Designation of the salt.	Boric acid. Per cent.	Grains per pound avoir.
Kansas No. 2 rock salt	0.005000	0.35
Foreign sea salt	0.010900	0.76
Foreign sea salt	0.006448	0.45
Cheshire salt	0.000992	0.07
XXX Casing salt	0.000620	0.0435
Kansas fine salt	0.000620	0.0435
Kansas rock salt No. 2	0.001240	0.0870
Louisiana rock salt	0.000992	0.06944

There is not a salt here but what would give a good qualitative test by the delicate method indicated in this paper, and some of them would show up under the less refined test of the steam-bath.

THE CUDAHY PACKING CO.,
SOUTH OMAHA, NEB.

[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

AVAILABILITY OF PHOSPHORIC ACID OF THE SOIL.[1]

BY G. S. FRAPS.

Received May 4, 1906.

THE availability of the constituents of a soil depends upon several factors. The chemical compounds which are capable of being absorbed by plants and are exposed to the action of the plant roots may be termed *chemically available.* The compounds enclosed in the soil grains, or otherwise protected from soil moisture or the action of plant roots, may be called *physically unavailable.* During the growing season of the plant, chemically or physically unavailable food is converted into chemically available forms. This may be termed *weathering availability.* Further, different plants have different powers of utilizing the plant food presented to them; this may be termed a *physiological availability.* All these factors are worthy of consideration in soil problems. Chemically available plant food has been given the greatest attention, but for success in solving the problems of the soil all factors must be considered and valued.

In seeking a method for the determination of chemically available phosphoric acid, several factors again must be considered: first, the solubility of the soil phosphates in the solvent; second, the solubility of other soil constituents; third, fixation by the soil; and fourth, availability of the chemically available plant food.

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[1] Read at the New Orleans meeting of the American Chemical Society.

Solubility of Phosphatic Minerals.—Phosphates of calcium, aluminum, and iron, the latter more or less basic, and the mineral apatite, are perhaps the most common phosphates in the soil, though vivianite, phosphorite, and, less often, phosphatic minerals, such as dufrenite, wavellite, triplite, and others may be present. These phosphates differ in the readiness with which they yield their phosphoric acid to plant roots, and, if possible, the solvent used for determining chemically available phosphoric acid should make some difference between them.

Dr. F. W. Clarke, Chief Chemist of the Geological Survey, considers that apatite makes up 99 per cent. of the phosphoric acid of igneous rocks. Vivianite is quite common in secondary clays as a mineral. Of course, in the soil, other secondary minerals are quite likely to occur, particularly in soils in which a portion of the phosphates have passed through plants.

The author determined the solubility of some mineral and precipitated phosphates in a few solvents, under the conditions of soil analysis. The method used was as follows:

The amount of material containing 0.2 gram phosphoric acid (equivalent to 100 grams soil containing 0.2 per cent. phosphoric acid) was brought in contact with 1000 cc. solvent, and maintained at 40° for five hours. It was then filtered, and phosphoric acid determined in 100 cc. of the filtrate by the volumetric method. The results are presented in Table I.

TABLE I.—PERCENTAGE OF PHOSPHORIC ACID PRESENTED DISSOLVED BY DIFFERENT SOLVENTS.

	N/200 HCl.	N/50 HCl.	N/5 HCl.	N/5 HNO_3.	1 Per cent. citric acid.
Aluminum phosphate precipitated	46.25	100	100	100	100
Calcium phosphate precipitated	100	100	100	100	100
Ferric phosphate precipitated	8.5	16.0	100	100	100
Phosphorite (Ca)	48.3	85	100	100	71
Wavellite (Al)	1.8	3.6	5.6	3.6	2.2
Vivianite (Fe)	28.0	36.0	100	97.8	94.8
Triplite (Fe, Mn)	16.8	41.2	98.8	99.5	25
Dufrenite (Fe)	0.8	2.0	4.0	1.5	2.0
Apatite (Ca)	15.8	47.0	100	100	25.5

Fifth-normal hydrochloric and nitric acids dissolve completely the precipitated phosphates of aluminum, calcium, and iron, and phosphorite, triplite, vivianite, and apatite. Wavellite and dufrenite are attacked only slightly.

One per cent. citric acid entirely dissolves the precipitated phosphates; it has only one-fourth the power of the mineral acids for apatite and triplite. It dissolves less vivianite and much less phosphorite than the mineral acids.

The high solubility of vivianite and triplite in the weak solvents is striking. According to these experiments, fifth-normal hydrochloric or nitric acid should dissolve from a soil containing 0.2 per cent. phosphoric acid, all the phosphorite, apatite, vivianite, triplite, and precipitated phosphates of calcium, aluminum and iron, with which the solvent comes in direct contact. These compounds are undoubtedly of different value to plants, but these acids make no distinction between them.

Fiftieth-normal hydrochloric acid has a greater solvent power than 1 per cent. citric acid for phosphorite, triplite and apatite, but not for vivianite or ferric phosphate. N/200 hydrochloric acid, as was to be expected, has the lowest solvent power.

As soils contain much less than 0.2 per cent. phosphoric acid soluble in N/5 mineral acids, and since decreasing the amount of phosphoric acid presented to the solvent should increase the *percentage* dissolved, the soil phosphates may have a higher solubility in N/50 and N/200 acid, or citric acid, than is indicated by the work just given. On the other hand, in these experiments the minerals were presented in fine powder, and all sides came in contact with the solvent. In a soil, part of the phosphatic material may be in the soil particles, so that only one side is exposed to the solvent.

Solubility of Other Soil Constituents.—The plant food in the soil is in part protected from plant roots and soil moisture by surrounding material, such as hydrated oxide of iron, carbonate of lime, mica, feldspar, etc. If any of these are dissolved, physically unavailable plant food is exposed to the solvent, and dissolves to a greater or less extent. It is impossible to select a solvent which does not have some action of this kind, and all practicable solvents dissolve the carbonates of lime and magnesia if present. For this reason the direct comparison of calcareous and siliceous soils does not appear allowable. If, for example, a calcareous and a siliceous soil expose the same amount of phosphoric acid to plant roots, on treatment with acid the calcareous soil would give up more phosphoric acid, as the carbonates, on dissolving, would expose an additional quantity of phosphates to the action of the solvent. The soil with the larger quantity of material soluble in the solvent used, would show a larger quantity of chemically available phosphoric acid than it really contains.

It might be necessary to divide soils into different classes, according to the amount of material soluble in the solvent used for determining available plant food.

The different amounts of phosphoric acid dissolved from the same soil by different solvents, must be due, in part at least, to their different powers of dissolving the silicates, oxide of iron, or other soil constituents which protect the phosphates.

Fixation by Soil Constituents.—If a solvent loses phosphoric acid to the soil, it is evident that it cannot be considered as reliable for determining the chemically available plant food. With such a solvent the solution obtained does not represent the solubility of the soil constituents, but contains the quantity dissolved less the quantity fixed. This consideration eliminates certain solvents, such as water, carbonated water, and acetic acid.

With *water* the phosphoric acid in solution represents a condition of equilibrium between the solubility of the soil phosphates and the fixing power of the soil. For example, the author[1] brought eight soils in contact with water and with a solution of potassium phosphate containing 4 parts of phosphoric anhydride per million. At the end of twenty-four hours, 3.1 and 2.5 parts per million, respectively, were present. Thus nearly the same result is obtained whether we start with water, or a solution of potassium phosphate. F. H. King[2] observed a great absorption in three minutes.

The aqueous soil extract does not represent the solubility of the soil phosphates in water; neither does it represent the strength of solution with which the roots come in contact. The solvent power of the water near the roots is increased by the carbon dioxide they excrete, and dissolved food may be taken up by the plant without ever coming in contact with fixing soil particles, and thereby having its strength reduced.

Carbonated water, according to P. Wagner,[3] loses phosphoric acid rapidly to carbonate of lime and hydrated ferric oxide, and a soil extract with carbonated water lost phosphoric acid in contact with the soil.

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[1] Bulletin 82, page 16, Texas Experiment Station (1906).

[2] Investigations on Soil Management, p. 159.

[3] J. Landw., 1871, 89.

Dilute *acetic* acid, according to Wagner and Gerlach,[1] behaves similarly to carbonated water.

Citric acid.—With 2 per cent. citric acid, Konig[2] recovered 73 to 84 per cent. of the phosphoric acid fixed by four soils. He also added different amounts of water-soluble phosphoric acid to soil and recovered all of it with the citric acid.

Experiments with Nitric Acid.—Solutions of N/50 nitric acid containing 0.2 gram phosphoric acid per liter were brought in contact with a number of materials, five hours at 40°. No absorption occurred with prehenite, siderite, hematite, or limonite. With 0.5 gram precipitated aluminum hydroxide per liter, 12.5 per cent. of the phosphoric acid was absorbed, and with ferric hydroxide, 25.5 per cent. Fixation during the treatment of a soil with this solvent thus appears possible; and still more probable with N/200 acid.

Availability of Phosphoric Acid in the Soil.—The most soluble phosphates placed in the soil are never completely removed by a single crop, so we cannot expect the natural phosphates of lime, etc., in the soil to have a high availability or approach 100 per cent. In other words, the chemically available phosphoric acid should be considerably more than is taken up by a single crop.

The writer made experiments on four soils of similar character, to determine the availability of chemically available phosphoric acid, assuming that the plant takes all its phosphoric acid from compounds soluble in N/5 nitric acid. These results are only comparative. In determining the availability of phosphatic fertilizers, the quantity of phosphoric acid recovered is not taken as the availability of the material, but is compared with one of the fertilizers taken as a standard. The same should hold good in the determination of the availability of the phosphoric acid in the soil, though a standard is difficult to decide upon. Tricalcium phosphate in pure sand might be used.

The experiments were carried out as follows:

Twelve and one-half pounds of each soil were placed in galvanized iron pots, which had previously received a layer of gravel. Each pot received 2 grams sodium nitrate, 5 grams calcium carbonate, and, after the plants had made some growth, 1 gram ammonium nitrate. In addition, one pot received 1.5 grams potassium sulphate containing 0.82 gram K_2O, a second 2.5 grams

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[1] Landw. Verss., 1905, 371.

[2] Ibid., 46, 201 (1896).

acid phosphate, containing 0.35 gram available phosphoric acid, and a third both potassium sulphate and phosphoric acid. Twelve cowpeas weighing 2.00 grams were planted in each pot on May 31st, came up June 2nd, and grew until August 4th, when the experiment was discontinued on account of red spiders. All leaves that fell off were saved. The pots were watered two or three times a week, weighing them from time to time to maintain an equal water content between the pots (40 to 80 per cent. of their water capacity).

At the end of the period, analysis was made of the plant, roots and seed, and phosphoric acid determined in the soil by N/5 nitric acid. The results are summarized in Table II.

TABLE II.—AVAILABILITY OF PHOSPHORIC ACID.

	Soil 174. Gram.	Soil 176. Gram.	Soil 178. Gram.	Soil 180. Gram.
Phosphoric acid in plant	0.0440	0.0302	0.0439	0.0340
Phosphoric acid in seed	0.0198	0.0198	0.0198	0.0198
Difference	0.0242	0.0104	0.0241	0.0142
In roots	0.0220	0.0136	0.0047	0.0060
Total from soil	0.0462	0.0240	0.0288	0.0202
	Per cent.	Per cent.	Percent.	Per cent.
Soluble in N/5 HNO_3 in soil	0.00235	0.00075	0.0028	0.0010
	Gram.	Gram.	Gram.	Gram.
In each pot	0.1333	0.0397	0.1587	0.0567
	Per cent.	Per cent.	Per cent.	Percent.
Comparative availability (entire plant)	35	60	17	28
Comparative availability (roots excluded)	18	26	15	23

The percentage of phosphoric acid soluble in N/5 nitric acid removed by the plants varies widely when the entire plant is considered; this is in part due to the difficulty in securing the roots from the soil, only a part of the roots being obtained from soils 178 and 180. When only the part of the plant above the surface is considered, the differences are less. The availability is greatest in the soil which contains the least chemically available phosphoric acid.

The high percentage of phosphoric acid soluble in N/5 nitric acid removed from these soils by cowpeas—particularly soil 176—leads one to question whether this solvent is not too weak. We could hardly expect 35 to 60 per cent. of the chemically available phosphoric acid to be absorbed by the plant.

Relation of Chemically Available Phosphoric Acid to Soil Deficiencies.—The amount of chemically available phosphoric acid present was compared with the soil deficiency as measured by pot tests with the cowpeas, with the striking result that the order of deficiency was found to be the order of chemically available plant food, and inverse order of the availability of the phosphoric acid.

TABLE III.—AVAILABILITY AND SOIL DEFICIENCY.

	Phosphoric acid.		Weight of crop. (Dry matter.)	
Soil.	In soil. Per cent.	Availability. (Roots excluded.)	With nitrogen and potash.	Phosphoric acid, nitrogen and potash.
176	0.0008	26	14.4	20.7
180	0.0010	23	15.7	20.1
174	0.0024	18	17.0	19.6
178	0.0028	15	20.9	20.1

It does not follow that the same results would be obtained in all types of soils, since different phosphates may be present. With 0.0028 per cent. P_2O_5 soluble in N/5 nitric acid, the soil was no longer deficient in phosphoric acid for cowpeas.

Physiological Availability.—Pot experiments with cotton, corn, rice, and cowpeas similar to those described above were carried on to compare the solvent powers of these plants for phosphoric acid. Only seven pounds of soil were used in this experiment. The rice soil was left saturated with water during the period of growth, while the other soils were treated as described before.

Cotton and cowpeas removed nearly the same quantity of phosphoric acid. Rice had a lower solvent power, and corn much lower. The results of the experiment are presented in Table IV. The soil contained 0.0021 per cent. phosphoric acid soluble in N/5 nitric acid, equal to 0.0666 gram per pot.

TABLE IV.—AVAILABILITY OF PHOSPHORIC ACID TO DIFFERENT PLANTS.

	Rice.	Cotton.	Cowpeas.	Corn.
Grams P_2O_5 taken up	0.0124	0.0200	0.0181	0.0032
	Per cent.	Per cent.	Per cent.	Per cent.
Relative availability	19	30	27	5
Crop produced:				
	Grams.	Grams.	Grams.	Grams.
With nitrogen and potash	5.4	5.7	12.4	4.0
With phosphoric acid, nitrogen and potash	15.0	13.7	12.7	36.3

It is seen from the size of the crop produced that the soil appears to be deficient in available phosphoric acid for rice, cotton, and corn, but not for cowpeas. Corn has the lowest solvent power, and phosphoric acid exerts its greatest effect in this plant. Cotton and cowpeas appear to have nearly the same solvent power, and take up nearly the same amounts of phosphoric acid, but the soil is deficient for cotton and not for cowpeas. This must be due to the cotton requiring more phosphoric acid than cowpeas. We must therefore consider not only the solvent power of the plants, but also their needs for the plant food in question.

The experiment just described brings out clearly the fact that the soil may be deficient in phosphoric acid for some crops, and not for others, and further shows that the deficiency is due not only to the different solvent power of plants for mineral phosphates (physiological availability), but also to difference in the amounts of phosphoric acid required for the growth of the plant. These factors have never been sufficiently regarded in studying the action of solvents upon soils, a soil being often considered as deficient or not deficient in phosphoric acid without regard to the crop used for the test.

Further experiments are required before the availability of phosphoric acid in the order given can be considered as true for all soils. Indeed, Gedroiz found varying relations with different soils in comparing several plants.

Weathering as Affected by Plants.—Still assuming that N/5 nitric acid dissolves the chemically available phosphoric acid of the soil, we determined the weathering effect of the plants on the soils. Subtract from the phosphoric acid (soluble in N/5 nitric acid) in the soil before planting, that present after the plants are removed, and the difference gives the loss (or gain) to the soil. Add the amount taken up by the plant, and we have the total amount rendered available. The results are given in Table V, expressed in per cent. of the amount originally present in the soil.

The amount of weathering depends upon the nature of the soil, being in these experiments proportionately more when the content of chemically available phosphoric acid is low.

The author[1] has found that moisture effects a slight average increase in the chemically available phosphoric acid (soluble in N/5 nitric acid) in three months. Calcium carbonate causes a decrease, calcium sulphate an increase, and decaying organic matter an increase. The weathering action of plants is very much greater than that of any of the other agencies studied.

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[1] Am. Ch. J. 32, 1 (1904).

TABLE V.—WEATHERING BY PLANTS AND AVAILABILITY.

Plant.	Soil.	Percentage increase by weathering. Per cent.	Comparative availability of phosphoric acid. Per cent.
Cowpeas	174	36	25
"	176	134	26
"	178	38	13
"	180	58	23
Cotton	.....	39	22
Corn	.....	24	4
Cowpeas	.....	42	19
Rice	.....	57	16

Comparing the plants on the same soil, the order of weathering, beginning with the most active, is rice, cowpeas, cotton, corn. Cotton and cowpeas are nearly the same. Rice acts vigorously.

The foregoing discussion is based on the assumption that all the phosphoric acid removed by the plant was soluble in N/5 nitric acid, which may not be entirely true, though no doubt partly true. Aside from this, however, the weathering action of the plant has undoubtedly changed marked quantities of phosphoric acid into chemically available forms, for more phosphoric acid is present as N/5 soluble after than before growing the plants, and a part of the phosphoric acid taken by the plant must have been in this form. Hence the plant has been active to convert a considerable part of the physically unavailable phosphoric acid into chemically available forms. This the plant could do by breaking down the soil particles, thereby exposing more phosphoric acid to the action of the solvent.

The comparative availability of the phosphoric acid has been calculated from the original content of the soil plus that rendered available by weathering. The results are presented in Table V. The comparative availability is high. We would not expect cowpeas to remove 13 to 26 per cent. of the phosphoric acid presented to them in the form of phosphates of calcium, iron or aluminum. Consequently, it would appear that N/5 nitric acid does not extract all of the chemically available phosphoric acid from these soils.

Pot Tests Compared with Chemical Tests.—The striking correspondence between the soil deficiencies as shown by the pot experiments with cowpeas and the chemically available phosphoric acid dissolved by N/5 nitric acid described in previous pages of this article led to the determination of phosphoric acid in a number of soils which had been subjected to pot tests. These pot tests were made at different times, and were only qualitative in scope, not being intended to measure the *extent* of any deficiencies. They are not strictly comparable.

These results are presented in Table VI. In most cases there is a relation between the amount of phosphoric acid, and the deficiency of the soil as measured by the ratio, crop without phosphoric acid divided by crop with phosphoric acid. The chief exception is soil 128.

TABLE VI.—POT TESTS AND PHOSPHORIC ACID SOLUBLE IN N/5.

		Nitric acid.	
Soil No.	Plant.	Phosphoric acid. Per cent.	Ratio of crop $\frac{\text{without}}{\text{with}}$ P_2O_5. Per cent.
97	Cotton	0.0007	42
108	"	0.0010	48
141	"	0.0018	66
137	"	0.0029	51
135	"	0.0029	84
128	"	0.0045	62
129	"	0.0065	28
131	Corn	0.0014	22
76	"	0.0022	51
176	Cow-peas	0.0008	70
180	"	0.0010	78
174	"	0.0024	86
178	"	0.0028	100
	"	0.0021	97
	Rice	0.0021	36
	Cotton	0.0021	44
	Corn	0.0021	11

Most of these soils are similar in nature. Some, however, are calcareous.

These experiments do not establish any standard for chemically available phosphoric acid in the soil. They do indicate, however, that the determination of chemically available phosphoric acid is of decided importance in soil analysis, and aids in detecting soil deficiencies, if due attention is paid to the nature of the soil, the kind of crop, and any characteristics which might retard or accelerate ordinary weathering of the soil. Extended series of careful pot experiments in a variety of soils, and much careful chemical work will be necessary before these relations are worked out in detail. Neglect of the other factors which should be considered may lead us astray, and cause us to condemn methods which might give valuable practical information.

SUMMARY.

(1) The factors to be considered in choosing a solvent for the chemically available phosphoric acid in the soil are (1) solubility of soil phosphates therein; (2) solubility of the soil constituents; (3) fixation by the soil; (4) availability of the chemically available food.

(2) Aluminum, calcium, and ferric phosphates, phosphorite, vivianite, triplite and apatite are completely soluble in N/5 hydrochloric and nitric acids under soil conditions. Some are completely soluble and others less soluble in N/50 HCl, N/200 HCl, and 1 per cent. citric acid.

(3) Other soil constituents, if dissolved, expose physically unavailable phosphoric acid to the action of the solvent, which thereby appears as chemically available. Calcareous soils must thus be placed in a different class from siliceous soils. It is necessary to group soils according to the amount of soluble matter they give to the solvent used for estimating available plant food.

(4) Where fixation takes place, the phosphoric acid in solution represents that dissolved less that fixed. The soil fixes phosphoric acid from water solutions, carbonated water, and acetic acid. Aluminum and ferric hydroxides fix phosphoric acid from N/50 nitric acid under the conditions of soil treatment, and it is possible that some phosphoric acid is removed by the soil from solution when this solvent is used.

(5) Since the soil phosphates are largely insoluble mineral phosphates, they cannot have a high availability; that is, the phosphoric acid extracted by the solvent must be considerably in excess of that consumed by the plant.

(6) Assuming that N/5 nitric acid is a correct measure of chemically available phosphoric acid, its availability was compared in four soils by means of pot experiments as follows: 35, 60, 17, 28 per cent. for the entire plant; 18, 26, 15, 23 per cent. for the aerial portion only.

(7) In the four experiments, the order of availability as measured by pot tests is the same as the order of chemically available plant food as measured by N/5 nitric acid.

(8) Physiological availability was compared in rice, cotton, corn and cowpeas. Corn had the lowest assimilative power, rice next, and cotton and cowpeas nearly equal; the soil was deficient

in phosphoric acid for rice, cotton and corn, but not for cowpeas. While cotton and cowpeas have the same solvent power, cotton needs more phosphoric acid in its growth.

(9) The sum of the phosphoric acid in the soil after growing the plants plus that in the plant, less the original content of the soil, is taken as the phosphoric acid made available by the plant. It varies from 24 to 136 per cent. of the original soil content in our eight experiments, thus varying widely according to the soil or the plant. No doubt, different soils are different in this respect.

(10) In experiments with 15 soils, there appeared to be a relation between the chemically available phosphoric acid as measured by N/5 nitric acid, and soil deficiencies as shown by pot tests.

(11) There is no doubt that the determination of chemically available plant food will give valuable indications as to the needs of soils in phosphoric acid, if due attention is paid to the factors which influence it, and to the other factors of availability.

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HIGH VACUA IN THE SCHEIBLER TYPE OF DESICCATOR.

BY H. C. GORE.

Received April 28, 1906.

THE ether-sulphuric acid method for obtaining high vacua in desiccators, which was invented by Benedict and Manning,[1] is shown by them to be of great value in the determination of water in foods and physiological preparations. The method consists essentially in expelling the air by evaporating ether in the desiccator under diminished pressure and subsequently removing the ether vapors by means of sulphuric acid. Vacua of less than 1 mm. of mercury are readily attained by this means.

The Hempel desiccator, in which the sulphuric acid is located in the upper part of the apparatus, has been the type of desiccator mainly used by Benedict and Manning. The main objection to this form, in the opinion of the writer, and one which it is believed will prevent its general use, lies in the fact that the sulphuric acid is apt to spill, particularly at the time when the

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[1] Am. Ch. J. 27, 340 (1902), and Am. J. Physiol. 13, 309 (1905).