Chapter (non-refereed)

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The determination of total phosphorus in soils by acid digestion

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1 Introduction

Phosphorus is of major significance in plant nutrition and the various forms in soil have long been studied intensively. Such investigations often require knowledge of the total content in soil, particularly as primary mineral levels are often quite low for this element. Hence, it is important that reliable estimates of the total level can be made.

Absolute chemical methods for bringing minerals, particularly silicates, into solution have always depended on fusion or hydrofluoric acid procedures, although it is well known that the commonest variants (Na_2CO_3 fusion and HF+ $HClO_4$) cannot bring all minerals into solution. Fortunately, the mineral phosphates are, as a group, relatively soluble in strong acids, and this property, coupled with a growing need for convenient procedures in soil analysis, led, many decades ago, to substitute methods being proposed for phosphorus. These methods were based on acid dissolution, and perchloric acid was a favourite because it is also a strong oxidizing agent for soil organic matter.

A common perchloric acid procedure involved digesting 2 g dried soil with 30 ml acid, with the option of a nitric acid pre-treatment if the organic content was high (Jackson 1958). However, although this digestion has been widely used, some workers have suggested that the phosphorus recovery might sometimes be low (Muir 1952; Syers *et al.* 1968). Various mechanisms could, in theory, be responsible for this loss, but there is evidence to suggest that incomplete release from the sample is involved (Sommers & Nelson 1972).

In addition to these problems, there appeared to be a safety risk in the large-scale use of neat perchloric acid, particularly if perchloric salts were allowed to accidently dry out. In more recent years, the need for adequate fume cupboard facilities when using this acid has also been stressed. The neat perchloric acid digestion was therefore not used on a routine basis at ITE's Merlewood Research Station. Instead, a nitric-perchloric-sulphuric system was adopted for soil phosphorus and was taken from the procedure already in use in the laboratory for vegetation. This system followed the method of Piper (1950), but on a smaller scale. Although it was a strong oxidizing system, it was safer to use because the presence of sulphuric acid greatly reduced the risk of drying out.

However, some comparison with a hydrofluoric acid method was required for soils analysed at that time. These tests involved 24 chalk soil samples from 6 sites in southern England, whose mean percentage total phosphorus content (with standard error) was 0.094 ± 0.005, following a hydrofluoric-perchloric digestion of 0.1 g sample, and 0.096 ± 0.004 with a nitric-perchloric-sulphuric digestion of 0.05 g. These particular digestions both included 1 ml sulphuric acid instead of 0.5 ml and dilution to 100 ml not 50 ml (see below). It was concluded that the 2 systems were equally effective for these soils.

At a later stage, the nitric-perchloric-sulphuric procedure was replaced by a sulphuric-peroxide system for vegetation. Although this system had somewhat less oxidizing power and required a catalyst, it had the advantage of recovering nitrogen in the same digest as used for other elements (Allen *et al.* 1974; Parkinson & Allen 1975). Recently this method has been adopted at Merlewood for estimating nitrogen and phosphorus in soils (Rowland & Grimshaw 1985). This paper records comparisons between the 2 systems which were made for the recovery of total phosphorus from a range of soil types, and includes supplementary data obtained with a hydrofluoric-perchloric system. Factors relevant to the overall performance of the sulphuric-peroxide method are also examined briefly.

2 Materials and methods

2.1 Soils and minerals

Samples (103) covering 8 soil types in the United Kingdom were originally taken as part of a soil fertility study led by Dr A F Harrison of Merlewood. The soil types were described pedologically by Dr M Hornung of ITE's Bangor Research Station. Samples were dried (40°C), sieved (<2 mm) and a subsample ground (<0.15 mm) prior to analysis. The approximate organic contents were estimated by loss-on-ignition at 550°C (2 hours). Mean values of the types ranged from 7% to 85% of the dry matter. Mineral samples of fluorapatite $Ca_5(PO_4)_3F$ (from Norway) and monazite (W Australia) were supplied by University College of North Wales (Bangor) and ground to a fine powder.

2.2 Nitric-perchloric-sulphuric digestion

An air-dried ground sample (0.05 g) was weighed into a 50 ml Kjeldahl flask and digested with 3 ml 5+1 nitric acid (SG 1.42) + perchloric acid (60%) and 0.5 ml sulphuric acid (SG 1.84). The digestion was controlled to avoid rapid loss of acid or excess heating. The flasks were gently boiled for about one hour with only a gradual loss of mainly nitric acid. As the white fume stage approached, heating was increased a little to remove white perchloric fumes and continued for about 15 minutes until mainly sulphuric acid remained. The digest was now more viscous but drying out was not permitted. When cool, the digests were diluted to 50 ml (using a Zippette), mixed and the silica residue allowed to settle. Blank solutions (acids only) were also digested. The final solution was 1% acid (v/v) and used without further dilution to estimate phosphorus.

2.3 Sulphuric-peroxide digestion

The digestion mixture was prepared by mixing 350 ml hydrogen peroxide (100 vol), 14 g lithium sulphate and 0.42 g selenium powder (catalyst), followed by the careful addition of 420 ml sulphuric acid. The mixture was stored at 2°C and was stable for 3–4 weeks. For digestion, 0.2 g air-dry ground samples were weighed into a 50 ml Kjeldahl flask. The digestion mixture was added (4.4 ml) and digested at low heat until the initial vigorous reaction subsided. Heat was then gradually increased and continued for 2 hours. When cool, the digest was diluted to 50 ml, mixed and the silica residue allowed to settle. Blank solutions (digestion mixture only) were also digested. The final solution was 5% acid (v/v) and was further diluted 5 times before estimating phosphorus.

2.4 Hydrofluoric-perchloric digestion

An air-dried ground sample (0.05 g) was weighed into a platinum crucible and 7 ml hydrofluoric acid (40%) and 1 ml perchloric (60%) added in succession. Crucibles were heated gently at 200–220°C for 2 hours with the lid on, followed by evaporation to white fumes. When cool, 3 ml nitric acid and 0.5 ml sulphuric acid were added and digested until white fumes reappeared and continued for about 15 minutes. Digests were finally made up to 50 ml in a volumetric flask.

2.5 Estimation of phosphorus

Phosphorus was determined using an automated molybdenum-blue colorimetric procedure with an AutoAnalyzer, as described by Allen et al. (1974). Standards were compensated with 1% sulphuric acid or digested sulphuric-peroxide reagents as appropriate.

2.6

Moisture contents were determined on separate subsamples of air-dry soil to correct analytical results to a dry (105°C) basis.

3 Results and discussion

3.1 Comparison of digestion procedures

The data in Table 1 show the mean phosphorus contents of each soil type, as recorded by both digestion systems. Differences between the 2 systems were minor for all soil types and none significant at P<0.05. The standard errors were also very similar for a given soil type. The digestions appeared to be equally effective, regardless of the organic content of the soil types. Further examination showed that the phosphorus levels themselves were not significantly correlated at P<0.05 with the organic contents over 103 soil samples (r=−0.029). This result, in turn, may reflect the fact that, on average, only 65% of the total phosphorus was organically bound as shown by data not presented here. It was concluded that the 2 digestion systems recovered comparable amounts of phosphorus from the soils tested. Further evidence was required to show if this was a full recovery.

3.2 Precision

Table 1 includes standard errors which represent the overall variations between 13 soil samples for

Table 1. Comparison of digestion procedures for 8 soil types showing mean percentage total phosphorus with standard errors (dry matter basis)

Soil type	Sites	LOI (%)	% phosphorus 'Peroxide'[1]	'Perchloric'[2]
Pleaty gley	13	35	0.073 ± 0.009	0.069 ± 0.009
Gley	13	10	0.105 ± 0.015	0.100 ± 0.015
Acidic brown earth	13	15	0.074 ± 0.008	0.074 ± 0.008
Basic brown earth	13	7	0.085 ± 0.014	0.080 ± 0.012
Podzol	13	9	0.018 ± 0.004	0.019 ± 0.004
Peaty podzol	13	50	0.064 ± 0.006	0.060 ± 0.006
Brown podzol	13	13	0.058 ± 0.007	0.063 ± 0.008
Peat	12	85	0.069 ± 0.008	0.062 ± 0.008
Overall mean ($\bar{x}$)	103		0.068 ± 0.004	0.066 ± 0.004

[1] 'Peroxide' = sulphuric-peroxide digestion
[2] 'Perchloric' = nitric-perchloric-sulphuric digestion

each soil type. These errors include both site and sampling variations, as well as the analytical component. A measure of the latter which will include both digestion and colorimetric variation can be obtained by digesting replicates of one sample. Four samples were selected as being representative of 4 soil types and 10 replicates from each sample were digested by the sulphuric-peroxide system and analysed as before. The mean values of the 10 replicates and their standard errors are given in Table 2. Although these errors inevitably include variation within a sample, Table 2 still indicates a very satisfactory level of precision for this digestion method.

3.3 Sample preparation

It is a general recommendation in the texts that only finely ground samples should be handled at the weights required for these types of digestion. The greater homogeneity of the ground sample allows a weight of 0.2 g to be reasonably representative of the sample, as shown by the narrow standard error limits in Table 2. Comparable data were obtained for seived but unground material which are not presented here, but they confirm that the precision is less satisfactory. These data also suggest that a slightly higher (6—9%) recovery of phosphorus was obtained from the ground samples of the soil types (peat and peaty gley). This was considered to be due to an increase in surface area presented to the sulphuric-peroxide mixture.

3.4 Digestive conditions

Digestion of 0.1 g and 0.2 g portions of soil showed that comparable recoveries were obtained. However, weights in excess of 0.2 g are not recommended for soil because excess mineral matter is undesirable for smooth control of the sulphur-peroxide system, although up to 0.4 g is acceptable for vegetation (Parkinson & Allen 1975). Although temperature control is not critical, only minimal heating should be used during the initial vigorous reactions and increased gradually after this stage, but avoiding excessive loss of sulphuric acid fumes.

The time required for the digestion of soil was also examined for periods up to 4 hours. Four soil types were selected and the data are presented in Table 3. The results suggested that the digestion is complete after 2 hours. This period was adopted in digesting the 103 soil samples, and only 2 digests had a yellowish tint at the conclusion. In these 2 cases, the colour was considered to be mineral rather than organic in origin.

3.5 Mineral phosphate

Data for mineral phosphate are presented in Table 4. They show that the sulphuric-peroxide digestion gave a phosphorus recovery of 103% from a fluorapatite sample of known composition, whilst hydrofluoric-perchloric and nitric-perchloric-sulphuric systems recovered approximately 95%. Recovery from the monoazite sample was more variable, and no theoretical phosphorus content was available because unknown amounts of the rare earth elements cerium, lanthanum and neodynium were present in this particular material. It left a white precipitate following the sulphuric-peroxide digestion which may have been a peroxide of one or more of the rare earth elements.

The results were satisfactory regarding fluorapatite because of the recovery and because the apatite group (including the chlor- and

Table 2. Precision of the sulphuric-peroxide digestion. Mean percentage phosphorus and standard errors for 10 replicates of one sample of a soil type (dry matter basis)

Soil type	% phosphorus
Pleaty gley	0.063 ± 0.000
Gley	0.044 ± 0.001
Podzol	0.0096 ± 0.0005
Peat	0.046 ± 0.000

Table 4. Recovery of phosphorus from replicates of a single fluorapatite mineral sample by various methods

Method	% phosphorus
Theoretical	18.4
Peroxide[1]	18.9
Perchloric[2]	17.6
HF-HClO$_4$	17.5

[1,2] see Table 1

Table 3. Recovery of total phosphorus from soil by the sulphuric-peroxide digestion over various time intervals. Mean percentage phosphorus for 3 replicates of one sample of each soil type

Soil type	Time (hours)					
	1.0	1.5	2.0	2.5	3.0	4.0
Gley	0.045	0.044	0.046	0.045	0.046	0.047
Acid brown earth	0.037	0.037	0.035	0.034	0.033	0.035
Podzol	0.012	0.012	0.012	0.012	0.012	0.012
Peat	0.076	0.080	0.082	0.080	0.080	0.080

hydroxy-forms) is the commonest source of primary mineral phosphorus in nature (Mason & Berry 1968). However, problems encountered in digesting monazite suggested that rarer forms of mineral phosphorus might not be fully recovered by these digestion procedures.

4 Conclusions

It was concluded that both digestion systems could recover total phosphorus satisfactorily from the 8 types tested. This would be a full recovery if apatite was the dominant form of primary mineral phosphorus in these soils, although direct evidence for this latter assumption was not available at the time. Forms of phosphorus which appear to be difficult to digest may be sufficiently scarce to suggest that they will rarely lead to a significantly low recovery. However, further work is required on soils containing non-apatite phosphate minerals to evaluate this point.

The paper ends with a caution. It was noted earlier that the sulphuric-peroxide digestion was adopted for vegetation because nitrogen can be determined in the same digest as is used for several other elements. This statement is valid for soil only as regards the estimation of nitrogen and phosphorus. Other mineral elements are not recovered from soil by wet digestion methods, unless hydrofluoric is present, because they are often bound up in silicates or other resistant minerals which, unlike phosphates, are largely insoluble in acids.

5 Summary

Two wet oxidation procedures are compared with regard to their effectiveness in the estimation of total phosphorus in soils. One method is a conventional procedure based on nitric, perchloric and sulphuric acids. The second is based on sulphuric acid and hydrogen peroxide, and has been widely used for plant materials but so far little used for soils. Eight soil types plus 2 mineral phosphate samples are examined and sample preparation is taken into account. Reference is made to a classical hydrofluoric plus perchloric acid procedure. The data suggest that a sulphuric-peroxide system is effective in assessing total phosphorus in soils.

6 References

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