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SOIL PHOSPHORUS AND ITS DETERMINATION: AN OVERVIEW

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Phosphorus (P) is an essential macro-element for optimum plant growth. It is present abundantly in the growing and storage organ of plants such as fruits and seeds. It promotes healthy root growths , fruit ripening by helping translocation and also increase in carbohydrate concentration. Compounds containing P e.g. ATP, ADP etc. play and important role in energy transfer reactions in different biological processes. Again deficiency of phorphorus$_2$ exhibits the following syndroms in plants:

1. Cambial activity is retarded.
2. Tillering of crop plants are reduced.
3. Dormancy period may be prolonged.
4. Crop production is reduced.

As plants absorb phorphorus from soils throguh roots, therefore, a knowledge of soil-P status is very important to ascertain the fertility of soil based on which management practice for P-fertilization can be formulated.

Determination of P-Basic principle:

Phosphorus is estimated as phosphates (PO_4^{-3}) that form a twelve-fold heteropolyacids with molybdate in acid medium. The Leteropolyacids are yellow in colour and can be precipitated out as ammoniumphos-phomolybdate by the following reaction:

$$H_3PO_4 + (NH_4)_2MoO_4 + HNO_3 \Rightarrow (NH_4)_3PO_4, Mo_{12}O_{36}\,ppt\downarrow + NH_4NO_3$$

This precipitation is then filtered through a gooch crucible and can be determined gravimentrically. Again the same ppt. can be dissolved in a known amount of standard base and the excess base can be back titrated by standard acid. A blank titration of known amount of base can be run. The difference of the two will give us the amount of P present in the solution.

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Calculation: 1ml of (N) NaOH = .001348g P

When phorphorus is present in very minute amount, the above methods will not hold good. phorphorus can be determined by spectro-photometric methods. The yellow solution of hetero-polyacid ($H_3PO_{12}O_{40}$) can be reduced by a suitable reducing agent when a blue color (moly-bdenum blue) appeared. The optical density or absorbity of this colour can be estimated spectro-metrically at 831 or 660nm and can be matched with a known standard curve of P for quantitative estimation. Sometime presence of As^{+5}, Si^{+4}, B^{+3}, F^{-1} may interfere for correct estimation of P. Suitable musking agent may be used to mask these ions before estimating phorphorus. Depending upon the reducing agents, nature of acid used etc. different spectrophoto-metric methods (SPM) have been employed for estimating phorphorus. The details are given in Table - 1.

The estimation of soil-P received extensive study in two lines:

a. Estimation of more active or available P.

b. Fractionation of the total of each chemical class or species of phosphate.

Estimation of available soil-P

The term available P of soil refers to that fraction of the soil phosphorus which remain in soil-solution phase and can be correlated with field response of crops. The P absorbed by plants from soil solution usually exists as inorganic orthophosphate ions viz., $H_2PO_4^{-1}$, HPO_4^{-2} and PO_4^{-3}. The most accessible ion is $H_2PO_4^{-1}$ followed by HPO_4^{-2}.

Importance:

- The available P is considered to be a fairly good indicator of the P-supplying capacity of soil.
- A knowledge of available P helps to determine its critical limit.
- The critical limit of soil phorphorus will help in predicting crop response to the applied phorphorus.

In soil testing work, the available soil-P can be determined by employing

Table -1

Sl.No.	Reductant	Acid medium	Acid normality with H_2SO_4	Colour	Sensitivity	Remarks
SPM -I	$SnCl_2$	H_2SO_4	~0.4N	Blue	High	High accuracy
SPM-II	$SnCl_2$	HCl	~0.7N	Blue	Medium	Suitable for chloride containing system
SPM-III	Mo	H_2SO_4	~0.4N	Blue	Medium	Eliminate the interference due to Arsenic
SPM-IV	1-amino-2-hydroxyna-pthalene-4-sulphonic acid	H_2SO_4 or $HClO_4$	~0.9N	Blue	Less	Eliminates the interference due to high Fe^{+3}
SPM-V	Vanadium (V)	HNO_3	----	Yellow	Least	Eliminates the interference due to all interfering ions.

suitable reagents, spccified soil to solution ratio, time of shaking and nature of soil used. For routine soil testing and soil fertility evaluation programme, the two most common methods, which are usually used, are described below:

Bray's method (Bray and Kurtz, 1945)

The method is usually employed for moderately to strong acidic soil. The soil is shaken with an extracting solution of 0.03 N NH_4F in 0.025N HCl which dissolves the fractions of phorphorus that are considered to be available to plant roots. Ammonium fluoride react with Al and Fe ions in acid medium with the consequent release of P, held by soil, by these trivalent ions.

$NH_4F + HF + AlPO_4 \Rightarrow H_3PO_4 + (NH_4)_3 AlF_6$

$NH4F + HF + FePO4 \Rightarrow H_3PO_4 + (NH4)_3 FeF_6$

$AlPO_4$ and $FePO_4$ represent various hydrated and hydroxyl phosphates of Al and Fe and oxides of Fe. In the filtered extract, P is estimated spectrophotometrically (SPM-II) by adding ammonium molybdate solution followed by reducing the phosphomolybdenum complex by stannous chloride. The heteropoly complexes (phosphomolybdates) are formed by co-ordinating atom, the oxygen of the molybdate radicals being substituted for that of PO_4.

The heteropoly complexes, before reductions, give a yellow hue to their water solution. In the solution of low P concentrations, the phosphomolybdenum complex is partially reduced to produce a characteristics blue colour, the intensity of the colour is a measure of concentration of P in the test solution. To extract more P from soil apatite in netural or calcareous soils or from rock phosphate additions, a higher concentration of HCl (0.1N) is needed. This is commonly known as Bray's II method for P-estimation.

Olsen's Method (Olsen et al., 1954)

This method is useful for neutral, alkaline, calcareous and slightly acidic soils. The soil is shaken with 0.5 M $NaHCO_3$, at a pH of 8.5 in 1:20 soil-solution ratio, for half an hour. Active charcoal or Darco-G60 is used to get a clear solution by dispersing organic matter. Phosphorus is then allowed to react with ammonium molybdate to form a heteropoly complex, which on reductions by $SnCl_2$ produces the characteristics blue colour (molybdenum blue). The intensity of the blue colour so obtained is proportional to the quantity of P present in the solution.

$Ca_3 (PO_4)_2 + NaHCO_3 \Rightarrow CaCO_3 + H_3PO_4 + Na_2CO_3.$

$(NH_4)_6 Mo_7 O_{24}, 4H_2O + 6HCl \Rightarrow 7H_2 Mo O_4 + NH_4Cl.$

$H_3PO_4 + H_2MoO_4 \Rightarrow H_3P (Mo_3 O_{10})_4 + 12 H_2O.$

Phosphomolybdenum complex + $SnCl_2 \Rightarrow$ Molybdenum blue

Inference

By measuring available P from soils, we can infer the following points :

P-content (ppm) (SPM-I)	Crop Responses	P-content (ppm) (SPM-II)
<5	Very low	<3
5-15	Low	3-7
15-25	Medium	7-20
>25	Adequately high	>20

Fractionation of Soil-P

Total inorganic P is divided in two forms viz. active and inactive. Al-P, Fe-P and Ca-P constitute active form and occluded, recductant

Table . 2. Scheme for fractional analysis of soil-P

<table>
<tr><td colspan="8">5 gms soil sample in 50 ml 1(N) NH_4Cl ⇒ Shaked for 30 minutes & filter</td></tr>
<tr><td rowspan="6">Filtrate (Highly soluble P can be estimated by SPM-II)</td><td colspan="7">Residue + 50 ml 0.5(N) neutral NH_4F - shaked for 1 hour and filter</td></tr>
<tr><td rowspan="5">Filtrate
(P for Al-P can be estimate through SPM-II)</td><td colspan="6">Residue is washed with saturated NaCl (thrice) solution and shaked with 50 ml 0.1 (N) NaOH for 6 hours and filter.</td></tr>
<tr><td colspan="2">Filtrate + conc. H_2SO_4 floccualte the OM & Filter</td><td colspan="4">Residue is washed with saturated (twice) NaCl solution then 20 ml 0.5 (N) H_2SO_4 is added and shaked and filter</td></tr>
<tr><td rowspan="3">Residue -Discard</td><td rowspan="3">Filtrate
P from Fe-P can be estimated by SPM-I</td><td rowspan="3">Filtrate
P from Ca -P can be determined by SPM -I</td><td colspan="3">Residue is washed with saturated NaCl solution Then 40 ml 0.3(N) Sodium Citrate, 5 ml (1N) $NaHCO_3$ and 1g Na_2SO_4 is added and heated to 80 °C for 15m in water bath & filter.</td></tr>
<tr><td rowspan="2">Filtrate
P for occluded Fe-P can be estimated by SPM-I</td><td colspan="2">Residue + 50 ml 0.5 (N) neutral NH_4F and shaked for 1 hour and filter.</td></tr>
<tr><td>Filtrate
P can be estimated for occluded Al-P by SPM-II</td><td>Residue - Discard</td></tr>
</table>

soluble and residual P from inactive-P. The active forms are usually considered as main source of available P for plants because when fertilizer are added to soil react with soil components and get transformed into Fe-P, Al-P and Ca-P. So, the availability of P thus largely dependent upon the amount of P-fractions presents in the soils. Again analysis of inorganic-P fractions are helpful in the field of soil genesis, soil chemistry and fertility. The fractionation procedures are based on the differential solubility of various inorganic-P in various extractants. A schematic assay of soil-P fractionation are presented Table II.

Some other important soil phorphorus parameters can be determined by following methods.

A. Total P in soil:

Total P in the soil can be determined by fusing with Na_2CO_3 and NaOH mixture and extracting with water. The SPM-I is applied for estimating phosphorus.

B. Total soluble Inorganic P:

Soil samples $\xrightarrow[\text{0.1 (N) HCl}]{\text{50 ml}}$ shaked for 30 minutes $\xrightarrow[NH_4F]{\text{1gm}}$ shaked for 1 hour and filter -- SPM-II is employed in presence of H_3BO_3 to eliminate the interference of F by complexing it as BF_4

C. Total soluble P in soil :

A known weight of soil sample is warmed with 15 ml 30% H_2O_2 in water bath. Then 15-ml water and 10 ml 0.5 (N) HCl is added to make whole solution to the capacity of 50 ml. Then 1 gm NH_4 is added and shaked for 30 minutes and filter. The filtrate is used for estimating soluble P (SPM-II is employed in presence of H_3BO_3).

D. A-C = Total insoluble P

E. C-B - Total soluble organic P

F. Saloid Phosphorus (SP)

This can be determined by extracting 0.5 gm of sieved soil with 25 ml 1(N) NH_4Cl for 30 mints. Phosphorus in the solution is then determined spectrophotometrically using ascorbic acid as reductant.

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