THE STRENGTH OF NITRIC ACID, PERIOD OF EXTRACTION, AND IGNITION AS AFFECTING THE GRAVIMETRIC DETERMINATION OF PHOSPHORIC ACID IN SOILS

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The question of a good measure of the available phosphorus in soils has long confronted chemists. The earlier investigators thought that by taking a solution of approximately the same strength as the plant acids they ought to get a correct estimate of the available phosphoric acid. In Europe, Dyer's¹ method of 1 per cent citric acid was extensively used, while the American chemists used $N/200$ HCl. Veitch² extracted soil first with water and then with citric acid. Maxwell³ used 1 per cent aspartic acid. As was pointed out by Hall⁴ other factors entered into the determination, giving discordant results. Dargast⁵ had already shown that the amount of phosphoric acid varied very much with the solvent. For a given soil he got the following results, in percentages: Aqua regia, 0.108; ammonium oxalate, 0.056; ammonium citrate, 0.042; acetic acid, 0.018; saturated CO_2 , 0.015; and distilled water, 0.012. Moreover, it was shown that a given method might show low P_2O_5 in a soil which would still show a good crop yield. This led to the conclusion that a weak acid does not get all of the soluble phosphates. Wood⁶ showed that strong HNO_3 removed much more P_2O_5 than the weaker acids; for example, strong HNO_3 extracted from the soil 0.23 per cent; 1 per cent citric, 0.08 per cent; 1 per cent citric in excess of enough to neutralize the lime, 0.085 per cent P_2O_5 . Other things being equal, the crop yield showed general agreement with the amount of P_2O_5 determined by analysis, when the strong acids were used.

Still there is considerable diversity in the strengths of acids used for extraction. Passernini⁷ used concentrated HNO_3 , Williams⁸ used HCl (sp. gr. 1.115), and Fraps⁹ used $N/5$ HCl. In 1880 Professor Karl Schmidt showed that the amount of P_2O_5 extracted varied with the strength of HCl employed. With 10 per cent hot HCl he got 0.562; with 5 per cent cold HCl 0.09; with 1 per cent cold HCl 0.084, in a soil containing 1.97 per cent total P_2O_5 . The first part of the present investigation is to determine the strength of HNO_3 necessary to obtain all the soluble phosphoric acid, or that included by Hilgard under the term "reserve" material.

Not only in the case of strength of acid used in the extraction is there great diversity of practice among chemists, but also in the length of time used in extraction. Williams¹⁰ used concentrated HCl at the temperature of boiling water for ten hours. Sigmon¹¹ rotated for one-half hour and allowed to stand for 16

hours, then rotated one half hour again. Pagnoul¹ digested for two hours. The official method of the U. S. Dept. of Agriculture² is to add the HNO_3 and evaporate to dryness. Passernini³ boiled on the sand bath for 1 hour.

The second part of this investigation is to determine the minimum time for the extraction of the soluble phosphates. Fraps⁴ found that ignition increased the phosphate soluble in $N/5$ HCl in both soils and phosphate materials. Lipman,⁵ however, found that ignition decreased the phosphoric acid in soils which are soluble in nitric acid.

The third part of this investigation includes a study of the effect of ignition on the amount of P_2O_5 set free by extraction with HNO_3 .

SOILS USED—The soil was powdered up and passed through a 0.5 mm. sieve, and thoroughly mixed. Three soils of quite different P_2O_5 content were selected.

1—A very rich, black, fine, silty loam, rich in phosphoric acid and humus from Arroyo Grande, San Luis Obispo County, California.

2—A light, sandy loam, of fairly good humus and P_2O_5 content, from Anaheim, Orange County, California.

3—Heavy black adobe soil, low in humus and phosphoric acid, from Porterville, California.

METHOD—Weigh out 3 g. of air-dry soil and extract with HNO_3 on the steam bath. Filter and wash until washings give no acid reaction. Evaporate to dryness and heat residue at 130°C . for 2 hours. Extract with 20 cc. HNO_3 (sp. gr. 1.2). Filter and wash with warm water until the washings give no test for $\text{Ca}_3(\text{PO}_4)_2$. Add NH_4OH until a precipitate remains and dissolve in a couple of drops of HNO_3 . Warm and add ammonium molybdate and stand at $50-60^\circ$ for 12 hours. Filter and wash with solution of NH_4NO_3 in HNO_3 . Dissolve in NH_4OH and slowly add magnesia mixture to slight excess and stand over night. Filter and wash free from chlorides with a solution of 1 vol. NH_4OH , 1 vol. alcohol and 3 vol. H_2O . Dry in air bath and carefully ignite to constant weight.

STRENGTH OF NITRIC ACID—Samples of No. 1 were extracted with 50 cc. HNO_3 and the rest with 20 cc.

TABLE I—STRENGTHS OF ACID VARIED
Per cent P_2O_5 found in soil

Strength of acid	No. 1	No. 2	No. 3
15 N.....	0.517		0.067
8 N.....	0.518		
4 N.....	0.501	0.177	0.065
2 N.....	0.517	0.187	0.074
N.....	0.516	0.154	0.059
N.....	0.488	0.155	None

HNO_3 . They were all heated for two days on the steam bath, with a watch glass over the soil cup to prevent evaporation of the liquid. The percentages given are computed to the air-dry basis and are averages of three checks on sample No. 1, and two in the other cases, which, with the exception of three instances, did not differ by more than 0.01 per cent.

From Table I it appears that 2N HNO_3 will give

¹ Trans. Lond. Chem. Soc., 65 (1894), 115.

² J. Am. Chem. Soc., 21, 1090.

³ Ibid., 21, 415.

⁴ Trans. J. Chem. Soc., 39, 205.

⁵ Ann. Agron., 9, 470.

⁶ J. Chem. Soc., 69, 291.

⁷ J. Chem. Soc. Abs., 1911, p. 535.

⁸ U. S. Dept. Agr., Bull. 43, 387.

⁹ THIS JOURNAL, 5, 416.

¹⁰ J. Am. Chem. Soc., 17, 925.

¹¹ Ibid., 29, 929.

¹ Ann. Agron., 25, 554.

² Div. of Chem., Bull. 43, 387.

³ Chem. Abs. [2], 1911, p. 535.

⁴ Fraps, THIS JOURNAL, 5, 416.

⁵ C. B. Lipman, Ibid., 4, 663.

as much soluble phosphoric acid as any stronger solution. The normal acid shows a slight decrease in yield in the second and third soils, and the $N/5$ acid shows a decrease in every case. This agrees with the experience of Wood in that a certain strength of acid is necessary to get all the P_2O_5 . However, it is not necessary to use the concentrated acid as did Passernini. The stronger nitric acids indeed are objectionable because they introduce certain difficulties by bringing down larger quantities of iron and aluminum.

PERIOD OF EXTRACTION—In each case 20 cc. of normal acid were used, and the per cent of P_2O_5 given is an average of two closely agreeing checks.

TABLE II—PERIOD OF EXTRACTION VARIED
Per cent P_2O_5 found in soil

Period of extraction	No. 1	No. 2	No. 3
1 hr.....	0.499	0.166	0.053
2 hr.....	0.513	0.173	0.054
4 hr.....	0.501	0.166	0.068
8 hr.....	0.517	0.154	0.059

In one hour practically all the soluble P_2O_5 is obtained. Two hours would be a liberal allowance and sufficient for all cases. Passernini boiled for 1 hour, which is about enough, but Williams boiled on the water bath for 10 hours, which was much longer than necessary. Pagnoul digested for two hours, which was about the right length of time. Hilgard employed the two-day period for digestion with concentrated HNO_3 .

IGNITION—Each sample was extracted for 2 hrs. with 20 cc. $N HNO_3$.

TABLE III—TIME OF IGNITION VARIED
Per cent P_2O_5 found in soil

Ignition at red heat	No. 1	No. 2	No. 3
0	0.513	0.18	0.054
1/2 hr.....	0.499	0.199	0.046
1 hr.....	0.487	0.193	0.041

In these cases the effect of ignition would seem to be similar to that obtained by Lipman, *i. e.*, to decrease the amount of P_2O_5 soluble in HNO_3 . Sample No. 2 shows practically no change, but the other two show appreciable decreases in the amounts of P_2O_5 extracted, as the period of ignition lengthens and as between ignition and no ignition.

SUMMARY

I—Acid weaker than $1N$ to $2N HNO_3$ will not extract all the soluble phosphoric acid from a soil.

II—It is needless to extract with the acid for a longer period than 2 hours on the steam bath.

III—Ignition decreases the HNO_3 soluble phosphoric acid in the soils.

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COMPARISON OF SILICATES AND CARBONATES AS SOURCES OF LIME AND MAGNESIA FOR PLANTS

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The amount of calcium carbonate in soils has long been considered a very important consideration in their chemical examination; but calcium silicate has not been accorded universal recognition as an important source of lime for growing plants. The same may be said of the corresponding forms of magnesia.

In determining soil carbonates by the present official method of the Association of Official Agricul-

tural Chemists, we find that practically every soil has an *apparent* occurrence of carbonates, but at the same time possessing, in most cases of humid soils, a *lime requirement* by the Veitch method.¹ These two conditions—presence of appreciable amounts of carbonates and lime requirements, which indicate need of carbonates—are diametrically opposite, and were a soil to contain carbonates under laboratory conditions it would have no lime requirement. It is hard to conceive of a soil having 0.27 per cent calcium carbonate and yet having a lime requirement of 3812 lbs. of $CaCO_3$ per acre (3,500,000 lbs. of soil); however, such results were obtained by the A. O. A. C. method for CO_2 and the Veitch lime requirement method, respectively, upon the loam soil of the farm at this Station. This is strongly indicative of erroneous results from either one or possibly both of the methods cited.

The work of Marr² and the results reported by the writers³ have shown that some soils absolutely free of carbonates, through elimination by dilute acid digestion, will produce heavy evolution of CO_2 from the action of boiling acid upon carbonaceous matter. Marr concluded from his work that the use of 1:50 HCl , and boiling with greatly reduced pressure, gave correct results. Until recently, practically all of the methods advanced for the determination of soil carbonates were based upon the supposed necessity of boiling the soil with acid to completely decompose carbonates and to expel from solution the liberated CO_2 . The more recent work of the writers³ has demonstrated that phosphoric acid is less active than hydrochloric acid upon soil organic matter and that 1:15 H_3PO_4 will liberate and expel from solution all carbonate CO_2 at room temperature with about a 4-inch vacuum. In recent unpublished work the writers are making determinations upon treatments of about 400,000 pounds of limestone per 2,000,000 lbs. of soil and the carbonates from this treatment are entirely liberated by 1:15 H_3PO_4 with suction and without heat.

The Association of Official Agricultural Chemists has recognized the incorrectness of its method and is now studying the two methods above cited.

It will thus be seen that in many cases all of the CO_2 found by analyses of soils when boiling with acid has been erroneously considered as in combination with lime, while the lime has occurred largely in the form of silicates and not as carbonates.

CORRELATION BETWEEN ACIDITY AND ABSENCE OF CARBONATES

Gaither,⁴ in a comprehensive study of a large number of Ohio soils, found that almost invariably there was a close correlation between acidity, as indicated by the litmus-paper test, and absence of carbonates by his modification of the Marr method. We should probably note, however, that the authors have found that soils rich in silicates of calcium and magnesium,

¹ Jour. Am. Chem. Soc., 24 (1902), 1120.

² Jour. Agr. Sci., Vol. III, Part 2, 155-160.

³ Tenn. Sta. Bull., 100.

⁴ THIS JOURNAL, 5 (1913), 138.