# DETERMINATION OF ORGANIC PHOSPHORUS IN SAMPLES OF PEAT SOILS

By

ARMI KAILA AND OILI VIRTANEN

*Department of Agricultural Chemistry, University of Helsinki*

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The determination of the total amount of organic bound soil phosphorus seems to be a difficult problem, not yet satisfactorily resolved. The first attempts to obtain a quantitative estimation of the organic phosphorus in soil were made at the end of the nineteenth century (6, 22) and since then numerous methods and modifications have been proposed (e.g. 4, 5, 10, 14, 16, 17, 19, 23). All these procedures are based on the same principles: the amount of organic phosphorus is indirectly determined either as the difference between the amounts of total and inorganic phosphorus in soil extracts, or as an increase in the amount of extractable inorganic phosphorus in soil samples owing to the destruction of organic matter. For the present, in spite of the marked progress in the analytical technique in general, there seems not to be a more reliable way to determine the total organic phosphorus in soil samples.

In the studies reported in this paper no new idea for the determination of organic phosphorus is presented. The main purpose of these experiments and examinations was to choose the most suitable method for the determination of organic phosphorus in peat soils. This was found to be necessary, because some observations indicated that there may exist marked differences in the extractability of organic phosphorus from peat soils and mineral soils .

## *General*

Probably the most widely employed methods are those consisting of an alkali extraction with a pretreatment with acid which renders soil organic matter more soluble in alkali. The acid treatment varies from the washing with diluted hydrochoric acid in the methods of POTTER and BENTON (19), PEARSON (17) etc. to the extraction with 4 N acid in the procedure by WRENSHALL and DYER (23) and with boiling concentrated hydrochloric acid in the modification of MEHTA et al. (14). The alkali extraction has been performed by cold ammonia (19, 23 etc.), or hot ammonia (17), by sodium hydroxide at room temperature (9), or at higher temperatures (4, 10), or as consecutive treatments both with cold and hot solutions (14). The total phosphorus in the combined extracts is usually determined after an incineration with magnesium nitrate, in some modifications a wet combustion by perchloric acid is used. The determination of inorganic phosphorus in these extracts may lead to errors, particularly in the dark-coloured extracts of soils rich in organic matter. These solutions have been discoloured by activated charcoal (17), or kieselguhr (4), by a treatment with bromine water at 100°C or at room temperature (4, 8), or by precipitation with acid (23). All these procedures have their weak points either in the risk of hydrolysis of some organic phosphorus or in the possibility that a part of the inorganic phosphorus is adsorbed by the precipitate or the absorbent. In any case, the determination of the organic phosphorus as the difference of two values, neither of them being of a very great accuracy, cannot lead to results of high precision.

The same is true with those methods in which the increase in the extractable inorganic phosphorus of soil samples due to the destruction of organic matter either by wet or dry combustion is considered to represent organic phosphorus. Usually the wet combustion has been performed with hydrogen peroxide (2, 5 etc.), This method is simple and rapid, but it gives vague results owing to the facts that the oxidation of organic matter is not always complete (20), that fixation of inorganic phosphorus during the extraction may occur (17, 23), and that the treatment with hydrogen peroxide seems to dissolve inorganic phosphorus more than the treatment with water thus giving results far too high (21). Also the dry combustion appears to change the solubility of soil inorganic phosphorus, an observation already made by FRAPS (7). Therefore the methods in which the soil sample is ignited have not been favoured. GHANI (9) with his modification of Odynsky's procedure, however, obtained results which were rather well in accordance with those yielded by his alkali extraction method.

As emphasized by MEHTA et al. (14), we are not able to prove the accuracy of the various methods, since there is no satisfactory absolute standard of comparison. These authors assume that the extraction method which gives the highest results is the most accurate. This, however, can be a valid criterion only if there are no factors disturbing the determination of the total and inorganic phosphorus in the extracts, as e.g. a too high concentration of silica or sulphates in the ignited solutions which leads to an increase in the values of total phosphorus, or a too low estimation of inorganic phosphorus due to the adsorption from the extract during the elimination of its own colour. BOHNE (1) is of the opinion that a good method for the determination of soil organic phosphorus must completely extract the soil phosphorus. This claim may be justified in so far as the analyses of organic soils are in question but not in the case of soils containing mineral matter since they release their total phosphorus only by fusion with sodium carbonate or by digestion with hydrofluoric acid (cf. 15, 21).

When new methods for the determination of soil organic phosphorus are reported their superiority to the older procedures is demonstrated by comparing the results obtained by these methods from various soils. But usually the conclusions are drawn without paying sufficient attention to the fact that none of the methods can give results of high precision. Even though the extractions were performed as correctly as possible, the treatment of the extracts before the determination of phosphorus may cause a marked variation and also the determinations cannot generally be made without errors much lower than 0.01 mg/l of P. The final results are obtained by multiplying the measured phosphorus values by 1000—3000 and by taking the difference between the data for total and for inorganic phosphorus. Thus it is obvious that the amounts of organic phosphorus cannot be reported at a greater accuracy than at 10—20 ppm of soil, and even this probably is a far too precise estimation. Thus there must consistently exist differences higher than 20 ppm of organic phosphorus between the respective results of various methods, before any of the methods can be considered superior to the other ones.

To illustrate this fact we have determined the organic phosphorus content of 12 soils by four alkali-extraction methods. These were the method of DEAN (4) as the modification by SALONEN (21), the method of PEARSON (17), the method of WRENSHALL and DYER (23) modified by KAILA (11), and the method of MEHTA et al. (14). The total phosphorus was determined from solutions obtained by ignition with sodium nitrate, the inorganic phosphorus from solutions discoloured by precipitation with acid. The molybdenum blue method was employed as the modification of KAILA (12). The results of the duplicate determinations are reported in Table 1 which also contains the 95% confidence limits for the data of the various methods calculated according to CRAMÉR (3, p. 211). This, however, is not quite reliable, since the computation is based on the supposition that the mean deviation of the respective series depends only on the analytical errors. Even then, the confidence limits for the series of figures obtained in routine analyses by the various methods are not very narrow thus indicating that on the basis of a slight inequality too bold conclusions must not be drawn.

### *Acid-alkali extraction methods*

In Table 1 no significant difference exists between the values of organic phosphorus obtained by the four methods for the respective mineral soils. For different peat soils the maximum values are yielded by different methods. On the average, the PEARSON method has given somewhat higher figures than the other ones, but no regular superiority of any method can be observed. Contrary to what was expected the extraction procedure introduced by MEHTA et al. (14), did not give particularly high values for these soils. It seems possible that some hydrolysis of organic phosphorus occurred during the rather drastic treatments of this method, since generally the amounts of inorganic phosphorus were higher than those obtained by the other methods, although the total amounts did not differ markedly.

Table 1. Organic phosphorus in soils determined by various methods. (Expressed as P ppm of air-dry soil).

| Soil | Dean | | Pearson | | Wrenshall-Dyer | | Mehta et al. | |
|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b |
| 1. Sand | 210 | 200 | 150 | 150 | 180 | 160 | 170 | 160 |
| 2. Silt | 400 | 410 | 390 | 390 | 400 | 420 | 400 | 400 |
| 3. Heavy clay | 480 | 490 | 540 | 530 | 530 | 530 | 500 | 470 |
| 4. Mud clay | 350 | 370 | 430 | 430 | 400 | 400 | 390 | 410 |
| 5. Silt loam | 70 | 60 | 50 | 60 | 60 | 80 | 40 | 40 |
| 6. Sandy mull | 610 | 620 | 680 | 650 | 670 | 680 | 600 | 600 |
| 7. Fen peat cultivated | 470 | 470 | 640 | 610 | 560 | 590 | 530 | 480 |
| 8. » | 790 | 800 | 870 | 850 | 960 | 940 | 840 | 780 |
| 9. CS-peat | 340 | 300 | 260 | 280 | 210 | 200 | 290 | 380 |
| 10. LC-peat | 800 | 790 | 930 | 950 | 930 | 950 | 860 | 880 |
| 11. SC-peat | 660 | 640 | 640 | 670 | 470 | 490 | 590 | 520 |
| 12. CS-peat | 550 | 540 | 560 | 580 | 540 | 520 | 550 | 550 |
| 95 % confidence limits | ±20 | | ±20 | | ±20 | | ±40 | |

In a previous publication (11) it was stated that the modified method of WRENSHALL and DYER, although satisfactory in the analyses of mineral soils, from some peat soils failed to extract all the organic phosphorus. This observation appears to be corroborated by the data for the peat samples 9 and 11 in Table 1 for which all the other methods have given markedly higher results. That these low values for organic phosphorus really arise from the poor extraction of the phosphorus from these samples is indicated by the fact that the total amounts of phosphorus extracted were only about 250 and 660 ppm resp., whereas the corresponding values obtained e.g. by the procedure of MEHTA et al. (14) were 470 and 970 ppm. The reason for this is probably found in the ineffectiveness of cold ammonia to extract the organic matter in these peat samples. When the ammonia extraction was performed at 50°C, the total amount of phosphorus extracted from the SC-peat sample 11 increased to 810 ppm and that of the organic phosphorus up to 630 ppm. The treatment with ammonia at 50° C did not change the amounts of organic phosphorus extracted from the mineral soils.

These preliminary experiments indicated that the modification of the WRENSHALL and DYER procedure must be improved if particularly virgin peat samples are to be analysed. In their paper MEHTA et al. (14) claim that only consecutive extractions with cold and hot alkali remove all the organic phosphorus without any significant hydrolysis of the phosphorus compounds. Because the same authors also emphasize the superiority of sodium hydroxide to ammonia, and because the former also is more convenient to use particularly in laboratories with poor ventilation, 0.5 N sodium hydroxide was chosen. After the extraction with 4 N sulphuric acid for 18 hours at room temperature the well-washed 1-g samples were treated at room temperature with 100 ml of 0.5 N sodium hydroxide for 18 hours, and then with an equal volume of 0.5 N sodium hydroxide at 90°C for 4 hours.

In addition to these changes in the extraction procedure, also some analytical modifications were made. In the original method of WRENSHALL and DYER (23) as well as in the modification proposed by KAILA (11) the acid and alkali extracts are separately analyzed. The purpose of this practice was to eliminate the possible adsorption of inorganic phosphorus on the precipitated organic matter of the alkali extracts. In mineral soils and usually also in cultivated peat soils the acid treatment dissolves the main part of the inorganic phosphorus, but it was found that in virgin peat soils often a considerable portion of inorganic phosphorus is first extracted by the alkali. Thus it seemed unnecessary to perform four determinations of phosphorus, particularly, since it was found that no significant differences existed between the values of total inorganic phosphorus obtained either by the separate determinations or by analysing the combined extracts. It appeared not, however, to be desirable to mix the acid extract with the combined alkali extracts before the aliquot parts were taken for the determinations, because there could arise some error from the possibility that the combined solution was not quite homogeneous owing to the precipitation of organic matter.

One tenth of the acid extract and of the combined alkali extracts were used for the determination of the inorganic and total phosphorus. Although these mixtures contained equal amounts of acid and alkali, and therefore a precipitation of organic matter occurred in them, it was on the basis of some experiments considered desirable to let the precipitation take place under more acid conditions. 5 ml of 1 N sulphuric acid was added to the mixture and the volume made up to 50 ml with distilled water. The well-mixed suspension was then filtered through hard paper, since it was found that clear solutions could not always be obtained only by letting the flocculated organic matter to settle.

The destruction of organic matter for the determination of total phosphorus was performed either by dry or wet combustion. In the former case the mixture of the extracts was evaporated to dryness with 1 ml of 2 N sodium nitrate, ignited in an electric oven at a temperature not higher than 600°C, and heated on a boiling water bath with 20 ml of 1 N sulphuric acid at least for two hours not allowing the ash solution to dry. The wet combustion was performed with the aid of 1.5 ml of a mixture containing two parts of 70 % perchloric acid and one part of concentrated sulphuric acid. The latter was added in order to prevent the explosive decomposition of perchloric acid (cf. 18, p. 273). The suspension was first evaporated on water bath to a residue of about 2 ml, then heated on the flame until the colour became a pale yellow.

Both of these combustion methods have their advantages. The wet method is more rapid but it requires more attention than the dry one. The perchloric acid concentration in the solution does not disturb the colour development in the method used, although the amount of perchloric acid in the 50 ml of solution to be reduced would correspond to 0.4 ml of 70 % perchloric acid. A considerable increase in the work arises from the fact that the digested solutions are of various acidity due to

Table 2. Total and organic phosphorus dissolved by different methods.

| Soil | Total P, ppm | | | Organic P, ppm | |
|---|---|---|---|---|---|
| | Kjeldahl digestion | Proposed method | Wrenshall-Dyer method | Proposed method | Wrenshall-Dyer method |
| 1. Sand | 420 | 360 | 360 | 200 | 170 |
| 2. Silt | 1130 | 1020 | 1010 | 440 | 410 |
| 3. Heavy clay | 1170 | 1000 | 1020 | 520 | 530 |
| 4. Mud clay | 1060 | 980 | 1030 | 380 | 400 |
| 5. Silt loam | 710 | 630 | 640 | 60 | 70 |
| 6. Sandy mull | 1120 | 1030 | 1030 | 660 | 670 |
| 7. Fen peat cultivated | 990 | 990 | 940 | 590 | 580 |
| 8. » | 1330 | 1330 | 1240 | 980 | 950 |
| 9. CS-peat | 470 | 420 | 250 | 380 | 210 |
| 10. LC-peat | 1080 | 1080 | 1000 | 940 | 940 |
| 11. SC-peat | 1010 | 1010 | 660 | 660 | 480 |
| 12. CS-peat | 760 | 750 | 600 | 610 | 530 |

the uneven evaporation of acid. Therefore their acidity must be determined by titration with alkali, whereas the acidity of the solutions obtained by ignition can be calculated. The weak point of the inceneration lies in the danger that losses due to spattering may occur.

The extraction method adopted was found to be rather convenient. When the twelve soil samples used above were analyzed by this method for organic phosphorus the results reported in Table 2 were obtained. This table also contains data for the total phosphorus dissolved by the proposed method, the old modification of the Wrenshall and Dyer method and by Kjeldahl digestion in which sodium selenate and sodium sulphate were substituted for copper sulphate and potassium sulphate resp. It must be emphasized that this digestion does not release all the phosphorus in mineral matter and that the results do not really represent the total phosphorus in mineral soils. In peat soils, however, this probably is the case.

The strenthening of the treatment has not improved the dissolution of total phosphorus from the mineral soil samples, but from most of the peat samples the proposed method has extracted as much phosphorus as the acid digestion, and sometimes nearly twice as much as the old method. Also the amounts of organic phosphorus obtained by these methods for the mineral soils are generally almost equal, but the treatment with hot alkali has markedly increased the quantity of organic phosphorus of some peat samples. In an experiment in which the proposed method was compared with an extraction procedure without the treatment with hot alkali, it was found that the latter gave results which were from 7 to 50 per cent lower than those of the proposed method when peat soils were analyzed. As to the mineral soils no difference existed in the amounts of organic phosphorus obtained. Therefore, it appears to be unnecessary to employ the successive extraction with cold and hot alkali on mineral soils for then the extra work connected with the second alkali treat-

Table 3. Organic phosphorus in soil determined by ignition methods with different kind of extraction. (Expressed as org. P ppm of air-dry sample.)

| Soil | $H_2SO_4$ | | | | | Ghani | Proposed acid-alkali extraction |
|---|---|---|---|---|---|---|---|
| | 1:100 | | 1:200 | | 1 : 40 | | |
| | 5 N | 0.2 N | 2 N | 0.2 N | 1 N | | |
| 1. Sand .............. | 190 | 190 | 220 | 190 | 200 | 60 | 200 |
| 2. Silt .............. | 440 | 500 | 480 | 520 | 470 | 260 | 440 |
| 3. Heavy clay ........ | 580 | 540 | 570 | 530 | 520 | 310 | 520 |
| 4. Mud clay .......... | 380 | 430 | 500 | 440 | 420 | 190 | 380 |
| 5. Silt loam .......... | 60 | 60 | 80 | 70 | 50 | 20 | 60 |
| 6. Sandy mull ........ | 660 | 710 | 740 | 630 | 660 | 250 | 660 |
| 7. Fen peat cultivated .. | 620 | 610 | 730 | 660 | 590 | 350 | 600 |
| 8. » .. | 1040 | 990 | 1110 | 1020 | 1020 | 710 | 980 |
| 9. CS-peat............ | 420 | 380 | 430 | 380 | 360 | 250 | 380 |
| 10. LC-peat .......... | 1030 | 940 | 1020 | 980 | 900 | 380 | 940 |
| 11. SC-peat............ | 780 | 850 | 850 | 840 | 820 | 740 | 660 |
| 12. CS-peat............ | 700 | 650 | 710 | 670 | 620 | 480 | 590 |

ment probably is wasted. This, perhaps is true also as regards to some peat samples, particularly those of old cultivated soils. Generally, however, the total organic phosphorus in peat soils cannot be extracted without the aid of hot alkali.

## *Ignition methods*

The extraction methods are rather laborious and owing to the many manipulations exposed to marked errors. Thus, the precision of the results cannot be very high. This being the case it appeared desirable to study the possibilities as offered by the rapid and simple combustion methods for the determination of soil organic phosphorus. In this work attention was paid only to the dry combustion procedure which has been used as several modifications by various authors. SCHMOEGER (22) used 12 % hydrochloric acid to extract the inorganic phosphorus from the untreated and the ignited samples. ODYNSKY (16) ignited one 1-g sample at 600°C for one hour before extraction with 2 N sulphuric acid, while the other sample was extracted without ignition with the same amount i.e. of 200 ml of acid. MADANOV (13) heated the other sample for 3 or 4 hours at a temperature not higher than 300°C and performed the extraction with 2 % citric acid. GHANI (9) used 0.5 N acetic acid instead of sulphuric acid in Odynsky's method to obviate the chance of error due to a change in acid-solubility of inorganic phosphorus compounds and phosphatic minerals. He also used 8-hydroxychinoline to prevent fixation during the extraction and performed ignition in the presence of magnesium oxide.

Some experiments with the ignition and acid extraction procedures were performed. The twelve soil samples used in the study of the extraction methods were ignited and extracted with acid under various conditions. Since the heating of the soil samples at 300°C burnt the organic matter incompletely and unevenly a higher temperature was chosen. In all the analyses reported in Table 3 the soil samples were ignited for one hour at 600°C. Different concentrations of sulphuric acid were used and also the ratio of soil to solution was varied, but the period for shaking was kept as half an hour. This time was rather short and it was chosen in order to prevent the readsorption of dissolved inorganic phosphorus which is known to increase with the time of contact. In addition to the results obtained as a difference between the sulphuric acid soluble inorganic phosphorus in the ignited and untreated soil samples Table 3 also presents data given by the method of GHANI (9) in which the extraction was performed by 0.5 N acetic acid containing 8-hydroxychinoline. For the sake of comparison also the results yielded by the proposed acid-alkali procedure are listed in Table 3.

The concentration of sulphuric acid and the ratio of extraction apparently have not exerted any marked effect upon the difference of the amounts of extractable inorganic phosphorus in the ignited and untreated samples. Some deviation exists, of course, but no uniform tendency can be found. Generally, the values are higher than those obtained by the acid-alkali extraction, but in several cases the difference between these values is almost insignificant. In view of the fact that due to incomplete extraction of organic phosphorus or to some hydrolysis of the most easily decomposable compounds the data obtained by the acid-alkali extraction method probably do not always represent the maximum amounts of organic phosphorus, the conclusion can be made that, at least for most of these soils, the ignition methods can be used. This does not include the method by GHANI which obviously gave results which were far too low for most of the soils, but a rather high value for the sample number 11. This sample appears to be somewhat problematic since also the other ignition methods yielded it considerable higher values than the acid-alkali extraction.

### *Comparison of extraction and ignition methods*

Since the purpose of this investigation was particularly to elucidate the determination of organic phosphorus in peat soils, it was necessary to apply these methods to a larger material of peat samples. The method of PEARSON (17), the proposed acid-alkali extraction method and an ignition method were used on 40 peat soil samples, the main part of which originated from virgin peat soils of different kinds. As in the previous experiments the ignition was performed at 600°C and the period of extraction was half an hour. Since the differences in the concentration of acid and in the ratio of extraction did not significantly affect the results 0.2 N sulphuric acid was used in the ratio of 1:100. This made it possible to determine inorganic phosphorus in the extracts without any extra work of dilution required in the case that markedly stronger acids were used. All the determinations were made only in duplicates, and generally the analyses were performed in series of 24 samples.

The results are listed in Table 4. They indicate that the proposed method (successive treatments with 4 N sulphuric acid, and hot and cold 0.5 N sodium hydroxide)

Table 4. Total and inorganic phosphorus in peat soils by different methods.

| Peat | H[1] | pH | Total P, ppm | | | Org. P, ppm | | |
|---|---|---|---|---|---|---|---|---|
| | | | Kjeldahl digestion | Proposed extraction | Pearson | Proposed extraction | Pearson | Ignition |
| 1. LCSp | 6 | 4.3 | 1340 | 1330 | 1150 | 1180 | 1050 | 1200 |
| 2. EuSCp | 3 | 4.4 | 1340 | 1330 | 1130 | 970 | 930 | 1150 |
| 3. LCSp | 4 | 4.4 | 1170 | 1170 | 1110 | 890 | 880 | 1090 |
| 4. LCp | 4 | 4.9 | 1200 | 1190 | 1010 | 870 | 710 | 990 |
| 5. CSp | 4 | 4.5 | 1330 | 1250 | 1130 | 1030 | 1030 | 990 |
| 6. BCp | 7 | 6.1 | 1180 | 1180 | 880 | 950 | 690 | 970 |
| 7. LCp | 8 | 4.7 | 1110 | 1080 | 1080 | 940 | 940 | 950 |
| 8. LCSp | 4 | 4.5 | 1150 | 1140 | 1020 | 930 | 820 | 930 |
| 9. LCp | 6 | 5.0 | 1180 | 1140 | 1180 | 880 | 910 | 920 |
| 10. SCp | 4 | 4.7 | 920 | 890 | 870 | 660 | 660 | 850 |
| 11. SCp | 5 | 3.5 | 990 | 920 | 880 | 750 | 740 | 860 |
| 12. SCp | 7 | 4.2 | 1140 | 1030 | 920 | 880 | 840 | 860 |
| 13. SCp | 4 | 4.8 | 1000 | 930 | 730 | 780 | 640 | 840 |
| 14. SCp | 3 | 3.6 | 860 | 830 | 850 | 710 | 680 | 800 |
| 15. SCp | 6 | 4.9 | 850 | 870 | 850 | 740 | 720 | 750 |
| 16. Cp | 6 | 5.1 | 890 | 910 | 860 | 730 | 730 | 740 |
| 17. LCp | 7 | 4.6 | 830 | 830 | 750 | 710 | 630 | 730 |
| 18. EuSCp | 3 | 5.6 | 730 | 750 | 640 | 580 | 490 | 680 |
| 19. CSp | 3 | 4.7 | 740 | 730 | 700 | 590 | 570 | 660 |
| 20. EuSCp | 5 | 4.7 | 660 | 580 | 440 | 480 | 370 | 590 |
| 21. LCp | 8 | 4.9 | 660 | 620 | 530 | 540 | 460 | 580 |
| 22. Sp | 7 | 4.2 | 570 | 570 | 490 | 460 | 410 | 530 |
| 23. Sp | 1 | 4.0 | 650 | 650 | 520 | 490 | 410 | 520 |
| 24. Sp | 5 | 3.8 | 590 | 520 | 400 | 360 | 330 | 510 |
| 25. Cp | 4 | 5.2 | 580 | 540 | 590 | 430 | 510 | 490 |
| 26. LCSp | 2 | 4.2 | 680 | 660 | 550 | 450 | 370 | 420 |
| 27. CSp | 3 | 4.2 | 500 | 450 | 440 | 360 | 320 | 410 |
| 28. BCp | 2 | 4.7 | 450 | 450 | 330 | 310 | 230 | 390 |
| 29. CSp | 5 | 5.1 | 450 | 440 | 390 | 380 | 270 | 380 |
| 30. EuSCp | 7 | 4.3 | 440 | 400 | 390 | 320 | 310 | 370 |
| 31. Sp | 3 | 3.6 | 390 | 360 | 280 | 250 | 190 | 310 |
| 32. Sp | 1 | 3.7 | 330 | 310 | 220 | 180 | 130 | 260 |
| Cultivated fen peats: | | | | | | | | |
| 33. | | 4.9 | 1770 | 1770 | 1730 | 1260 | 1240 | 1290 |
| 34. | | 4.7 | 1440 | 1410 | 1320 | 960 | 920 | 1020 |
| 35. | | 4.5 | 1330 | 1330 | 1330 | 980 | 860 | 990 |
| 36. | | 4.7 | 1290 | 1250 | 1130 | 860 | 810 | 930 |
| 37. | | 4.1 | 1060 | 1060 | 1000 | 860 | 840 | 860 |
| 38. | | 4.6 | 1090 | 1050 | 980 | 750 | 700 | 790 |
| 39. | | 4.4 | 960 | 880 | 800 | 640 | 640 | 720 |
| 40. | | 4.7 | 990 | 990 | 970 | 600 | 610 | 610 |

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[1] v. Post's degree of decomposition

has extracted from the soils almost as much total phosphorus as the acid digestion which can be supposed to dissolve practically all the phosphorus in organic soils. On the average, the amounts of total phosphorus obtained by the extraction method are about 97 per cent of those yielded by the digestion. In view of the analytical errors this difference appears to be almost insignificant. The PEARSON method, extraction with 0.1 N hydrochloric acid and hot ammonia, has rendered soluble markedly less of the total phosphorus, on the average of only about 88 per cent of the amount given by the acid digestion. This by the Pearson method insoluble phosphorus may be partly inorganic, but probably some of the organic compounds have resisted the quantitative extraction.

As to the organic phosphorus the relation between the amounts obtained by the proposed method and the Pearson method is almost equal to that found to exist between the corresponding values for total phosphorus: on the average, the latter method has given about 92 per cent of the organic phosphorus yielded by the former one. This corroborates the opinion that Pearson's method does not extract all the organic phosphorus of most of the uncultivated peat soils. The ignition method, on the contrary, has given results generally somewhat higher than those of the proposed method. On the average the increase in the 0.2 N sulphuric acid soluble phosphorus due to ignition represents values which are about 8 per cent higher than those obtained by the acid-alkali method proposed in this paper. This difference does not exist for all the soils: there are several samples on which the both procedures have given equal results, but then for some soils the differences are quite high even almost 200 ppm. On the basis of this scarce material it is, however, impossible to draw any valid conclusions of the reasons for the higher results given by the ignition procedure. Of course, it can be explained on the basis of the old observation that ignition increases the solubility of soil inorganic phosphorus, but also other reasons can be given. Equally well the incomplete extraction of organic phosphorus or a hydrolysis of organic compounds in the acid-alkali procedure may decrease values obtained by it.

In lack of a reliable criterion it is impossible to conclude which of the two methods gives better results in the contradictory cases. The safest way is probably to take averages of the values obtained by both the methods. The most reliable results are obtained if the methods yield equal amounts. Generally the determination of soil organic phosphorus by two methods requires too much work and it is necessary to choose one of the methods. One must remember that the extraction methods can give values which are slightly lower than the true ones, and the ignition methods tend to yield somewhat higher data than the ideal procedure not yet developed.

## *Summary and conclusions*

Attention was paid in the present paper to the fact that the precision of the values obtained by different methods for the total organic phosphorus in soil cannot be very high. Even the variation caused by the treatment of the extracts and connected with the colorimetric estimation of phosphate in the solution makes it impossible to report the results more accurately than by 10—20 ppm organic P, at least if routine analyses are in question.

Although the somewhat modified methods of DEAN, WRENSHALL and DYER, PEARSON, and MEHTA et al. yielded equal results for the organic phosphorus content of the respective mineral soils and of most of the peat soils analyzed, the treatment with cold alkali in the Wrenshall and Dyer procedure apparently failed to extract the organic phosphorus from two peat samples as quantitatively as the treatment with hot alkali in the other methods.

On the basis of this observations a new modification of the method of WRENSHALL and DYER was proposed. It consists of an extraction of 1-g sample with 25 ml of 4 N sulphuric acid at room temperature for 18 hours, followed by washing with water and two successive extractions with 100 ml of 0.5 N sodium hydroxide, the first of them for 18 hours at room temperature, the second for 4 hours at 90°C.

This method was found to extract from 40 peat soil samples on the average about 97 per cent of the total phosphorus dissolved by the Kjeldahl digestion and about 9 per cent more organic phosphorus than the method of PEARSON.

Experiments concerning the ignition and acid extraction procedures indicated that the method of GHANI was not suitable for the determination of organic phosphorus in the twelve samples analysed. The extraction with sulphuric acid showed no marked differences between the increase in the soluble phosphorus due to the ignition when the ratio of extraction was varied from 1:40 to 1:200, and the extractant from 0.2 N acid to 5 N acid. The results obtained for 40 peat samples by ignition for one hour at 600°C and extraction of the ignited and untreated samples with 0.2 N sulphuric acid in a ratio of 1:100 for half an hour were on the average 8 per cent higher than those given by the proposed acid-alkali extraction.

The total organic phosphorus content of soil may probably be somewhat higher than the figure yielded by the acid-alkali extraction and slightly lower than the value obtained by the ignition method. For the present, the most reliable result seems to be found in the average of the data given by these two methods.

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## SELOSTUS:

## TURVENÄYTTEIDEN ORGAANISEN FOSFORIN MÄÄRITTÄMISESTÄ

Armi Kaila ja Oili Virtanen

*Yliopiston maanviljelyskemian laitos, Helsinki.*

Tutkimuksessa vertailtiin eräitä käytössä olevia maan orgaanisen fosforin määritysmenetelmiä. Todettiin, että muutamista turvenäytteistä uuttui ainoastaan kylmän emäskäsittelyn sisältävällä Wrenshallin ja Dyerin menetelmän muunnoksella paljon vähemmän orgaanista fosforia kuin Deanin, Pearsonin sekä Mehtan ja kumppanien metodeilla, joissa käytetään kuumaa emästä. Kivennäismaista ja toisista turvemaista saatiin kaikilla menetelmillä suunnilleen samanlaisia tuloksia.

Aikaisemmin käytettyä Wrenshallin ja Dyerin menetelmän muunnosta parannettiin siten, että kylmä ammoniakkiuutto korvattiin kahdella peräkkäisellä uutolla, joissa käytettiin 0.5 n natriumhydroksidia ja joista ensimmäinen suoritettiin huoneen lämpötilassa ja toinen 90°C:ssa. Tämä menetelmä uutti 40 turvenäytteestä keskimäärin 97 % happopolton liuottamasta kokonaisfosforin määrästä ja noin 9 % enemmän orgaanista fosforia kuin Pearsonin metodi.

Tutkimuksessa selvitettiin myös niitten menetelmien käyttömahdollisuuksia, joissa orgaaninen fosfori määritetään happoon liukenevan epäorgaanisen fosforin lisääntymisenä näytteen polttamisen vaikutuksesta. Todettiin, että tällaiset metodit antavat hiukan suurempia arvoja kuin happo-emäsuutto: tutkituissa 40 turvenäytteessä ero oli keskimäärin 8 %. Todennäköisesti polttomenetelmät antavat hiukan liian suuria, uuttomenetelmät taas hieman liian pieniä orgaanisen fosforin arvoja. Oletettiin, että paras tulos saadaan molempien menetelmien tulosten keskiarvoista.