Determination of soil reaction

The test for soil reaction or pH is by far the simplest and is commonly made in all soil testing laboratories. It is widely used for estimating the lime needs of soil.

Methods for determining soil reaction may be divided into two classes:

Colorimetric and electrometric. The colorimetric method makes use of suitable dyes or indicators, the colour of which changes in a very definite way with the hydrogen-ion concentration. The results obtained by this method agree within 0.2 pH units with those of the electrometric method. In the electrometric method, the potential of the hydrogen-ion-indicating electrode is measured potentiometrically against another standard electrode. The observed electrometric force of such a cell is a direct function of hydrogen-ion activity of the solution or soil suspension into which the electrodes are immersed.

For the determination of pH of soils in the laboratory, glass-electrode pH meters (Buckman model) are extensively used. It is convenient to use for fairly accurate determination of the small potentials produced at the gas-liquid interface. The soil Reaction Committee of the International Society of Soil Science (1935) recommended the use of glass-electrode pH meter which gives satisfactory values for pH for all soils.
Although glass-electrode generally used for pH measurement employs a special and chemically pure glass membrane, it is normally necessary to standardise the instrument before use. This is done by adjusting the controls until the correct readings are obtained for two buffer solutions of known pH-values. Once the instrument is adjusted it may be used for two to three hours for continuous use.

Hydrogen-ion concentration or pH varies considerably with changes in the soil-water ratio. Since the pH value determined with 1:5 soil-water ratio does not differ greatly from that at 1:1 ratio, the author has maintained 1:5 soil-water ratio in the determination of pH of the soil samples of the study area.
Determination of organic matter

For its complex nature numerous difficulties beset the accurate determination of the soil organic matter. Estimation of organic matter content based on loss on ignition does not give an accurate value since it includes water of hydration of the clay fraction. In Robinson's method, the soil is treated with 15% H₂O₂, washed, dried and weighed (Robinson, W.O., 1927). The organic matter is destroyed or rendered soluble by this treatment, and hence the difference between the dry weight of the soil and that of the dried residue represents the organic matter content of the soil. By this method, elementary carbon is slightly attacked. This method, therefore, gives a good measure of organic matter in those soils for which it is applicable.

Because of its limitations of direct methods, organic matter is more commonly estimated indirectly from organic carbon which is determined very accurately by dry or wet combustion methods. The amount of organic matter is then obtained by multiplying the organic carbon by the conventional factor 1.72, which is based on the assumption that the soil organic matter contains 53% carbon.

The dry combustion method gives a very accurate determination of carbon but the method includes all elementary carbon. This is a tedious, more expensive and time consuming method.
For this reason, simpler and more rapid methods based on oxidation of soil organic matter with a mixture of potassium dichromate and sulphuric acid and subsequent titration of the unreduced dichromate serves the purpose well. In such methods the advantage lies in their incomplete attack on elemental carbon, such as charcoal and graphite which may be present in appreciable amount in some soils and which correctly should not be included with soil organic matter.

The Walkley-Black's method (1934) further modified by Walkley (1947) is of course simple and the results are fairly accurate. Chronic acid method based on spontaneous heating by dilution of H$_2$SO$_4$ involves essentially the same procedure as Schollenberger (1927) except that the heating is less than externally supplied. So somewhat less of the total organic matter is oxidised. The author, therefore, prefers the Schollenberger's method with applied heat, for it gives a higher recovery of carbon compared to Walkley-Black (96% recovery against 77% for Walkley-Black).

Detailed Procedure:

Reagents -

1) N/2 K$_2$Cr$_2$O$_7$ (24.5175 gms. of K$_2$Cr$_2$O$_7$ per litre)  
2) N/2 Fe$_2$SO$_4$ (NH$_4$)$_2$SO$_4$, 6H$_2$O (196.06 gms. of pure salt per litre)  
3) 0.5% Diphenylamine in conc. H$_2$SO$_4$.  
4) Conc. H$_2$SO$_4$ (Fresh stock)  
5) Conc. H$_3$PO$_4$.

Method:

0.3 gm. (for top soil) or 0.6 gm. (for bottom soil) of finely powdered soil are taken in a 250 ml. 'Pyrex' conical flask, 20 ml. N/2 K$_2$Cr$_2$O$_7$ soln. and
20 ml. conc. $\text{H}_2\text{SO}_4$ are added. The flask is gently shaken for half a minute and then heated on a hot plate or Bunsen burner in such a way that a temperature of 175°C is reached in about 5 minutes. The temperature of the digest is kept constant at 175°C for 10 minutes (A thermometer is used for correct temperature regulation). After heating for 10 minutes the flask is cooled under the tap and 100 ml. of distilled water added. The flask is cooled again. 10 ml. $\text{H}_3\text{PO}_4$ and 20 ml. $\text{N/2}$ Ferrous ammon-sulphate soln. are added. The quantity of ferrous-ammon sulphate soln. is so adjusted that it is in excess of dichromate soln. present in the flask after digestion. A few drops of diphenylamine indicator are added, and excess of ferrous salt is titrated back with the standard $\text{K}_2\text{Cr}_2\text{O}_7$ soln. The end point of titration is indicated by a very sharp change from green to deep violet blue colour.

Knowing the exact amount of dichromate reduced, the organic carbon present in the soil is calculated on the basis of $1$ ml. $\text{N K}_2\text{Cr}_2\text{O}_7 = 3$ mgm. of organic carbon. Assuming that the peat contains 58% organic carbon, the percentage of organic matter present = 1.724.

Calculations of results:

1 ml. of N. Potassium dichromate is equivalent to 3 mgm. of carbon. The amount of carbon oxidised, expressed as percentage of soil, is therefore given by the expression:

$$\frac{V_1 - V_2}{W} \times 0.003 \times 100$$

where $V_1$ = the volume of $\text{N K}_2\text{Cr}_2\text{O}_7$, $V_2$ = the volume of Normal Ferrous ammon-sulphate (in ml.), and $W$ = weight of the soil taken.

The result is multiplied by 1.72 to get the percentage of organic matter in the soil.
APPENDIX - A3

Determination of soil nitrogen

In most soils the great bulk of the nitrogen is in the form of ammonium compounds and their organic derivatives and it may without appreciable error be estimated by the standard Kjeldahl technique (Piper, 1950; Jackson, 1958). In this method organic matter is destroyed by oxidation with hot strong sulphuric acid with a catalyst, so that all tricovalent nitrogen is converted into ammonium sulphate.

Anhydrous sodium or potassium sulphates are added to raise the temperature and a catalyst used to speed the oxidation. Amongst the catalysts mercury and copper are frequently employed but Selenium or a mixture of selenium and mercury is more efficient in shortening the digestion period. In the latter case, it is necessary to add a reagent to precipitate mercury before distilling the ammonia otherwise the ammonia is retained as a stable mercury ammine co-ordination complex. Piper (1950) recommends Fal's procedure of preliminary moistening of the soil with water specially on heavier soils to ensure release of all nitrogen from the clay aggregates.

When nitrogen is fully converted into ammonium sulphate, it is heated with excess of 40% caustic soda solution to give off nitrogen which is then absorbed in a standard sulphuric acid solution. Finally the amount nitrogen present in the soil is calculated, from the fact that 1 ml. of normal sulphuric acid when acted with ammonia will contain 0.014008 gm. of nitrogen.
Method:

10 gms. of soil is taken in a Kjeldahl flask and 20 ml. conc. H₂SO₄ is added to it. Then the flask is heated gently for 10 minutes and after that 2.5 gms. of sodium sulphate and a small amount of CuSO₄ are added to the flask. The whole content is strongly heated for 2-3 hours till the contents of the flask attains gray colour. The flask is cooled and 200 ml. of distilled water is added to the flask. The supernatant liquid is then transferred to a distilling flask, care being taken to keep as much solid particles in the Kjeldahl flask.

Then 40% strong NaOH is added to the distilling flask, and it is heated. Ammonia is collected in 50 ml. N. H₂SO₄ with a drop of methyl orange in the conical flask (the flask is cooled in cold water) when no more ammonia evolves (Nestler's reagent test), the contents of the conical flask is titrated against N.NaOH. At the end point it will turn from pink to yellow.
APPENDIX - A

Determination of citric soluble phosphorus

Part-I: Preparation of a calibration curve showing the relationship between phosphorus concentration and deflection (optical density) on the Eel Absorption meter.

Part-II: Extraction of available phosphorus from soil with 1% citric acid followed by colorimetric determination (University of Nottingham, 1954):

Part-I

In this determination, phosphorus is estimated colorimetrically by means of an Eel absorption meter and the principle on which this instrument operates is as follows: coloured substance in solution absorb light in parts of the spectrum, the extent of absorption being proportional to the concentration of coloured material. Such substances are said to obey "Beer's Law" which may be expressed as:

\[ l_t = l_0 e^{-kct} \]

Where \( l_0 \) = intensity of unabsorbed light and \( l_t \) = intensity of transmitted light after passing through \( t \) cm. thickness of solution of concentration \( c \), it is more convenient to express the relationship as \( \log l_0/l_t = K'tc \) = optical density.

Such an equation enables the concentration of coloured substance to be determined by means of its absorptive properties, or, by comparing the unknown colorimetrically against a standard, the relative concentrations may be found. Such methods are only justified if Beer's Law is obeyed, i.e. if
plotting \( \log \frac{l_0}{l_t} \) against \( c \) gives a straight line. It is, therefore, necessary to prepare a calibration curve showing relationship between \( \log \frac{l_0}{l_t} \) and concentration, a series of standard solutions is prepared under the same conditions as those to be employed for unknown. Their optical densities are measured, and plotted against concentration.

**Preparation of a calibration curve from standard phosphate solution.**

In acid solution low concentration of phosphate react with excess of molybdate to give a phospho-molybdate complex which may be reduced (with stannous chloride in this case) to produce intense blue colour proportional to the phosphate concentration.

**Re-agents:**

1. **Standard phosphate solution:** 3.834 gm. dried A.R. potassium dihydrogen phosphate, \( \text{KH}_2\text{PO}_4 \), per litre. For actual use this solution is diluted 20 times so that 1 ml. of the diluted solution is equivalent to 0.1 mg. \( \text{P}_2\text{O}_5 \).

2. **Stannous chloride:** 20 gm. of solid dissolved in 50 ml. Conc. HCl. The dilute solution (6 drops of this in 25 ml. water) should be freshly prepared.

3. **Molybdic acid:** 20 gms. of A.R. ammonium molybdate dissolved in 100 ml. of water. 600 ml. \( \text{H}_2\text{SO}_4 \) (275 ml. Conc. \( \text{H}_2\text{SO}_4 \) in the 600 ml.) is cooled, added and made up to the litre. 75 ml. of this made up 1 litre gives the working solution.

4. **2 : 4 dinitro phenol solution:** 0.5 gm. solid dissolved in 40 ml. N/10 NaOH and made up to the litre with distilled water.
Calibration curve from standard phosphate solution:

Into 100 ml. graduated flasks the following amounts of phosphate solutions are placed.

<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>Phosphate Amount (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>3.0</td>
<td>0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>0.4</td>
</tr>
<tr>
<td>5.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

To each is added approx. 10 ml. N. H₂SO₄ and made up to 70 ml. 3 drops of dinitro-phenol indicator are added and it is made just alkaline with 8% ammonia solution, and finally acid with 1.0 ml. 5N.H₂SO₄. It is made up to the mark with distilled water and thoroughly mixed.

5.0 ml. of the standard is pipetted into the test tube and to this 5.0 ml. of the molybdic acid solution is added. 5 drops of the diluted stannous chloride solution are added, the tube is shaken and allowed to stand for 10 minutes for full colour to develop.

With a red OR I filter in the Bécl absorption meter, and using distilled water in the test tube, the micrometer reading is brought over to zero and the instrument is allowed to stabilize for two or three minutes; the pointer is again brought to the zero mark, and the test tube containing the water is removed and replaced by another containing a standard; the meter reading is noted, and the test test tube containing distilled water then replaced to verify that the
reading returning to zero, indicating stable operating conditions. Readings for remaining standards are taken and the concentration of $P_2O_5$ in each sample against the corresponding optical density is plotted.

**Part-II.** Extraction of phosphorus from soil.

About 10 gms. of air-dry soil sample is weighed into a shaking bottle (1/2 pint) and 100 ml. of 1% citric acid solution is added to it. It was shaken for 12-24 hours. The solution is then filtered and 30 ml. solution was placed into a 50 ml. evaporating basin. The solution is evaporated to dryness on a sand bath and ignited at 600°C to destroy organic matter. When cooled 10 ml. of approx. $NH_2SO_4$ is added and gently boiled for 10 minutes to reconvert pyrophosphates formed by ignition into orthophosphate.

The solution is then filtered through a smaller filter paper (Whatman 29 cm. m) into 100 ml. graduated flask and washed with distilled water until the combined volume of filtrate and washing is not greater than about 70 ml. 3 drops of indicator (dinitrophenol) are added and it is just made alkaline with 3% ammonia and finally acid with 1 ml. 5N. $H_2SO_4$. It is then made up to the mark with distilled water.

**Determination of Phosphorus:**

After the extract was made upto 100 ml., a 5 ml. portion is pipetted into the absorptionmeter tube and the colour developed in the same way as used for phosphorus standard.

The Eel absorptionmeter is used to measure the colour intensity and by interpolation from the calibration curve the phosphorus concentrations is determined. From the weight of the soil used and the dilution employed the result is calculated as % of $P_2O_5$ (citric acid soluble).
APPENDIX - A

Determination of potassium (as dipotassium sodium cobaltinitrate)

10 ml. extract of soil (citric soluble) is taken, 1 ml. of N. Nitric acid and a solution of 1 g. of A.R. sodium cobaltinitrate in 5 ml. of water are added to the soil extract. It is then thoroughly mixed allowed to stand for 2 hours.

The solution is then filtered through a weighed sintered glass or porous porcelain filter crucible and the ppt. is transferred completely with the aid of 0.01 N. nitric acid. (It is washed ten times with 2 ml. of 0.01 N. nitric acid and 5 times with 2 ml. portion of 95% ethyl alcohol).

The ppt. is washed into 250 ml. beaker, the crucible is placed in it and diluted to 100 ml. with water.

20 ml. of N. sodium hydroxide solution was added and boiled for three minutes.

A slight excess of standard 0.05 N. (about 20 cc.) potassium permanganate solution is placed into another beaker, diluted to 50 ml. with water and then 5 ml. of conc. sulphuric acid is added to it.

The hot potassium cobaltinitrate solution is poured into the cold potassium permanganate solution. The crucible is also transferred and the beaker is washed with a small amount of water.

* Jackson (1958), Vogel (1951), Wright (1934).
An excess of standard 0.05 N sodium oxolate solution is added and the titration is completed with standard potassium permagnate solution. From which it may be followed that:

\[ \text{ml. of } \text{KMnO}_4 \times \text{normality of } \text{KMnO}_4 \times 7.1084 = 2 \text{ mg of } K. \]
Mechanical analysis of soil

Although many methods and modifications have been proposed for the mechanical analysis of soil, the author has adopted here the principles recommended by the International Society of Soil Science (Wright, 1934; Piper, 1950). The standardization effected by the International Society of Soil Science has been a great value in efforts to secure uniformity in the methods of mechanical analysis of soils.

The method consists in boiling a measured amount of air dry soil sample with hydrogen peroxide to destroy humus, treatment with dilute hydrochloric acid and washing to remove carbonate and bases combined with clay and humus and final dispersion by shaking with normal sodium-hydroxide. Dispersion having been effected by preliminary treatment, the coarsest fraction, namely that consisting of particles between 0.2 mm and 2.0 mm in diameter separated by means of seiving, usually a 70-mesh brass wire cloth sieve whose apertures are slightly less than 0.2 mm square.

The finer fractions are determined by the application of the principle enumerated in Stocke's Law*, namely, that the limiting velocity of a particle

\[ V = \frac{2 g r^2}{n (D - d)} \]

Where, \( V \) = Velocity of sedimentation; \( g \) = Acceleration due to gravity; \( r \) = Radius of the spherical particles; \( D \) = Density of spherical particles; \( d \) = Density of the fluid; \( n \) = Coefficient of viscosity of the fluid.

* Stocke's Law
falling in a fluid is proportional to its diameter. The separation can
be effected by taking a measured amount of the soil suspension by an automatic
or ordinary pipette choosing approximately setting time and depths for 'clay'
and 'silt and clay'. Finally fine sand is recovered by repeated washing and
decantation of the soil suspension.

Procedure in detail (International Method):  

1. An air dry soil sample, measuring 10 gms, is taken in a 600 ml.
beaker and boiled with 50 ml. of 6% H$_2$O$_2$ as originally proposed by Robinson to
destroy organic matter and the volume is made 30 ml.

2. The contents of the beaker is then sieved through 1 mm. 70 mesh
brass wire sieve, washed with a jet of hot water. The coarse sand in the sieve
is dried at 105° - 110°C, carefully removed from the sieve and weighed, the
result is expressed in the percentage of the total weight of the sample taken.

3. After the peroxide treatment, the soil is treated with 20 cc.
HCl to remove the calcium carbonate or gypsum, if present. The material is
then filtered through Buchner's funnel connected with a pump, and the soil
standing on the funnel is washed three times with 25- 30 ml. of distilled water.
Washing with 10% ammon. acetate followed by two 25 ml. washing with distilled
water should be made.

4. The acid filtrate is then treated with little HNO$_3$ to oxidize
the ferrous compound, and after concentrating the solution to 100 ml., excess
of ammonia is added. The precipitation is ignited in a nickel crucible, cooled
and carefully weighed giving the percentage of lose by solution which is not
usually more than 1- 2%.
The residue is then transferred to a shaking bottle and to which 4 ml. N.Na(OH) is added and the bottle is shaken for 5-6 hours in a mechanical shaker for a complete dispersion of the soil particles. The content is then transferred to a 500 ml. tall cylinder, made up to the mark, shaken for one minute with repeated inversion and allowed to stand away from the source of heat and direct sun light.

After standing for 4 min. 48 sec. at 20°C or equivalent time at any other temperatures, 20 cc. pipette sampling is carried out at a depth of 10 cm. The sampling is collected in a weighed porcelain dish dried to a constant weight at 105-110°C. The weight of the dried residue in milligram divided by 4 is the percentage of silt and clay.

The suspension is then thoroughly shaken and allowed to settle for 8 hours at 20°C, or corresponding time at any other temperature, for clay sampling which is carried out at a depth of 10 cm. The weight of the dry residue in milligram divided by 4 is the percentage of clay. This figure is subtracted from the percentage of silt and clay to obtain the percentage of silt.

After this, the greater part of the suspension is poured away and the sediment is washed with distilled water, decanted after allowing to stand for 4 min. 48 sec. at 20°C (or corresponding time at any other temperature) for several times. The clean fine sand standing with water is then dried and weighed for percentage of fine sand. Finally the results are expressed in percentages as the following:

5. Loss on solution; 6. Organic matter*

* Percentages of organic matter and moisture present in the soil are calculated from the results obtained in separate procedures (Appendix-A, Page 91).