Section II

Soil Analysis

Chapter 3

Chemical Analysis of Soil

3.1 Available Nitrogen (Alkali KMnO$_4$ Method)

(1) What is Available Nitrogen

Nitrogen (N) is found in the horizon of the soil, mostly in organic materials. In the soil solution, organic N is gradually transformed into ammoniacal (NH$_4^+$), nitrite (NO$_2^-$) and nitrate nitrogen (NO$_3^-$)-N by microbial processes. Organic-N is, in itself, of very little use to plants, as it cannot be absorbed as such. It is therefore, necessary to estimate the different forms of mineralized or available N. The NO$_2^-$ - N and NO$_3^-$ - N together, hardly, exceed 1% of the total N in normal soil.

The available N in soil refers to a fraction of the total N which is converted into forms accessible to the plants. This constitutes, on an average, only 0.5-2.5 % (rarely 5%) of the total N in a soil at any given time.
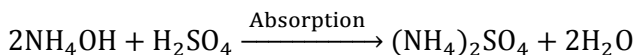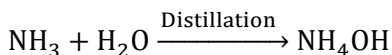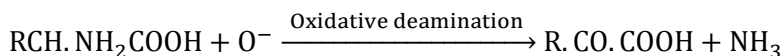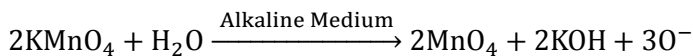
(2) Principle

Potassium permanganate (KMnO$_4$) in alkaline medium (in presence of NaOH here) acts as a weak oxidizing agent. Hence when KMnO$_4$ and NaOH are added to a soil, KMnO$_4$ oxidizes the organic forms of N (e.g. protein) to amines. Thus in presence of alkali (NaOH), NH$_3$ volatilizes. During distillation NH$_3$ comes out from the distillation flask and is absorbed in a known volume of a standard acid, i.e. H$_2$SO$_4$, the excess of which is titrated with a standard alkali (0.02NaOH) using methyl red as the indicator. The known volume of H$_2$SO$_4$ taken in the conical flask is in excess so that only a portion reacts with NH$_3$ and another portion remains unchanged. The volume of this unchanged H$_2$SO$_4$ is measured by titration with the standard NaOH (N/50) solution. By mathematical deduction of this volume from the volume taken, the volume of H$_2$SO$_4$ that

reacts with NH_3 is found out.

(3) Reactions

(a) Distillation

$$2KMnO_4 + H_2O \xrightarrow{\text{Alkaline Medium}} 2MnO_4 + 2KOH + 3O^-$$

$$RCH.NH_2COOH + O^- \xrightarrow{\text{Oxidative deamination}} R.CO.COOH + NH_3$$

$$NH_3 + H_2O \xrightarrow{\text{Distillation}} NH_4OH$$

$$2NH_4OH + H_2SO_4 \xrightarrow{\text{Absorption}} (NH_4)_2SO_4 + 2H_2O$$

(b) Titration

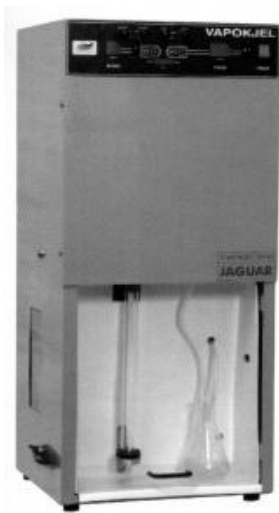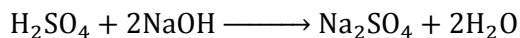$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

Fig. 2. Portable Kjeldahl distillation unit.

(4) Materials Required

(i)   Kjeldahl distillation set

(ii) Measuring cylinders

(iii) Pipette

(iv) burette

(v)   Conical flask (less than 250ml)

(vi) Heater

(5) Reagents Required

0.32% $KMnO_4$ solution: Dissolve 3.2gm of $KMnO_4$ in distilled water, make up the volume to 1 litre.

2.5% NaOH solution: Dissolve 25gm of NaOH pellete in distilled water. Make up the volume to 1 litre.

N/50 (or 0.02N) H_2SO_4: Add water upto 1000ml to 0.55ml concentrated H_2SO_4.

N/50 NaOH : Dissolve 0.80gm NaOH in a 600ml distilled water. Stir to dissolve NaOH. Add distilled water upto 1000ml.

Methyl red indicator (0.15%): Dissolve 0.15%gm of methyl red indicator powder in 50ml ethyl alcohol and make up the final volume to 100 with distilled water.

(6) Procedure

- Place 20gm of soil in a distillation flask.
- Moisten the sample by adding 20ml of distilled water.
- Add 100ml of 3.2% $KMnO_4$ solution.
- In conical flask, take 30ml N/50 H_2SO_4. Add 2-3drops of methyl red indicator and dip the end of the delivery tube into it.
- Pour 100ml of 2.5% NaOH solution into the distillation flask and cork it immediately.
- Distill ammonia by steadily heating the distillation flask and collect enough distillate in a conical flask.
- Titrate the excess of the standard H_2SO_4 in the conical flask with 0.02% N NaOH (or N/50 NaOH)). The end point is reached when the colour changes from pink to yellow.

(7) Calculation

Weight of the soil taken = 20gm
Volume of N/50 H_2SO_4 taken = 30ml

Volume of N/50 NaOH used in titration = Xml

Volume of N/50 acid used for NH_3 absorption = (30-x)ml

(1ml of N/50 H_2SO_4 = 0.02mg of N = 0.028mgN= 0.00028gm N)

(a) % available N = (30-x) × 0.00028 ×100/20

(b) Available N in the soil (kg/ha) = percentage N value × 22400

(For expressing available N in kg/ha, I ha/g furrow slice (0-15cm) of the soil is assumed to be 2.24 million kg in weigh.)

(8) Interpretation

Amount of available N (kg/ha)	Comments
< 272	Low
272-544.1	Medium
> 544	High

3.2 Organic Carbon and Organic Matter (Walky and Black, 1934)

(1) What is Soil Organic Matter

All plants, animal and microbial residues both decomposed and endecomposed in the soil constitute the organic matter, most of which is of plant origin.

(2) Importance

The Organic Matter (OM) is the source of plant nutrients which are released in assimilable forms during microbial degradation. A major proportion of N (95-99% of the total), occurs in organic combinations, which mineralize to release the nutrients in inorganic forms to be used by plants. Thus OM is an index of the productivity. It is also a source of cation exchange capacity besides retention and aeration of soils.
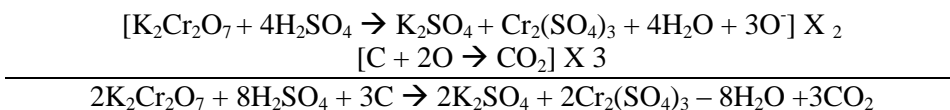
3.2.1 Titrimetric Method

(1) Principle for Titration Method

The soil is digested with chromic and sulphuric acid making use of the heat of dilution of strong H_2SO_4 so as to oxidize the humus. The highest temperature
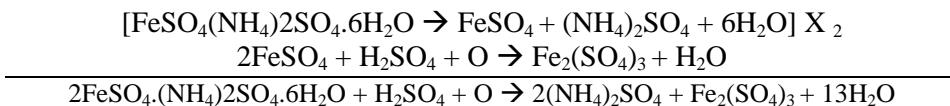
attained by the heat of dilution reaction, produced on the addition of H_2SO_4 is approximately 120^0C, which is sufficient to oxidize the active forms of the soil organic C. On oxidation potassium dichromate is reduced to potassium sulphate. Cr^{6+} is reduced to Cr^{3+}. The colour of the oxidized form of chromium Cr^{6+} is yellow and that of reduced form Cr^{3+} is green. Appearance of yellow (or organic) colour after completion of oxidation (i.e. after 30 minutes of addition) indicates that only a small fraction of dichromate is reduced and major fraction remain unchanged. An appearance of green colour indicates that entire amount of Cr^{6+} has been reduced to Cr^{3+}. There might have some possibility that an amount of C remain unoxidized. (Therefore, in this case the procedure is repeated taking small amount of soil or increased volume of $K_2Cr_2O_7$ so that after completion of oxidation, a considerable amount of $K_2Cr_2O_7$ exists unchanged that shows yellow or orange colour) The volume of unchanged $K_2Cr_2O_7$ solution is determined by titration with ferrous iron sulphate. During titration, ferrous iron sulphate reduces unchanged or excess of $K_2Cr_2O_7$ present in the solution. In the procedure, H_3PO_4 and NaF are used as a redox titration. Diphenylamine added is oxidized first to colourless diphenylbenzidine which is further oxidized to diphenylbenzidine violet.
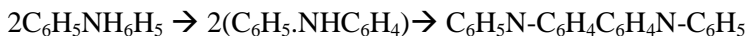
(2) Reactions

(i)   The oxidation of Carbon

$$[K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O^-] \text{ X } 2$$
$$[C + 2O \rightarrow CO_2] \text{ X } 3$$

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3C \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 - 8H_2O + 3CO_2$$

(ii)   The titration procedure

$$[FeSO_4(NH_4)2SO_4.6H_2O \rightarrow FeSO_4 + (NH_4)_2SO_4 + 6H_2O] \text{ X } 2$$
$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$2FeSO_4.(NH_4)2SO_4.6H_2O + H_2SO_4 + O \rightarrow 2(NH_4)_2SO_4 + Fe_2(SO_4)_3 + 13H_2O$$

(iii) The action of diphenylamine indicator

$$2C_6H_5NH_6H_5 \rightarrow 2(C_6H_5.NHC_6H_4) \rightarrow C_6H_5N\text{-}C_6H_4C_6H_4N\text{-}C_6H_5$$

(3) Materials Required

(i)   Conical flask

(ii)   Pipette

(iii) Burette

(iv)   Analytical balance

(4) Reagents Required

1. 1N Potassium dichromate: Dissolve 49.04gm of AR grade $K_2Cr_2O_7$ in distilled water and make up the volume to 1 litre.

2. 0.5N ferrous ammonium sulphate (Mohr's salt): Dissolve 392gm of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 15ml of conc.H_2SO_4 and make up the volume to 2litre with distilled water.

3. Conc.H_2SO_4. For saline soil, 1.25gm of Ag_2SO_4 in 100ml of conc.H_2SO_4 is dissolved and the solution (1.25% $AgSO_4$ in H_2SO_4) is used instead of only conc.H_2SO_4.

4. Orthophosphoric acid (H_3PO_4) 85%.

5. Sodium fluoride.

6. Diphenylamine indicator: Dissolve 0.5 gm of diphenylamine indicator in a mixture of 20ml of water and 100ml of conc.H_2SO_4.

(5) Procedure

- Take 1gm of soil in 500ml conical flask.

- Add accurately 10ml of $K_2Cr_2O_7$ solution with a 10ml pipette. Gently rotate the flask to mix them.

- Add 20ml conc. H_2SO_4 with a measuring cylinder and swirl the flask 2 or 3 times.

- Allow the flask to stand for 30minutes on an asbestos sheet for the reaction to complete. After 30 minutes, a yellow colour would be observed. If green colour appears, through the content and repeat with less amount of soil (<1g) or adding more volume of $K_2Cr_2O_7$ solution.

- Add 200ml of distilled water to dilute the suspension. Filter, if it is expected that the end point of the titration will not be clear.

- Add 10ml of Orthophosphoric acid and 2gm of sodium fluoride. Shake vigorously to mix.

- Add about 1ml of diphenylamine indicator.

- Immediately back-titrate the solution with 0.5N ferrous ammonium sulphate, till the colour flashes from violet through blue to bright green.

- Note the volume of the ferrous ammonium sulphate used.

- Carry out a blank titration (i.e. without soil) in a similar manner.

Since dichromate is reduced to oxidize diphenylamine, an error appears if diphenylamine is allowed to stay with potassium dichromate for long time.

Therefore, diphenylamine should be added just before titration.

Note: If the titration value is <4ml, repeat the experiment with <1g soil.

(6) Calculation

Weight of soil = Wgm

Volume of 0.5NFe(NH$_4$)$_2$(SO$_4$)$_2$ solution used = Bml for blank solution

Volume of 0.5NFe (NH$_4$)$_2$(SO$_4$)$_2$ solution used = Sml for sample solution

Volume of 1N K$_2$Cr$_2$O$_7$ used for oxidation of C = 0.5 × (B-Sml (or B-S/2ml)

(1 ml of 1N K$_2$Cr$_2$O$_7$ oxidizes 3gm of C or 0.003g C)

% of Organic C in the soil (uncorrected) = 0.5 × (B-S) × 1 × 0.003 × 100/W = Q

% Organic C in the soil (Corrected) = Q × 1.3 = R

(Walky averaged a 77% recovery of organic carbon by this method. Thus the correction factor is 100/77 = 1.3.)

Hence, % of organic matter in the soil = R × 1.724.

(Since organic matter, on an average, contains 58% carbon, the percent organic matter is multiplied by 1.724 (100/58) is known as the 'Von Bemmlen factor.)

3.2.2 Colorimetric Method

(1) Principle

The oxidation of soil organic matter is carried out by dichromate sulfuric acid mixture. The intensity of the chromium sulphate found is measured to give directly the amount of carbon oxidized.

(2) Materials Required

Photoelectric colorimeter, conical flask, volumetric flask, pipette, AR grade potassium dichromate, concentrated H$_2$SO$_4$, sucrose (anhydrous).

(3) Procedure

- Take 1gm of soil in 100ml conical flask.
- Add 10ml of 1NK$_2$Cr$_2$O$_7$, swirl the flask, followed by addition of 20ml

H_2SO_4, swirl again.

- Allow the flask to stand for 30minutes and then centrifuge the contents to clear state.
- Read the green colour of the chromium sulphate on the supernatant layer on a colorimetet after, adjusting the blank solution to zero, using 660nm red filter.

(4) Standard Curve Preparation

Take 1 to 25mg of anhydrous sucrose in 100ml conical flask, develop the colour and read on a colorimeter as per the procedure outlined for the sample. Draw a curve by plotting the concentration of carbon as sucrose on the abscissa and the colorimeter reading (%T) on the ordinate in log scale.

(5) Interpretation

Organic C (%)	Comments
<0.50	Low
0.50-0.75	Medium
> 0.75	High

3.3 Available Phosphorous (Olsens et al., 1954)

(1) Introduction

The term available Phosphorous (P) refers to the inorganic form, occurring in the soil solution, which is almost exclusively orthophosphate. This orthophosphate occurs in several forms and combinations, and only a small fraction of the total amount present may be available to plants, which is of direct relevance in assessing P fertility level.

The phosphate concentration in soil solution is governed by heterogeneous equilibrium in which it takes part. This situation can be represented as:

P adsorbed in solid phase $\leftrightarrow$ P in soil solution $\leftrightarrow$ P precipitate
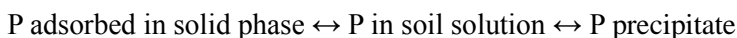
The phosphorous absorbed by plants from soil solution comes as inorganic orthophosphate ions, viz. $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. The most available ion is H_2PO^{4-}, followed by HPO_4^{2-}. The accessibility of P by plants is influenced by a series of soil properties. The relative abundance of ions is, however relatively dependent on the soil pH. For soil having a pH between 4.7 and 7.5, ions of $H_2PO_4^-$ as well as of HPO_4^{2-} exists in soil solution. At a pH of 7.2, $H_2PO_4^-$ and

HPO_4^{2-} ions have an equal activity, and when the pH is strongly alkaline (>8.3) ions of HPO_4^{2-} predominates the solution. Above pH of 9.0, the trivalent ion (PO_4^{3-}) becomes more important than $H_2PO_4^-$, but even at a pH of 12, the HPO_4^{2-} concentration is still greater than that of PO_4^{3-}.
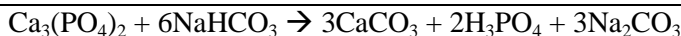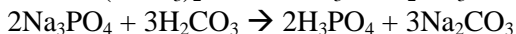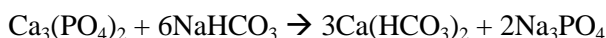
(2) Importance

The available P indicates fertility level of soil. The knowledge of critical limits of soil is necessary for better soil - crop response. The evaluation of the soil critical limit of available P would help in developing P-fertility ranges for effective fertilizer recommendation schedule.
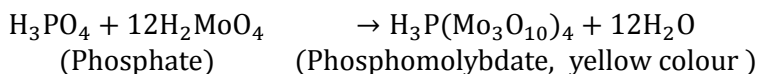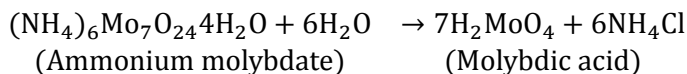
(3) Principle

The soil is shaken with 0.5M $NaHCO_3$, at a nearly constant pH of 8.5, in 1:20 ratio for half an hour, in presence of Darco-G60 (which absorbs the dispersed organic matter in the sample and helps giving a clear extract) and the extract is obtained by filtering the suspension. Phosphorous in the extract is treated with ammonium molybdate (a complexing agent), which results in the formation of a heteropoly complex, known as 'phosphomolybdate' (faint yellow colour). This 'faint yellow colour' is not visible, and hence, it is unsuitable for colorimetry or spectrophotometry. To make it suitable, the heteropoly complex is partially reduced by stannous chloride that given a blue colour. With increasing P concentration in the soil extract, the amount of molybdo-phosphoric acid complex increases and hence, on partial reduction of the complex, the intensity of blue colour increases. Thus, a faint blue colour indicates low P content and a deep blue colour indicates high P content of soil.

1. Extraction

$$Ca_3(PO_4)_2 + 6NaHCO_3 \rightarrow 3Ca(HCO_3)_2 + 2Na_3PO_4$$
$$3Ca(HCO_3)_2 \rightarrow 3CaCO_3 + 3H_2CO_3$$
$$2Na_3PO_4 + 3H_2CO_3 \rightarrow 2H_3PO_4 + 3Na_2CO_3$$
$$\overline{Ca_3(PO_4)_2 + 6NaHCO_3 \rightarrow 3CaCO_3 + 2H_3PO_4 + 3Na_2CO_3}$$

2. Colour development

$$(NH_4)_6Mo_7O_{24}4H_2O + 6H_2O \rightarrow 7H_2MoO_4 + 6NH_4Cl$$
(Ammonium molybdate)　　　(Molybdic acid)

$$H_3PO_4 + 12H_2MoO_4 \rightarrow H_3P(Mo_3O_{10})_4 + 12H_2O$$
(Phosphate)　　(Phosphomolybdate, yellow colour)

3. Reduction

$$\text{Phosphomolybdate} + \text{SnCl}_2 \quad \rightarrow \text{Reduced Phosphomolybdate}$$
$$\text{(Molybdenum blue)}$$
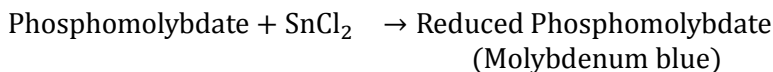
(4) Apparatus

Photoelectric colorimeter, pipette (5ml), volumetric flask (25 or 50ml), funnel, Whatman No 42 or 44 filter paper.

(5) Reagents

0.5M $NaHCO_3$: Dissolve 42gm of Sodium bicarbonate in distilled water and make up the volume to 650ml approximately. Adjust the pH of the solution to 8.5 with dilute NaOH solution and make up the volume to 1liter with distilled water.

Darco-G60 (activated charcoal): This is to be made free from soluble P first by following procedure:

1. Take about 1g of charcoal in a 250ml conical flask.
2. Take about 15-20ml of 0.5M $NaHCO_3$ (pH 8.5) solution in the flask.
3. Stoppered the flask and shake for about 30 minutes.
4. Filter through Whatman No1 filter paper.
5. Take 10ml of the filtrate in a 50ml volumetric flask.
6. Add 1-2 drops of 2, 4 dinitrophenol. It turns filtrate to yellow in colour which indicates pH above 3.
7. Add 4N HCl drop by drop until yellow colour disappears to adjust pH at 3.
8. Add 5 drops of $SnCl_2$ and shake.
9. Wait for 5-6 minutes.

If no blue colour appears, then it may be concluded that the charcoal is free from phosphorous. If blue colour appears, it indicates the presence of excess P in charcoal. Such charcoal is made free from P by the method as follows:

1. Take required amount of charcoal in the beaker.
2. Add 0.5M $NaHCO_3$ (pH 8.5) to submerge the charcoal and stir for 30 minutes.
3. Keep it overnight and decant the $NaHCO_3$ solution next day.
4. Again add 0.5M $NaHCO_3$ (pH 8.5) solution to submerge the charcoal, stir with glass rod, decant the $NaHCO_3$ solution. Repeat the decantation process 6-8 times.

5. Place a whatman No1 filter paper on a buckner funnel and transfer the entire amount of charcoal from the beaker to the buckner funnel.

6. Connect the buckner funnel with a water suction apparatus.

7. Repeatedly leach the charcoal with 0.5M NaHCO$_3$ (pH 8.5) solution.

8. Take about 10ml of the leachate in a 50ml volumetric flask.

9. Follow the procedure to test the presence of P in the leachate by the method as already described.

10. After the charcoal is made free from P, the excess of NaHCO$_3$ solution present in charcoal is removed by leaching the charcoal with P free warm water several times.

11. Dry the charcoal in an oven at low temperature.

Dickman and Brays' reagent in excess of acid: Dissolve 15g of ammonium molybdate (AR grade) in 300ml of warm water (about 60^0C), cool and filter, if turbidity exists. Add to it 400ml g 10N HCl, and make up the volume to 1 litre.

40% Stannous Chloride (Stock solution): Dissolve 10g of SnCl$_2$.2H$_2$O (AR) crystals in 25ml of concentrated HCl. Warm the solution, if necessary to dissolve Stannous Chloride. A watery look of solution indicates SnCl$_2$ solution. Store it in a brown bottle. This is 40% SnCl$_2$ stock solution. Addition of a piece of tin metal (AR), will keep the stock solution for long time.

Stannous Chloride working solution: Dissolve 0.5ml of the 40% SnCl$_2$ stock solution to 66ml with distilled water, Prepare this solution just before use.

Standard P solution: Dissolve accurately 0.439g of Potassium dihydrogen Phosphate (AR), KH$_2$PO$_4$, in about half a liter of distilled water. Add to it 25ml of 7N H$_2$SO$_4$ (approx.) and make up the volume to 1 litre with distilled water. This gives 100ppm stock solution of P.

(6) Other Necessary Reagents

1. 4N NH$_4$OH: Take 27ml of ammonium hydroxide in a 100ml volumetric flask and add distilled water upto 100ml mark.

2. 4N HCl: Take 34.5 ml of concentrated HCl in a 100ml volumetric flask and make the volume to 100ml by adding distilled water.

3. 2,4-dinitrophenol indicator: Take an amount of (app 1g) 2,4, dinitrophenol indicator in abeaker and add approximately 200ml distilled water and stir for sometime. Filter or decant the solution to obtain a clear solution.

4. 7N H$_2$SO$_4$: To 50ml of distilled water pour 19.5ml of concentrated H$_2$SO$_4$

very slowly in a 100ml volumetric flask. Cool and then add distilled water upto 100ml mark.

(7) Procedure for Standard Curve

- Take 9 numbers of 50ml volumetric flasks.
- Take a little volume of distilled water in one flask (blank) and 1, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0 and 20.0 of 2ppm P solution in individual flask. (For 2ppm standard solution of the volume 500ml, 20ml of 50ppm P solution is diluted to 500ml.)
- Add 1-2 drops of 2,4-dinitrophenol in each flask. No colour appears in P solution except yellow colour in distilled water.
- Add 4N NH_4OH drop wise to each solution of P until yellow colour appears.
- Add drop wise 4N HCl to each flask until yellow colour disappears.
- Add 10 ml ammonium molybdate solution to each flask.
- Fill each flask with 20ml of distilled water.
- Add 1ml of $SnCl_2$ working solution to each and gently stir to mix. Fill each flask with distilled water upto 50ml mark. Blue colour appears within 4-5 minutes and the colour intensity remains unchanged for 20 minutes. The flask in which only distilled water was taken instead of P solution doesn't show blue colour. This is blank.
- Place red filter in the colorimeter or set it to 660nm.
- Set zero with blank and take readings of each P solution.
- Complete the work within 20 minutes.
- Find out the concentration of P solution (i.e. ppm of P) in each flask. Plot P concentration on a graph paper on X axis and optical density of each corresponding P solution on Y axis. The graph obtained will be stratight line and it is the standard curve of P.

(8) Procedure of P Estimation

- Take 25g soil in a 250ml conical flask.
- Add 50ml of 0.5M $NaHCO_3$ (pH 8.5) solution with a 50ml bulb type pipette in the flask.
- Add 1-2g of P free charcoal.
- Close tightly the mouth of the flask with a rubber cork and shake for 30 minutes. Filter with a Whatman No 42 filter paper till a colourless filtrate is obtained. (P free charcoal can be added while filtering the extract through

filter paper.)

- Whatman No 1 filter paper may be used, if a clear filtrate is not obtained.
- Take two 50ml volumetric flasks. (For more samples, a maximum of 10 volumetric flasks can be arranged. More than 10 flasks may take more time in colorimetric reading. The colour may be deteriorated after 20 minutes of development.)
- Take 10ml of extract (filtrate) with a 10ml bulb type pipette in one flask and 10ml of distilled water in another flask (blank).
- Adjust their pH to 3 with 2, 4 dinitrophenol, 4N NH$_4$OH and 4N HCl by the method as described earlier for standard curve preparation.
- Add 10ml of ammonium molybdate solution to each flask.
- Add distilled water (about 15ml) so that the total volume of solution becomes about 35ml in each flask.
- Add to each 5 drops of stannous chloride stock solution (For NaHCO$_3$ extract), and shake gently.
- Add distilled water upto 50ml mark to each flask.
- After 5 minutes, set the colorimeter to zero optical density reading using red filter (i.e. 660nm) with blank. Take reading of all samples within 20minutes of SnCl$_2$ addition.
- Put the values of OD in standard curve and find the corresponding P.

(9) Calculation

a. Weight of soil taken = Agm
b. Volume of 0.5M NaHCO3 solution added = Xml
c. First dilution = A/X times
d. Volume of soil extract taken = Bml
e. Final volume following colour development=50ml (Volume of volumetric flask)
f. Second dilution = 50/B times
g. Total dilution = A/X × 50/B times
h. Concentration of P as read from standard curve = S ppm (say)
i. Available P in ppm = S × A/X × 50/B ppm
j. Available P in kg/ha = S × A/X × 50/B × 2.24 kg/ha
k. Available P$_2$O$_5$ in kg/ha = S × A/X × 50/B × 2.24 × 2.29 kg/ha

(10) Interpretation

P (kg/ha)	Rating
<11.2	Low
11.2 - 22.4	Medium
>22.4	High

(11) Precaution

- Always use fresh $SnCl_2$ working solution.

- Before P testing, glasswares should be washed with 6N HCl or Chromic acid followed by washing with tap water and finally dips in distilled water for 24hrs. Washing powder containing P should not be used for cleaning the glass wares.

- After completion of P estimation, the 50 ml volumetric flasks should be washed with tap water at least 4-6 times and then filled with Chromic acid cleaning solution. (16g of $K_2Cr_2O_7$ in about 60ml of hot water + 200ml L.R. grade H_2SO_4 slowly with stirring) and kept overnight. Next day the volumetric flasks should be washed with tap water several times (4-6 times) followed by washing with distilled water at least 3 times.

- If blue colour appears in blank though all reagents are P free, the 50ml volumetric flasks should be washed properly. If blank colour still appears, this may be due to poor quality of Ammonium molybdate reagent.

3.4 Available Potassium

(1) Introduction

The total K content of a soil varies from 0.05 to 2.5 %. The total K is distributed in mineral from (lattice K, 90-98%) fixed non-exchangeable or temporary retrograded K (1-10%), and exchangeable plus water-soluble K (1-2%). Available K in soils is generally the sum of water soluble and exchangeable K which can be readily taken by plants.

Extraction of K with Ammonium acetate (CH_3COONH_4 or NH_4OAc): A solution of neutral (pH 7.0) normal (1N) Ammonium acetate (CH_3COONH_4) is generally used for extracting both water soluble and exchangeable K. This extract contains only water-soluble and exchangeable K. K extraction by this extractant is considered as a suitable index of K availability in most soils, based on crop response correlation study, and, thus, K extract by this method is

equated as the available K.

(2) Principle

The method is based on the principle of equilibrium of soils with an exchangeable cation made of the solution of neutral normal NH_4OAc, in a given soil: solution ratio. During the equilibrium, ammonium ions exchange with the exchangeable K ions of the soil. The K content in the equilibrium solution is estimated with a flame photometer. Since NH_4^+ holds highly charged layers together just as K, the release of the fixed K, in an exchangeable form, is retarded during NH_4OAc extraction.

(3) Reaction

$$\text{Clay} \begin{vmatrix} K \\ K \\ K \\ K \\ K \end{vmatrix} + 5CH_3COONH_4 \leftrightarrow \text{clay} \begin{vmatrix} NH_4 \\ NH_4 \\ NH_4 \\ NH_4 \\ NH_4 \end{vmatrix} + 5CH_3COOK$$
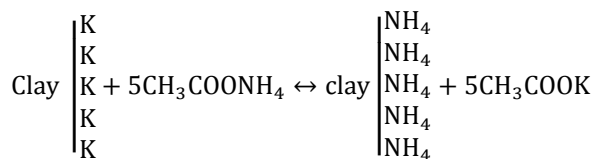
(4) Materials Required

Flame photometer with potassium filter, conical flask, Pipette, Mechanical shaker, Funnel, Filter paper (Whatman No 42 or 1), balance.

(5) Reagent

Neutral 1N Ammonium acetate (1N CH_3COONH_4, pH 7.0): Dissolve 77.08g of solid Ammonium acetate in distilled water and make up to one litre. Adjust its pH to 7.0 with dilute NH_4OH or dilute CH_3COOH with universal indicator or pH paper or glass electrode pH meter.

Standard Potassium (K_2O) solution: Dissolve 1.5829g of AR grade KCl in the flask (if possible dry at 60^0C for 1hr) and make up the volume upto 1000ml. It gives 1000ppm of K solution.

Butyl alcohol: Available in the market.

(6) Preparation of Standard Curve

From the stock solution take measured aliquots and dilute with NH_4OAc solution to give 15 to 50 ppm of K. This can be done using the following formula:

$$S_1V_1 = S_2V_2$$

Here,

S_1 = Final strength of solution (in ppm);

V_1 = Final volume of standard solution to be prepared;

S_2 = Strength of K solution taken (1000ppm here);

V_2 = Volume of K solution (1000ppm) to be taken to make solution of desired strength.

How to prepare desired solution: Example of preparation of aliquots from stock solution is given in Table 1.

Table 1. Preparation aliquots of K solution from 1000ppm stock solution.

S_2 in ppm (Known)	S_1 in ppm (desired)	V_1 in ml (Known)	V_2 in ml (to be taken)
1000	50	50	2.5
1000	40	50	2.0
1000	30	50	1.5
1000	20	50	1.0
1000	15	50	0.5

(7) Procedure

- Take five numbers of 50ml (V_1) volumetric flask.
- The range of standard K solution to be prepared is 15-50ppm (S_1). Now, from the calculations of table 1, take 0.5, 1.0, 1.5, 2.0 and 2.5ml of 1000ppm solution in volumetric flasks.
- Make the volume of each flask to 50ml by adding NH_4OAc solution.
- Take 50ml of NH_4OAc in another 50ml volumetric flask as blank.
- Set up the flame photometer by atomizing blank in 0 and 50 in 100 reading scale.
- Atomize the other solutions and record the readings.
- On a graph paper, plot the readings against the respective ppm. The graph thus drawn will be a straight graph.

(8) Extraction of K_2O

- Take a 250ml conical flask.

- Take accurately 5g of soil sample in the flask.
- Take 25ml of 1N CH_3COONH_4 (pH 7.0) solution in the flask. The soil extracted ratio is 1:5.
- Close tightly the mouth of the flask with a rubber cork.
- Shake the flask for about 30 minutes on the mechanical shaker.
- Filter only through Whatman No 42 filter paper.
- Collect the filter (i.e. soil extract) to estimate K_2O concentration.

(9) Estimation of K_2O

- Add 2 drops of butyl alcohol to the filtrate. It improves spraying properties of the solution.
- Place the K filter in the flame photometer.
- Atomize the filter and record the reading.
- Find the K_2O in ppm by putting the reading in standard curve.

(10) Observation and Calculation

The K_2O content is calculated as follows:

a. Weight of the soil =5g
b. Volume of the neutral 1N NH_4OAc =25g
c. Reading of the flame photometer for the test solution=R (say)
d. Concentration (ppm) as read from the standard curve= c(say)
e. Dilution factor= 25/5= 5 times
f. Now, available K in soil (ppm) = $C \times 5$
g. Available K in soil (kg/ha) = $C \times 5 \times 2.24$
h. Available K_2O in soil (kg/ha) = $C \times 5 \times 2.24 \times 1.20$

(11) Interpretation

Available K	Available K_2O	Comments/rating
<120	<136	Low
120-280	136-337.5	Medium
>280	>337.5	High

(12) Precaution

- See that filtrate is purely clear.

- Maintain the air pressure in flame photometer between 0.4 to 0.6 kg/cm^2. Air pressure must not fluctuate during analyses.

3.5 Soil pH

(1) Principle

The potentiometer determination of pH is based on the measurement of the electrical potential developed by an electrode whose potential depends on the hydrogen ion concentration of the solution. The single electrode potential of any electrode should be measured with the second electrode (reference electrode) dipping into the same solution. Glass electrode is the most convenient among different pH electrodes. The reference electrode commonly used is the saturated calomel type. The pH meter measures the voltage developed by the combination of glass electrode and reference electrode and the scale is graduated in pH units as well as in milivolts. The pH meter is to be calibrated using standard buffer solution.

(2) Materials Required

Balance, Beaker, (100ml/250ml), measuring cylinder, Glass rod, pH meter, Buffer solution (pH 4.0, pH 7.0 and pH 9.2).

(3) Procedure

- Take a 100ml beaker and place 20gm of air dry soil into it.
- Add 50ml distilled water in the beaker (soil:water = 1:25). Stir with a glass rod occasionally for about 30 minutes. If mechanical shaker is available, shake the suspension continuously for 4-5 minutes.
- Make the pH meter ready for pH measurement following the instructional manual.
- Standardize the pH meter at 4.0 by buffer solution. First take 7.0 solution and then 4.0. Repeat the procedure two or three times. Wash the electrode after each immersion with strong stream of distilled water.
- Immerse the glass rod into soil-water suspension in the beaker. Note the reading.
- Wash the electrode immediately after reading.

(4) Interpretation

pH	Interpretation
<6.5	Acidic reaction
6.5-7.5	Normal
>7.5	Alkaline

(5) Comment

- Drying changes the soil pH. For convenience, the air-dried soil samples are used for pH determination. In soil testing report, whether the dried or field-moist samples were used must be mentioned.

- The pH value in soil-water suspension increases with increasing dilution. The soil:water ratio may vary from 1:1, 1.0:2.5, 1:5 and 1:10. Therefore, in soil testing report the ratio of soil:water should also be mentioned.

3.6 Electrical Conductivity of Soil

(1) Principle

The measurement is based on the principle that ions being the carriers of electricity the electrical conductivity of a solution increases with soluble salt concentration. Thus, it is possible to measure electrical conductivity of a soluble salt.

(2) Equipment

Beaker (100ml/250ml), glass rod, Balance, Conductivity meter.

(3) Procedure

- Take 20g of soil in a 100ml beaker.
- Add 50ml of distilled water into it (soil: water =1:2.5).
- Stir with glass rod occasionally for about 30 minutes. If mechanical shaker is available shake for 4-5 minutes.
- Stand the suspension for few minutes (2-3) so that soil particles settle down.
- Use the supernatant liquid to measure conductivity by conductivity meter.

(4) Interpretation

Electrical Conductivity (mmhos/cm)	Interpretation
<0.8	Normal for all crop
0.8-1.6	Critical for salt sensitive crop
1.6-2.5	Critical for salt tolerant crop
>2.5	Injurious to all crop

(5) Comment

- The supernatant solution of soil:water suspension used for pH determination can be used for electrical conductivity measurement.
- Soil: water ratio and type of soil used (air dry/moist) must be mentioned in the report.