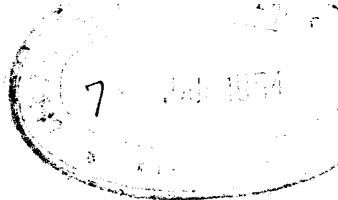


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RECENT WORK ON THE CHEMICAL DETERMINATION OF READILY SOLUBLE PHOSPHORUS IN SOIL. PART I

This account is for the most part limited to work published since Behrens (1937, 1940) reviewed about 180 papers dating between 1935 and 1940 on the chemical, biological and mixed methods of determining P and K requirements. The present section covers work relating to extractions in which only one solvent solution is used and papers comparing these methods of extraction. Sections on extraction methods for carbonate soils and organic P will appear in part 2, in the next issue of *Soils and Fertilizers*. This second part will deal mainly with fractionation methods, in which several extractions with different solvents are made, with methods of determining the quantities extracted, interference by various ions etc.

Methods of extraction

Water, H_2CO_3 and similar extractants find considerable use. Blenkinsop (1938) discusses the use of water extraction for advisory purposes in the rather special conditions of south-west England. McGeorge (1939) in south-west Arizona, where soil P is readily soluble near or just below the neutral point, reported that the small variations in the soil:solvent ratio likely to occur in field methods could greatly affect the amount of P extracted, the errors being greater with acetate buffer than with CO_2 solution. In the laboratory, CO_2 gave useful correlations with field response. With peat soils in Florida, Forsee (1945) found it necessary to use a soil: water ratio of 5 or 10 : 100 because of the excessive amounts of organic matter which interfered with Mo-blue colour development. At such ratios, distilled water extracted as efficiently as CO_2 . Bingham (1949) from correlations of the response of pasture, field and market-garden crops with the P_2O_5 content of filtered and centrifuged aqueous extracts of a great number of

Californian soils (soil:water ratio 1 : 10) concludes that on soils whose filtrates contain less than 0.30 p.p.m. or more than 0.50 p.p.m. these crops would respectively be likely and unlikely to respond to P. Mention may be made of the older work of Dobresco and Russev (1937) in Rumania, who used a ratio of 1 : 60 (a) without adding P and (b) after adding 8 mg. of P_2O_5 as $Ca(H_2PO_4)_2$ to 100 g. of soil. The effect of fertilizing should be insignificant, perceptible and effective respectively if the increase of water-soluble P in (b) is less than 20 per cent, 20-30 per cent and more than 30 per cent of that found in (a).

Mineral-acid extractants appear to be favoured for the highly buffered silt loams and clays of the Middle West of the U.S. Thus, for rapid tests, Baver and Bruner (1939) reported that 0.3 n. HCl gave results very like those of the detailed Truog laboratory analysis, the two methods placing 80 per cent of the samples into the same group. Olson (1946), using 0.7 n. HCl mixed with NH_4 molybdate on various soils in Georgia, found good agreement with the Truog method. Correlation between cotton response and acid-soluble P was erratic, but response of maize, lespedeza and groundnut showed a better correlation. Peech, Alexander *et al.* (1947) record the attempt of a number of U.S. Experiment Stations and the U.S. Department of Agriculture to develop a standardized set of methods to enable workers in one State to compare work directly with that of other States confronted with the same problem. For P, Truog's method is used, somewhat modified (a ratio of 1 : 100 is used instead of 1 : 200 because a modification of Zinzadze's Mo-blue method is used, which is rather less sensitive than Truog's $SnCl_2$ method). It is recognized that

other chemical methods are "capable of giving an equally satisfactory evaluation of P status" and that some of the methods adopted would be less satisfactory on calcareous or alkaline soils. Smith (1939) used dilute HCl in a survey of P requirements in the east of Scotland. In Natal, Beater (1949) extracted air-dry soils (1 : 10 for normal soils) for 30 seconds at 30°C. with N/21 H₂SO₄ containing about 0.36 g. of Na borate per litre at a pH of 1.5. Results were highly correlated with those of the 1% citric-acid method. Beater gives tentative ranges and symbols for readily soluble P in lb./acre and for the fixation rate in lb./acre on these soils. Schollenberger (1947) in investigations of arsenate displacement of phosphate, considers that extraction by arsenate may provide a method to supplement others designed for attack on a definite fraction of the P content of soil. The displacement can be carried out at any desired pH over a range wider than that natural to soils, with less tendency to re-adsorption or precipitation of P than with dilute acid extractions and with less organic P entering solution than when alkaline solvents are used. Bondorff (1950), whose method utilizing dilute HNO₃ at a final pH of 2.5 has hitherto formed the basis for advisory work in Denmark, reports that the HNO₃ method is now replaced by one using 0.2 n. H₂SO₄. The new P values are strongly correlated with the old, but the new method offers analytical advantages.

There are many references to the use of organic acids, often buffered with the sodium or other salt. Brown (1940) uses an extraction with two ratios of sodium-acetate buffer (5 : 1 and 10 : 1). From the results it is possible to grade the soils very satisfactorily as to their P status and the probable response of sugar beet to P fertilizers. Fyn (1941) in Uruguay recommended as a quick test for Ca and P that 100 g. of soil should be treated with 100 c.c. of acetic acid (10% of glacial acid by volume) for 12-15 hours, P to be determined by a Mo-blue method. He found a correlation of 0.926 with the common methods. Ghani (1943), working with 22 soils from different parts of India, found a marked increase of phosphate solubility through the admixture, which he recommends for acid soils containing much active sesquioxide, of 8-hydroxyquinoline in

the acetic acid used as extractant. As the pH rises to neutrality, the effect of this admixed substance vanishes. Lemmermann and Rauterberg (1949) often found less P₂O₅ in 1 % acetic-acid extracts after 24 hours than after 1½ hours. Reversion of this sort, possibly due to the presence of Ca, Fe etc., detracts somewhat from the usefulness of this acid in determining the fertilizer needs of soils. They observed, however, that results with acetic acid agreed much more closely with those of field experiments than did those with the citric-acid method. Peech and English (1944) present a test making use of Morgan's solution, and of activated C to remove organic matter. The determination is colorimetric after reduction of the phosphomolybdate with stannous oxalate. If, as with very calcareous soils, the pH of the extract is above 5.8, it is adjusted to 4.8 with HCl. Dames (1949) notes that 2% citric acid is in general use in Java today. In Kenya, according to Jones (1949), 0.5 n. NaOH is now preferred to citric acid, which on fertile red soils showed only little available P.

Egnér's (1941) lactate method, using Ca lactate and HCl at pH 3.5 as extractant, has been the subject of numerous studies, mainly in Germany, where it has now, in Riehm's modification using twice Egnér's concentration, become the standard method for advisory purposes. Ermolev (1939), in Russia, found that Egnér's determinations agreed with those obtained with the Mitscherlich method. Várallyay (1940) recommended this method for determining the small changes in soil P occurring on fertilizing (or even those changes in soil P that follow biological decomposition). For advisory purposes he suggested allowing 5 g. of soil (or more if insoluble P fertilizers are used) to stand 48 hours with a solution containing 0.1 mg. of P₂O₅, and determining P by Egnér's method on the treated soil and on a control. Okác (1943) studied the effects of shaking. 1 and 3 hours' machine shaking (40 r.p.m.) gave similar results, but occasional hand shaking even up to 20 hours gave low results. Rheinwald and Constantin (1939) described a systematized serial method for large numbers of analyses. It is a conveyor-belt type of team process by which, it is claimed, 400 P determinations per day can be made by 3 workers and 2 manual assistants, or 800 with a second shaking machine and

2 or 3 extra personnel. Riehm (1944) summarized 27 papers on the lactate method which, he stresses, deserves to be regarded as a universal method, valid for non-calcareous, calcareous and strongly organic soils. Behr (1949) maintains that the applicability of the Egnér-Riehm (double-lactate) method depends more on the size than on the content of the CaCO_3 particles. In the first minutes of shaking calcareous soils with lactate much P_2O_5 dissolved, but was mostly re-precipitated as neutrality was approached. Some soils with more than 5% of CaCO_3 give double-lactate extracts which remain acid, e.g. extracts of the finer separates of shell-lime soils remained very acid (pH 4.2), and the P_2O_5 values obtained were always higher than those from the whole soils giving extracts of final neutral reaction. Such a separation procedure (rubbing in water and decanting) may hold promise of extending the applicability of the method to highly calcareous soils. Lederle (1947) comparing the solution of P from various sources in (a) the lactate and (b) seedling tests found (a) to be of much stronger dissolving power for the P of basic slag, tertiary Mg and secondary Ca phosphates. Al and Fe phosphates were the least soluble, and Mg pyrophosphate only slightly soluble, in both tests. K metaphosphate after 28 days in moist soils was more dissolved by (a) which also gave as good or better indications of the solubility of organic P compounds after 28 days in or without soil.

Comparison of methods

Mukherjee (1941) recommended Truog's method for use with non-calcareous red soils in India. This method gave figures about twice as high as those obtained by 1% citric acid and several times higher than with acetic acid. Weeks and Karraker (1941) with U.S. soils of known treatment and performance, and using mineral and organic acids and mixtures of these as well as alkaline solutions, found no extractant appreciably better than another. Choice of solvent should be on the basis of convenience and experience. Fineness of grinding and length and number of extractions offered little to influence the choice of extractant.

In Denmark, Bondorff and Damsgaard-Sorensen (1942) found good agreement, as indicators of available P in soil and of field

response to super., between the "phosphoric-acid number" derived from Bondorff's HNO_3 extraction, the "lactate number" (Egnér) and the "permutite" or "phosphate number" obtained by shaking with a synthetic Na zeolite and determining the P content of the centrifugate. The phosphate number was often useless for judging the P needs of soil and the phosphoric-acid number was the most certain for calcareous soils. Atkinson *et al.* (1945), with Ontario soils, concluded that each method tested tended to give results within a certain range regardless of the soil type. Spurway's showed low readings for P; Morgan's and Thornton's gave high, and a modification of Thornton's very high, readings. On Iowa soils Bower *et al.* (1945) compared H_2CO_3 , Bray's fluoride No. 1 and Truog's methods. All, especially H_2CO_3 , were valuable in differentiating responding from non-responding soils when response was determined with oats, lucerne or red clover, but with maize they were less reliable. The reliability of the methods varied with the soils; where the P was apatitic, H_2CO_3 and Bray's method showed better correlation with response than Truog's method. All three were satisfactory for acid soils containing Fe and Al phosphates. The Iowa Station (1946), using rock-, super- and non-phosphated plots, found that large amounts of easily soluble P were removed from rock-phosphate plots by 0.03 n. NH_4F in 0.1 n. HCl (soil:solvent ratio 1 : 7), and smaller amounts by CO_2 agitation of a 1 : 100 soil-water suspension. Carbonated water, 0.03 n. NH_4F in 0.025 n. HCl (ratio 1 : 7) and 10% Na acetate in 3% acetic acid (1 : 5) extracted little of the apatite form. Fraps and Fudge (1945) studied the P solubility of 34 soils and several phosphatic minerals in 0.2 n. HNO_3 , 0.75 n. HCl, 0.002 n. H_2SO_4 and 0.5 n. $\text{C}_2\text{H}_4\text{O}_2$. None gave quantitative measures of the amounts of P available to plants. Sometimes, e.g. with maize, the amount extracted shows a relationship to crop uptake, but the relationship varies widely for different soils and has to be determined by field experiments in each case. These authors point out that because rock phosphate is almost completely soluble in mineral-acid extractants and is practically insoluble in Morgan's solution, soils heavily fertilized with rock phosphate cannot be usefully analysed by the mineral-acid

extractants. Rubins and Dean (1946), comparing several methods, found that the acetic-acid, Morgan, Truog and lactate methods gave results very significantly correlated with each other. Salonen (1946) found that Spurway's 0.025 n. acetic acid gave results which agreed best with cultivation results in Finland. A calcium-acetate buffer solution at pH 3.7 also gave good results, but Truog and Dean's solution (0.002 n. $H_2SO_4 + 3$ g./l. of $(NH_4)_2SO_4$) appeared to dissolve too much Fe and Al phosphate.

Kaila (1949), compared yield responses to fertilizers with the results using (a) Bondorff's

HNO_3 method, (b) citric acid, (c) 0.5 n. acetic acid (1 : 10, 1 hour), (d) 0.09 n. acetic acid + 0.01 Na acetate (1 : 5, 1 hour) and (e) lactate. Method (e) gave low results, (d) high and low, and the other methods gave results usually too low. Hende (1950) found that soil deficiency and plant uptake were best reflected with Morgan's sodium-acetate extraction, and to a lesser degree with citric-acid and calcium-lactate extraction. Forsee (1945), using celery plots responding markedly to P, reports that the curves for CO_2 and water extractions paralleled the tissue test curves, whereas the 0.5 n. acetic-acid curve diverged considerably.—W. D. B.

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