soil are weighed into a 125 mL Erlenmeyer flask and 25 mL of extractant added.
3. The soil mixture is then shaken on a reciprocating shaker for 15 minutes at 180 cycles/minute with flasks kept open.
4. The extracts are then filtered through Whatman 42 filter paper.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analyzed for all elements.
2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn and Cu.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.
5. Ca & Mg can be analyzed by complexometric titration method.
6. Boron estimated by colorimetric method.

20.4 Multi-nutrient Extraction Procedure: WOLF (P, K, Ca, Mg, Zn, Fe, Cu, Mn)

The Morgan extraction reagent was modified by Wolf (1982) who added the chelate DTPA (diethylenetriaminepentaacetic acid) to the extractant for the determination of the micronutrients Cu, Fe, Mn and Zn irrespective of texture as the soil aliquot measurement is by volume. As with the Morgan's solution, it is possible to determine all important elements except sodium in a single extract but with better correlations of extracted trace elements with plant growth. The extraction reagent is a mixture of 0.073 *M* sodium acetate ($NaC_2H_3O_2$), 0.52 *N* acetic acid (CH_3COOH) and 0.001 *M* diethylene-tri-amine-penta-acetic acid (DTPA) buffered at pH 4.8. The extraction reagent is best suited for the assay of well fertilized soils and most effective for monitoring their fertility level.

REAGENTS:

1. 0.073 *M* Sodium acetate
2. 0.52 *N* Acetic acid
3. 0.001 *M* DTPA

PREPARATION OF EXTRACTING SOLUTION:

1. Weight 100 g sodium acetate into a one litre volumetric flask.
2. Add 300 mL pure water and 30 mL glacial acetic acid (CH_3COOH) and 0.05 g DTPA.
3. Dilute to 950 mL with pure water and adjust the pH to 4.8.
4. Dilute to volume with pure water.

EXTRACTING PROCEDURE:

1. Scoop 20 cm^3 soil into a 250-mL Erlenmeyer flask or other suitable extraction vessel.
2. Add 40 mL Morgan-Wolf* Extraction Reagent.
3. Vigorously shake the soil-extraction reagent for 5 minutes.
4. Filter and save the filtrate.

5. The obtained extract (filtrate) is ready for elemental (P, K, Ca, Mg, B, Cu, Fe, Mn, Zn and Al) content determination as well as for nitrate, ammonium and sulfate.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analyzed for all elements.
2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn and Cu.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.
5. Ca & Mg can be analyzed by complexometric titration method.

Note: The extraction composition (mixture of 0.062 *N* NH_4OH and 1.25 *N* HOAc, pH 4.8) mentioned in the detailed project report is different from the original reference article (Wolf, 1982)

20.5 Multi-nutrient Extraction Procedure: CDTA-GLYCEROL

(P, K, Ca, Mg, S, B, Zn, Fe, Cu, Mn)

Recently, Seth (2016) tailored diamino-cyclo-hexane-tetra-acetic acid glycerol (CDTA), a new complex multinutrient extractant that combines 0.002 M trans-CDTA, 0.05 M glycerol, 0.1 *M* NH4-acetate, and 0.01 *M* NH_4F, buffered at pH 4.8. The premise for this extractant is the CDTA forms stronger complexes with almost all metals than does EDTA or DTPA, and the low buffering pH (4.8) could extract cationic micronutrients (Zn, Cu, Fe, and Mn), mimicking plant's extraction of nutrients. The suitability of different extractants for assessing plant available soil Zn is a function of the nature of soils and the crop type. For example, the DTPA method of Lindsay and Norvell (1978) has gained wide acceptance because of good Zn correlations in calcareous soils (Wendt, 1995; Schmisek et al., 1998).

REAGENTS:

1. 0.002 *M* trans-CDTA
2. 0.05 *M* Glycerol
3. 0.1 *M* NH_4-acetate
4. 0.01 *M* NH_4F

EXTRACTING PROCEDURE:

1. Take soil and extractant in the ratio of 1:2 in Erlenmeyer flask or other suitable extraction vessel.
2. Vigorously shake the soil-extraction reagent for 15 minutes.
3. Filter and save the filtrate.
4. The obtained extract (filtrate) is ready for elemental (P, K, Ca, Mg, B, Cu, Fe, Mn, Zn and Al) content determination as well as for nitrate, ammonium and sulfate.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analyzed for all elements.

2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn and Cu.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.
5. Sulphur estimated by turbidometric method.
6. Ca & Mg can be analyzed by complexometric titration method.
7. Boron estimated by colorimetric method.

20.6 Multi-nutrient Extraction Procedure: AMMONIUM ACETATE-EDTA UNIVERSAL EXTRACTANT (P, K, Zn, Fe, Cu, Mn, Mo, Co)

The acid ammonium acetate-EDTA universal extractant developed at Agricultural Research Centre of Finland. This method has already been globally used in soil testing and pollution studies.

REAGENTS:

1. 0.5*N* Acetic acid: 28.7 mL
2. 0.5*N* Ammonium acetate: 38.54 gm
3. 0.02*M* Na_2EDTA: 6.72 gm added to the final concentration of one litre.

PREAPARATION OF EXTRACTANT:

The extraction solution is made with 28.7 mL acetic acid and 38.54 g ammonium acetate added to 800 mL distilled water in a 1000 mL volumetric flask. The pH is adjusted to 4.65 and 6.72 g of Na_2EDTA is added to the final concentration and made upto the mark.

EXTRACTING PROCEDURE:

1. Take soil and extractant in the ratio of 1: 10
2. 5 grams of soil are weighed into a 125 mL Erlenmeyer flask.
3. 50 mL of extracting solution is added to it.
4. The soil mixture is then shaken on a reciprocating shaker for 60 minutes at 27 rpm.
5. The extracts are then filtered through Whatman No. 1 filter paper.

NUTRIENT ANALYSIS:

1. The filtrate may be stored and analysed for all elements.
2. Atomic absorption spectroscopy may be used for analysis of Fe, Mn, Zn, Cu, Mo and Co.
3. Phosphorus can be analysed by ascorbic acid method.
4. Potassium in the soil extract is determined directly by flame emission.

REFERENCES

Aitken R.L, Jeffrey A.J. and Compton B.L. (1987) Evaluation of selected extractants for boron insome Queensland soils. *Australian Journal Soil Research.* 25:263-273.

Berger, K.C. and Truog, E. (1939) Boron determination in soils and plants using the quinalizar in reaction. *Industrial Engineering Chemistry and Analytical Edition* 11:540-545.

Bray, R. H. and Kurtz, L. T. (1945) Determination of total, organic, and available forms of phosphorus in soils. *Soil Science,* 59(1):39-46.

Chiba, A. and Shinke, H. (1977) Estimation of lime requirement of soil with calcium carbonate and aeration method, Japanese. *Journal of Soil Science and Plant Nutrition*: 48:237–242

Datta, N. P., Khera, M. S. and Saini, T. R. (1962) A rapid colorimetric procedure for the determination of organic carbon in soils. *Journal of the Indian Society of Soil Science*, 10(1):67-74.

Datta, S. P., Bhadoria, P. B. S. and Kar, S. (1998) Availability of extractable boron in some acid soils, West Bengal, India. *Communications in Soil Science and Plant analysis*, 29(15-16):2285-2306.

Datta, S.P., Meena, M.C., Dwivedi, B.S. and Shukla, A.K. (2018) Manual on Advanced Technique for Analysis of Nutrients and Pollutant Elements in Soil, Plant and Human WestvillePublishing House.

Dhyan, S., Chhonkar, P.K. and Dwivedi, B.S. (2005) Manual on soil, plant and water analysis. Westville Publishing House.

Goswami, N.N., Rattan, R.K., Dev, G., Narayanasamy, G., Das, D.K., Pal, D.K. and Rao, D.L.N.(2009) Fundamental of Soil Science by Indian Society of Soil Science.

Grigg, J.L. (1960) The distribution of molybdenum in the soils of New Zealand. New-Zealand. *Journal of Agricultural Research* 3:69-86.

Gupta, J. P. and Jalali, V.K. (1998) Manual for Soil, Plant and Irrigation Water Analysis. Soil Science Section, SKUAST, Jammu.

Jackson, M. L. (1973) Soil Chemical Analysis. Prentice Hall of India Pvt. Ltd., New Delhi, pp. 263-393. John, M.K., Chuah, H.H. and Neufeld, J.H. (1975). Application of improved azomethine-H method to the determination of boron in soils and plants. *Analytical letters* 8(8):559-568.

Johnson, C.M. and Ulrich, A. (1959) Analytical methods for use in plant analysis. California Agricultural Statistical Bulletin, 766.

Lindsay, W.L. and Norvell, W.A. (1978) Development of DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal* 42: 421-442.

Mehlich, A. (1984). Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis*, *15*(12), 1409-1416.

Merwin, H.D. and Peech, M. (1951) Exchangeability of soil potassium in the sand, silt and clay fractions, as influenced by the nature of complimentary exchangeable cations. *Soil Science Society of America Proceedings* 15:125-128.

Morgan, M. F. (1941). Chemical soil diagnosis by the universal soil testing system. CONNECTICUT AGRICULTURAL EXPERIMENT STATION BULLETIN 450.

Nelson, L.B. and Heidel, H. (1952) Soil analysis methods as used in the Iowa State College Soil Testing Laboratory.

Olsen, S. R., Cole, C.V., Frank, S. W. and Dean, L.A. (1954) Estimation of available phosphorus by extraction with sodium bicarbonate, United States Development of Agriculture Circular number, 939.

Piper, C.S. (1950) Soil and plant analysis. The University of Adelaide, Australia.

Rattan, R.K., Katyal, J.C., Dwivedi, B.S., Sarkar, A.K., Bhattacharyya T., Tarafdar, J.C. and Kukal, S.S. (2015) Soil Science -An Introduction by Indian Society of Soil Science.

Richards, L.A. (1954) Diagnosis and improvement of saline- alkali soils. Agriculture Handbook No. 60, USDA, Washington.

Schofield, R. K. and Taylor, A. W. (1955(The measurement of soil pH. *Soil Science Society of America Journal* 19 (2):164-167.

Seth, A., Sarkar, D., Datta, A., Mandal, B., Chowdhury, A., Masto, R. E., ... & Saha, S. (2017). Suitability of complex extractants for assessment of available soil zinc for nutrition of rice (*Oryza sativa* L.) in subtropical India. *Soil Science*, *182*(1), 28-35.

Singh, A.K., Khan, S.K. Nongkynrih, P. (1999) Transformation of Zinc in Wetland Rice Soils inRelation to Nutrition' of Rice Crop. *Journal of the Indian Society of Soil Science* 47(2):248-253.

Sippola, J. (1994) Acid ammonium acetate-EDTA universal extractant in soil testing and environmental monitoring. *Communications in Soil Science and Plant Analysis*, *25*(9-10), 1755-1761.

Snell, F.D. and Snell, C.P. (1949) Colorimetric Methods of Analysis.3rd Ed. Vol. 2nd D. Van Nostrand Inc. New York.

Soltanpour, P. N., & Schwab, A. P. (1977) A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. *Communications in Soil Science and Plant Analysis*, *8*(3), 195-207.

Soltanpour, P.N. and Workman, S.M. (1981) Soil testing methods used at Colorado State University Soil Testing Lab for evaluation of fertility, salinity, sodicity, and trace elementtoxicity. Colo. State Univ. Exp. Sta., Fort Collins, Tech. Bull. 142.

Subbiah, B.V. and Asija, G.L. (1956) A rapid procedure for determination of available nitrogen in soil. *Current Science*, 25:259-260.

Walkley, A.J. and Black, I.A. (1934) Estimation of soil organic carbon by chromic acid titrationmethod. *Soil Science* 37:29-38.

Williams, C.H. and Steinbergs, A. (1959) Soil Sulphur fractions as chemical indices of available Sulphur in some Australian soils. *Australian Journal of Agricultural Research* 10: 340-52.

Wolf, B. 1982. An improved universal extracting solution and its use for diagnosing soil fertility. COMMUN. SOIL SCI. PLANT ANAL. 13:1005- 1033.