

XV.—*On the Analytical Determination of probably available "Mineral" Plant Food in Soils.*

(*Illustrated by Examination of the Permanent Barley Soil of Hoos Field, Rothamsted.*)

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THE chemical analysis of soils, which in the early days of agricultural chemistry was looked upon as likely to be of very great practical use in agriculture, was soon found to be, as ordinarily practised, of very limited value. Determinations in the soil of the total quantities of the more important mineral elements of plant food have been long recognised as affording useful information only in exceptional cases: and even in these exceptional cases the results obtained have rather afforded "probable indications" than absolute information. Thus the fact that a soil contains much less phosphoric acid than is contained in average soils is a "probable indication" that it is in need of phosphatic manure; and the fact that another soil is much poorer in potash than average soils is regarded as a "probable indication" that it needs potassic manure; and in extreme cases these indications, read by experienced interpreters, may assume a degree of probability so great as to become all but certain. On the other hand, there are soils in which the proportions of total phosphoric acid or of potash are so large as to leave an experienced agricultural chemist no difficulty in forming an opinion that special applications to them of phosphates or of potash would be superfluous. But in the great majority of cases a soil analysis, as usually carried out, leaves us really in the dark, except as to such broad (and admittedly valuable) general facts as richness or poverty in lime, preponderance of sand or clay, or peat, &c.

The reason, as has often been pointed out, is that an analysis of soil, as ordinarily made, shows the total percentage of its constituents,

or, at any rate, the percentage dissolved by strong mineral acids, without reference to the fact that only a *very small proportion of this total may be available for plant use.*

For example, it is very usual to find about 0.15 per cent. of phosphoric acid in an ordinary average English agricultural soil. An average loamy soil, 9 inches deep, in its dry state, may, roughly, be said to weigh 1200 to 1500 tons per acre. Such a soil, containing 0.15 per cent. of phosphoric acid, would accordingly contain somewhere about 2 tons of phosphoric acid to the acre, disregarding the subsoil altogether. Such a soil contains as much phosphoric acid per acre as would be contained in about 17 tons of superphosphate, or in nearly 10 tons of bone-dust: and yet on such a soil the addition of a mere few hundredweights of phosphatic manure may make the difference between a full crop of turnips and a bad one! And similar statements would apply to other constituents of the soil.

The obvious and thoroughly well recognised explanation of such anomalies is that it is not the total proportion of phosphoric acid, or of potash, or of nitrogen, that rules a soil's fertility, but the proportion of each of them that is present in an *immediately available condition.* It is true that the presence of a large *total* of any constituent renders it, under many circumstances, *probable* that there is present a larger available quantity than is likely to exist where the total is small; but this merely brings us to the "probable indications" which have been referred to as generally all that are afforded by the ordinary soil analysis.

By far the greater part of the work done of late years in soil chemistry has had reference more especially to nitrogen, and quite an army of brilliant workers, at home and abroad, have engaged themselves on this branch of the subject.

Much less general attention has, however, been given to the mineral chemistry of the soil, no doubt for the reason that, both scientifically and economically, it is less interesting, and that its unsolved problems have lacked the magnitude of those which till lately were involved, and indeed may still be said to be involved, in the chemistry of nitrogen assimilation.

The desirability, however, of adopting, if possible, some mode of analysis that should distinguish between total mineral constituents and those small portions of them probably available as plant food has not only been recognised, but has formed the subject of many suggestions and of some investigation. Closely allied to this question is that of the "available" as distinguished from "total" ingredients in manures, and among those who have specially worked in the laboratory on one or both of these allied subjects from one point of view or another will be found the names of Berthelot,

Dehérain, Dugast, Eggertz, Fleischer, Fresenius, Grape, Gladding, Hilgard, Joulie, Lechartier, H. von Liebig, Lloyd, Luck, Maercker, Mallet, Neubauer, Nilson, Ollech, Petermann, Karl Schmidt, Stutzer, Thomson, Tollens, Voelcker, Vogel, P. Wagner, R. Wagner, Way, Wiklund, &c.; whilst a vast storehouse of data of information for future use has been accumulated, and is being yearly accumulated, in the field experiments of Lawes and Gilbert, at Rothamsted, followed up by those of late years carried on at Woburn by A. Voelcker and J. A. Voelcker.

Most of the memoirs touching these subjects published by the various authors have, however, had to do rather with manures than directly with soils, and for the moment it is proposed to select for consideration such work as has borne more directly on the question of soil analysis, so far as concerns phosphoric acid and potash.

The memoirs coming strictly under this head to be found in modern chemical literature are comparatively few.

The earliest paper of any importance that the author has been able to find is that of H. v. Liebig (*Zeitschrift d. Landwirth. Vereines*, 1872), who worked on soils obtained from the permanent wheat field at Rothamsted. The attention of the present author was directed to Liebig's investigation by Dr. (now Sir J. Henry) Gilbert, when some three or four years ago he discussed with him the lines on which it was proposed to pursue the investigation which forms the principal subject of the present paper. In the light of the results of the experiments since made with soils from other Rothamsted plots, plots not only more numerous, but experimentally nearly twenty years older, than those worked on by Liebig in 1872, it appears to be desirable to quote here some of Liebig's figures.

The specimens of soil used by Liebig were from Broadbalk Wheat-field, Rothamsted, and represented the 1st and 2nd depths of 9 inches each.

No. 3 soil had been continuously unmanured for nearly thirty years. Liebig determined in it several of the mineral constituents soluble in "dilute hydrochloric acid" and in "dilute acetic acid." As the present paper is concerned only with potash and phosphoric acid, it is unnecessary to quote Liebig's determinations of lime, magnesia, soda, &c.

The other soils were 10 A, which for nearly 30 years had received an annual dressing of 400 lbs. ammonia salts, without mineral manure; 5 A, which for a like time had received a complete annual dressing of mineral manures, without nitrogen; 7 A, which had received annually both 400 lbs. ammonia salts and a complete mineral manure; and 2, which had received an annual dressing of 14 tons of farm-yard manure.

The following are his results:—

	Potash soluble in "dilute hydrochloric acid."	Potash soluble in "dilute acetic acid."	Phosphoric acid soluble in "dilute nitric acid."
No. 3. Continuously unmanured.			
1st 9 inches	0·085	0·015	0·075
2nd 9 inches	Not determined	0·018	0·047
No. 10 A. Ammonia salts only.			
1st 9 inches	" "	0·013	0·076
2nd 9 inches	" "	0·019	0·047
No. 5 A. Mixed mineral manure without nitrogen.			
1st 9 inches	" "	0·038	0·108
2nd 9 inches	" "	0·022	0·058
No. 7 A. Mixed minerals and ammonia salts.			
1st 9 inches	" "	0·039	0·126
2nd 9 inches	" "	0·018	0·061
No. 2. Farm-yard manure.			
1st 9 inches	" "	0·041	0·093
2nd 9 inches	" "	0·026	0·065

These results afford indications that the investigation might have presented considerable interest had it been at the time systematically worked out. As it stands, however, its interest is greatly diminished owing to the facts that no information is given about the degree of dilution of any of the acids used; and that only in one case is any comparison afforded between the action of the two acids—of unknown dilution—used to extract the potash.

In 1880, Professor Karl Schmidt, of Dorpat, published a series of analyses of eight Russian soils, determining the total potash and phosphoric acid and also the percentages of these constituents soluble in hot 10 per cent. hydrochloric acid, cold 5 per cent. hydrochloric acid, and cold 1 per cent. hydrochloric acid. The following average results of his determinations on three soils will illustrate his general results:—

	Total.	Soluble in hot 10 per cent. HCl.	Soluble in cold 5 per cent. HCl.	Soluble in cold 1 per cent. HCl.
Potash.....	1·970	0·562	0·090	0·084
Phosphoric acid.....	0·171	..	0·051	0·049

In 1881, P. P. Dehérain observes (*Ann. Agron.*, 6, 392—393) that in the neighbourhood of Grignon phosphatic manures are found of no use. The soil, he says, does not contain more than an average quantity of phosphoric acid, but from one half to one quarter of the total phosphoric acid present is soluble in acetic acid. He thinks it may be true generally that soils which contain phosphoric acid removable by acetic acid will not be benefited by phosphatic manures.

Leaving chronological order for the moment, it is interesting to record that Dehérain has recently published—eleven years after the observations just cited—a further paper on this subject (*Ann. Agron.*, 17, 445—454). In plots, at Grignon, unmanured since 1875, he still finds 0·1 per cent. of phosphoric acid; yet on such plots a moderate dressing of phosphatic manure now suffices to nearly treble the yield of wheat, showing, in accordance with general observation and experience, that a soil fairly rich in its total mineral contents may nevertheless be exceedingly poor in *assimilable* mineral food. Pursuing the suggestion given in his earlier paper, viz., to use acetic acid as a means of diagnosing between assimilable and non-assimilable phosphates, he finds that, while the plots manured with phosphatic manures yield appreciable quantities of phosphoric acid to the action of acetic acid, the phosphate-exhausted soils yield only insignificant quantities. Plots that in 1879 contained as much as 0·03 per cent. of P_2O_5 soluble in acetic acid, and that have been continuously unmanured, now yield but traces.

In 1882, A. Vogel (*Bied. Centr.*, p. 852) suggests that if a sample of soil tested with acetic acid yields no indications of phosphoric acid, its percentage of phosphates should be regarded as abnormally low.

In 1884, Dugast (*Ann. Agron.*, 9, 470—478) publishes the results of an elaborate investigation into the composition of three soils (from Marché Neuf, Loire Inférieure), A, B, and C, which, in their cropping, show different degrees of fertility. The only points that need here be quoted are the comparative proportions of phosphoric acid extracted from A and B by various reagents as follows:—

Phosphoric acid (per cent. on fine dry soil) dissolved by						
	Aqua regia.	Ammonium oxalate.	Ammonium citrate.	Acetic acid.	Water saturated with CO_2 .	Distilled water.
A.	0·108	0·056	0·042	0·018	0·015	0·012
B.	0·072	0·048	0·034	0·013	0·013	0·011

There appears to be not very much here to lay hold of beyond the fact that the phosphoric acid exists in various conditions of solubility. (The phosphoric acid soluble in water is so enormously disproportionate to the water-soluble phosphoric acid found in fertile soils by the present author, that these numbers appear to him scarcely credible, unless perhaps in the case of soils containing an enormous quantity of vegetable remains, which does not appear to have been the case here.)

In the same year (1884), G. Lechartier (*Compt. rend.*, **98**, 1058—1061) suggests that a 2 per cent. solution of ammonium oxalate may be used as a means of determining the degree of solubility of the fertilising constituents of a soil.

In 1889, Eggertz and Nilson (*Bied. Centr.*, 1889, 664—668) published experiments indicating that extraction of a soil with hydrochloric acid of 2 per cent. strength so far removed available plant food that barley could not grow in the washed soil, while extraction with 4 per cent. acid rendered it sterile to oats.

In 1892 (*Landw. Jahrb.*, **20**, 909—923), Wiklund published a work in the same direction, and expresses dissatisfaction with the method of Eggertz and Nilson as one for general adoption. He deals, however, mainly with the distinction between organic and inorganic phosphorus and sulphur in the soil.

Lately, Berthelot and André have worked a good deal (see various papers in *Comptes rendus*) at the subject of the condition of the mineral ingredients of the soil, but apparently with more negative than positive results, so far as regards any conclusion as to the best mode of distinguishing between available and non-available plant food.

The classical experiments of Way and A. Voelcker on the action of various saline solutions on soils, which are to be found in the back volumes of the *Journal of the Royal Agricultural Society*, are familiar to most agricultural chemists. They dealt rather with the power of soils to retain various manurial substances added to them, and with the liberation of locked-up plant food by the action of such indirect manures as soda salts, than with means for distinguishing between "available" and "latent" mineral "food."

The literature of agricultural chemistry has become a wide one, and there are no doubt in existence many other contributions to this particular branch of soil chemistry. The papers that have been referred to, however, include all of any considerable importance that the present author has been able to find. Many papers, however, as has been already said, exist on the kindred question of the assimilability of manures, which will be referred to in a later section of this

paper, the attention of the reader being, for the present, directed rather to the soil.

It may be said to have been pretty widely recognised that some very much weaker solvent than strong mineral acid ought to be used in soil analyses, if these are to be of much use as indications of the proportion of available mineral plant food. Most of the suggestions made have, however, been arbitrary in the sense of not having any definite, or at any rate not any defined, basis beyond the recognised necessity that the solvent should be *weak*—weak, that is to say, compared with concentrated mineral acids.

For the commercial distinction between phosphates presumed to be presently available and those presumed to be not presently available *in manures*, it has for some years been customary in some Continental countries, and also in America, to use as a solvent an ammonium citrate solution, originally, no doubt, because “precipitated” phosphate, known from experience to be a readily available plant food, is soluble in such a solution. But much discussion has been spent on the point, and great diversity of views expressed, although in certain countries agreements have been come to for the arbitrary use for such purposes of citrate solutions of prescribed strengths and degrees of acidity or alkalinity.

In 1884, Stutzer (*Chem. Ind.*, 1884, Feb.) raised an emphatic protest against the, by that time, widely accepted use of a strong solution of ammonium citrate as a means of estimating available phosphoric acid in manures, while granting that it might well serve to determine “precipitated” phosphate. He accordingly experimented with *citric acid*, which had been previously suggested by Tollens (*Journal für Landwirt.*, 30. Bd.)* on various phosphatic materials in use as manures. The details of Stutzer's results need not here be given, since they deal not with the soil itself, but with manurial materials, the consideration of which for the moment is deferred. It suffices here to say that Stutzer's results showed that while there was in many cases but little coherence between the fertilising value of phosphatic materials as determined by practical experience and their solubility in ammonium citrate, there was, on the other hand, a much more satisfactory correspondence between their solubility in weak citric acid and their known manurial efficacy. The strength of the solution Stutzer employed in his experiments was 1 per cent., *i.e.*, 10 grams of citric acid per litre of water. He suggested that such a solution might best be adopted as a test of the probable solubility of

* This journal is not in the Library of the Chemical Society, and Tollens' paper is not reproduced in contemporary journals, so that the present author has not had the advantage of consulting the original.

manures in the soil (Bodenlöslichkeit). A. Thomson later (*Chem. Ind.*, 1885) endorsed Stutzer's suggestions. Neither Stutzer nor Thomson, however, appears to give any reason for the strength of citric acid solution adopted, beyond the fact that the results obtained with a solution of this strength (1 per cent.) showed a fair correspondence with the comparative efficacy accredited by practical experience to the fertilisers examined.

The general question of solvents as bearing on soil analysis was taken up in 1884 by the present author, and has from time to time been the subject of a good deal of intermittent work. Much of this was tentative and disappointing, and its results not worth transcribing. Some of the earlier experiments may, however, be recorded before passing on to the more systematic enquiry to which they led up.

PRELIMINARY EXPERIMENTS.

Among these earlier tentative experiments were determinations of solubility in various solvents of the phosphoric acid and potash contained in a clay soil from the neighbourhood of Tewkesbury. It was a soil about which the author had no very special information. It happened to be sent to him for advice or suggestions as to manurial treatment, with the information that it had been lately cropped with beans after wheat, following vetches heavily manured with dung and fed off with cake-fed sheep. Beyond these facts, and those ascertained by its analysis, the author had no information, and the soil was used for these tentative experiments merely because there happened to be a large bulk of the sample, and because it was a fair average specimen of a good heavy clay soil, with a good deal of reserve mineral food in it. On account of this very limited knowledge of its history and capabilities, any such interest as attaches to the soil experiments to be described later is not to be expected, but, as far as they go, the facts ascertained as to the condition of solubility of some of the constituents are chronicled for what they are worth.

The dry soil subjected to a tolerably complete analysis was found to contain, per cent. :—

	Soluble in HCl without incineration of soil.	Insoluble in HCl before incineration, but rendered soluble by incineration.	Insoluble in HCl, even after incineration.	Total.
Silica	—	—	—	70·745
Oxide of iron	4·320	0·360	0·313	4·993
Alumina	4·749	3·400	3·272	11·421
Lime	0·873	0·123	0·367	1·363
Magnesia	0·860	0·160	0·164	1·184
Potash	0·544	0·355	0·913	1·812
Soda	0·138	none	0·439	0·577
Phosphoric acid	0·211	—	—	—
Sulphuric acid	0·151	—	—	—

The solubility in water of the more important constituents was determined in each case by shaking up a weight of air-dried soil corresponding to 250 grams of dry soil with 1000 c.c. of water in a stoppered bottle, and allowing to stand with occasional agitation. At the conclusion of each experiment, an aliquot part of the liquid was filtered, and the clear liquid evaporated for analysis.

Percentage (in the dry soil) of Constituents dissolved by Distilled Water.

$$\frac{\text{Water}}{\text{Soil}} = \frac{4}{1}.$$

	In 2 days.	In 8 days.	In 28 days.
Phosphoric acid	0·0006	0·0006	0·0006
Potash	0·0046	0·0058	0·0059
Soda	0·0060	0·0139	0·0111
Lime	0·0302	0·0382	0·0637
Magnesia	0·0040	0·0040	0·0080
Sulphuric acid	—	0·0288	—

The question afterwards arose as to how far the quantity of water used might be responsible for variations in experimentally indicated water solubility.

Fresh experiments therefore were made in the same way, but using varying quantities of water.

Dissolved by Water in 8 days.

	$\frac{\text{Water}}{\text{Soil}} = \frac{2}{1}$	$\frac{\text{Water}}{\text{Soil}} = \frac{4}{1}$	$\frac{\text{Water}}{\text{Soil}} = \frac{10}{1}$
Phosphoric acid.....	0·0007	0·0009	0·0018
Potash.....	0·0035	0·0050	0·0077
Soda.....	0·0056	0·0059	0·0121
Lime.....	0·0955	0·1025	0·1148
Magnesia.....	0·0070	0·0050	0·0200

Evidently the quantity of water used for a given weight of soil produces variations which, if there were any object in pursuing such a mode of soil examination, would render it desirable to work under definite conditions. Probably the frequency of agitation would also bring about discrepancies (and there are some discrepancies here) when dealing with such small figures. Temperature too should have been regarded. As in each case the experiments were made at the ordinary temperature of the laboratory, and as some months elapsed between the first and second set of water solubility determinations, some of the differences may be due to this. This point, however, is of little consequence, since mere water solubility is not an index of fertility.

An attempt was next made to determine the solubility of the various constituents in carbonic acid water. Accordingly, a set of experiments was made precisely like the last, except that the water used was saturated with carbonic acid.

Constituents Dissolved by a Solution of CO₂ in Water. $\frac{\text{Water}}{\text{Soil}} = \frac{4}{1}$

	In 2 days.	In 8 days.	In 28 days.
Phosphoric acid.....	0·0010	0·0007	0·0009
Potash.....	0·0067	0·0085	0·0073
Soda.....	0·0139	0·0150	0·0087
Lime.....	0·1204	0·1266	0·2072
Magnesia.....	0·0150	0·0120	0·0300

Later, the following determinations were made of the quantity of phosphoric acid dissolved from this soil by solutions of ammonium citrate.

The ammonium citrate was made from specially purified citric acid. In each case a quantity of air-dried soil equal to 250 grams of dry soil was shaken up with 1000 c.c. of water containing ammonium citrate, rendered alkaline by the addition of 25 c.c. of 0·880 ammonia.

The liquid remained in contact with the soil for seven days (in late spring) with frequent shaking.

Ammonium Citrate Experiments.

	Solvent = 4 Soil = 1	Per cent. on the soil.	
		Phosphoric acid.	Potash.
Water only		0·0009	0·0050
Water and ammonia only		0·0034	0·0047
0·1 per cent. alkaline solution of ammonium citrate.....		0·0036	0·0059
0·25 " "		0·0042	0·0079
0·5 " "		0·0046	0·0089
1·0 " "		0·0056	0·0139
2·5 " "		0·0080	0·0156
5·0 " "		0·0090	0·0212
10·0 " "		0·0131	0·0253
15·0 " "		0·0161	0·0268
20·0 " "		0·0154	0·0261
30·0 " "		0·0194	—
40·0 " "		0·0220	0·0223
50·0 " "		0·0260	0·0223

Some similar determinations of solubilities were also made in a clay loam soil from the neighbourhood of Chelmsford—the soil, indeed, of Mr. Rosling's farm, on which have been carried out for some years, with the co-operation of the author, the various series of field experiments made for the Essex Agricultural Society.

This soil, on analysis, yielded the following results, the solvent, except for Cl and N₂O₅, being the usual one, viz., hydrochloric acid acting on the incinerated soil:—

Fine Soil, Dried at 212° Fahr.

Silica and silicates insoluble in hydrochloric acid..	86·480
Oxide of iron.....	3·721
Alumina.....	3·202
Lime.....	0·571
Magnesia	0·319
Potash	0·305
Soda.....	0·074
Carbonic acid.....	0·121
Phosphoric acid.....	0·141
Sulphuric acid.....	0·031
Nitric acid	0·001
Chlorine.....	0·002
*Organic matter, water of combination, &c.....	5·032

100·000

* Containing nitrogen, 0·176.

The farm was one that had for some years been kept in good condition by careful farming and liberal manuring, and the particular field sampled showed itself able, in the year in which this sample was drawn, to produce some 16 tons of mangolds per acre, without the addition of any manure, after a preceding crop of oats. This shows it to have been pretty rich in available mineral food as well as in nitrogen.

Determinations of the phosphoric acid and potash, soluble in ammonium citrate solutions of various strengths, were made (as in the case of the soil already mentioned) with the following results:—

Ammonium Citrate Experiments.

Solvent = $\frac{4}{1}$ Soil = $\frac{1}{1}$ Time of contact 7 days.	Per cent. on the dry soil.	
	Phosphoric acid.	Potash.
Water only	0·0003	0·0011
Water and ammonia only	0·0036	—
0·1 per cent. alkaline solution of ammonium citrate..	0·0047	—
0·25 " "	0·0046	0·0037
0·5 " "	0·0060	—
1·0 " "	0·0084	0·0077
2·5 " "	0·0128	0·0054
5·0 " "	0·0140	0·0065
10·0 " "	0·0149	0·0093
15·0 " "	0·0163	0·0077
20·0 " "	0·0207	0·0082
30·0 " "	0·0232	0·0104
40·0 " "	0·0237	0·0097
50·0 " "	0·0248	0·0110

These results are, on the whole, not dissimilar from those obtained with the Tewkesbury soil, except in potash, in which constituent the Tewkesbury soil was much richer.

At about this time the author had become convinced, by experiments of his own on phosphatic manures (see later), that the contention of Stutzer was right, and that the solvent action of an ammoniacal salt did not give a reliable index of availability. Weak organic acid had shown itself to give far more consistent and intelligible results with manures, and why not with soils, as suggested by H. v. Liebig, Dehérain, and others already quoted? But the first difficulty to be met—a very considerable one, as shown by the following experiments with the Chelmsford soil—was to decide the strength (or weakness) of the acid to be used.

Citric Acid Solution Experiments.

	$\frac{\text{Solvent}}{\text{Soil}} = \frac{40}{1}$	Phosphoric acid (per cent. on dry soil).
0.125 per cent. citric acid solution.....		0.0200
0.25 " " 		0.0250
0.5 " " 		0.0264
1.0 " " 		0.0312
2.5 " " 		0.0728
5.0 " " 		0.0896
	$\frac{\text{Solvent}}{\text{Soil}} = \frac{20}{1}$	
0.25 per cent. citric acid solution.....		0.0197
	$\frac{\text{Solvent}}{\text{Soil}} = \frac{20}{1}$	
0.5 per cent. citric acid solution.....		0.0193
	$\frac{\text{Solvent}}{\text{Soil}} = \frac{10}{1}$	
1.0 per cent. citric acid solution.....		0.0161

It is obvious that if citric acid be used the variations are great, as might be expected, in accordance with the degree of dilution and the proportion of acid to soil, at any rate where the contact with the soil is of short duration, as in the case of these last enumerated experiments, in which *only three days* were allowed.

Seeing that the end in view was a means of distinguishing between matter that a plant can take up and matter that a plant cannot take up, the possibility suggested itself of arriving at some conclusion from a closer study of the means by which a plant collects its mineral food. The mere solvent action of water, or even of water saturated with carbonic acid, at all events of the very limited quantity of water that exists in even a wet soil, is altogether insufficient to account for the solution of all the mineral plant food required by a crop. No doubt the action of decaying organic matter and of "humic" and "ulmic" acids, &c., produces some effect, but it seems probable that, useful as humus is in a soil for many purposes, the solvent action of its decomposition products on the minerals of the soil in actual fact has been overrated, and that the chief solvent agent for soil minerals is the root sap of the plant.

EXPERIMENTS ON THE ACIDITY OF ROOT SAP.

It has long been accepted as a fact that plants help themselves to a part of their mineral food by means of the solvent action of their

acid root sap on the particles of soil with which the rootlets come into contact. The observations most frequently quoted in support of this are the classical ones of Sachs, who showed that the acid of the root sap was sufficient to etch, by its corrosive action, the surface of polished marble buried beneath the soil.

But the mere observation that roots have an acid sap is much older than any recognition of the significance of their acidity. For example, Philip Miller (gardener to the Society of Apothecaries) wrote in 1733:—"When the juice enters the root, it is earthy, watery, poor, and acid." He also speaks of "that *tart* liquor oozing from the root of the walnut tree when cut off in the month of May."

The subject of the acidity of root sap and of its solvent action on certain soil constituents, but more especially on nitrogenous organic matter, is dealt with at some length in the paper "On the Present Position of the Question of the Sources of Nitrogen of Vegetation," published in 1889 in the *Phil. Trans.*, by Sir John Lawes and Sir Henry Gilbert. I have since learned from Sir Henry Gilbert that, in the course of their investigation, the authors experimented on the acidity of the root sap of about 75 different plants. None of the quantitative determinations, however, have been published, and few, if any, other attempts appear to have been made to determine the *degree* of acidity of root sap. In order, therefore, to obtain some information on this point, the determinations that are now recorded were undertaken.

The plants were, as far as possible, taken at a time when they were in vigorous growth. Gramineous plants—cereals and grasses—were selected just before, or in the first stage of, inflorescence, and so also were leguminous plants. Potato plants were taken when the tubers were beginning to develop, mangolds and turnips when the bulbs had developed to a diameter of 1 to 2 inches, and cabbages and other crucifers at a corresponding stage of growth. In addition to ordinary agricultural plants, a large number of garden plants were examined—annuals, biennials, and perennials—all being taken, as far as was practicable, during active growth.

The author desires here to tender his special thanks to Messrs. Sutton and Sons, Reading, for kindly placing at his disposal their pure cultivation plots of grasses and clovers, from which separate growths of the chief pasture grasses were obtained.

The problem of ascertaining the acidity of the root sap is by no means a simple one. In the case of large, fleshy, tuberous, or bulbous roots, it is, of course, easy to express the juice. But the examination of such juice does not necessarily throw much light on the real question under investigation, because it is the acidity of the sap, not of the main or tap roots, but of the small roots and rootlets, which

determines the soil-solvent functions of the plant. It by no means follows that we know the acidity of the rootlet sap when we know the acidity of the juice of the fleshy tap root from which the rootlets spring. To mechanically express the sap from fine roots and rootlets is practically impossible.

It is necessary, therefore, to proceed in some other fashion, and it is not easy to find one that is free from objection. The rootlets of most plants form a matted mass which clings intimately to the soil, and, seeing that soil abounds in basic substances, it is necessary to free the rootlets from the adherent particles. The plan finally adopted was to dig up a large block of the soil in which the plant was growing (or, in the case of pot-grown plants, to take the whole potful of earth and roots), and to rapidly wash the earth off with a good flow of water over a bowl. After a little practice, it is not difficult to effect the washing very rapidly and without much bruising of the roots. After the removal of the earth, the mass of moist roots and rootlets is lightly disentangled and freed from external moisture by pads of blotting paper and by blowing on the roots with bellows. When the roots no longer moisten new blotting paper, they are taken as "dry." In living and unbruised roots, the probability of losing soluble constituents during the process of rapid washing is small, because transfusion through the walls of living cells takes place very slowly, and even the vessels whose open ends may be exposed to the water are of such capillary fineness that there is little likelihood of rapid diffusion taking place. At all events, no better method of obtaining the rootlets free from soil and in a condition likely to be little changed presented itself.

A portion of the externally dry roots and rootlets is weighed and dried in the water oven. The moisture determined by loss in weight is taken as a sufficient approximation to the original "moisture" of the roots to furnish a basis for calculation of the sap.

Another portion of the roots is quickly snipped up with scissors (not "minced," so as to expose any material portion of the sap to the action of the metal) and boiled in distilled water for some time. The liquor is then strained off, and the exhausted rootlets rubbed to a pulp in a porcelain mortar, and again boiled. The total extract is boiled down to a small bulk to boil off carbonic acid, and the fixed acidity taken by titration with standard alkali, using phenolphthalein as an indicator.

After a good many determinations had been made in this way, it was thought possible that a more rapid and satisfactory extraction might be made if the *dried* rootlets could be used, as transfusion would be necessarily more easy. In a large number of cases, therefore, the portion dried for the moisture determination was ground to

powder in a mortar—a very quick process in the case of the crisp dry roots—and the powder boiled with water, and the decoction concentrated. It is not necessary to filter or pour it off, as neither the dark colour nor the turbidity interferes with the reading when so strongly reacting an indicator as phenolphthalein is used. In most cases the determination of acidity in the dried roots agreed very well with that in the moist roots, and in future it would probably be adopted as more convenient. Of course it is open to the objection that some mutually destructive action may occur between organic acids and the various other organic substances present when dried together, but the drying occurs very rapidly, and the total quantity to be determined is so very small, that even a considerable percentage error in the total acid present would little affect the percentage on the sap.

On the whole, although the whole process may be scientifically open to some objections, it appears sufficient to afford a fairly approximate idea of the percentage of total fixed acidity in the roots, and the moisture being known, the acidity for 100 parts of moisture may be taken as giving some approximate figure for the "sap acidity" of the roots.

No attempt has been made in any of these experiments to identify the acid to which the acidity was due. Probably, a considerable variety of organic acids exist in the rootlets of a single species, and in different orders of plants different acids would predominate. For the special purpose the author had in view, it was convenient to calculate the acidity into the form of citric acid, but in the record of results now given the acidity is also stated in terms of hydrogen.

In each case will be found stated—

- i. The percentage of moisture in the root.
- ii. The percentage of acidity in terms of hydrogen.
- iii. The percentage of acidity in terms of citric acid.
- iv. The ratio of acidity to 100 parts of moisture ("sap acidity") in terms of hydrogen.
- v. The ratio of acidity to 100 parts of moisture ("sap acidity") in terms of citric acid.

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).			"Sep acidity" of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.	
RANUNCULACEÆ.						
<i>Caltha</i> (Marsh Marigold)	71.0	0.0116	0.81	0.0163	1.14	
" "	70.9	0.0113	0.79	0.0159	1.41	
CRUCIFERÆ.						
<i>Brassicæ</i> —						
White Turnip (half grown)	88.6	0.0087	0.61	0.0099	0.69	
" "	81.0	0.0083	0.58	0.0103	0.72	
White Turnip (very young)	86.8	0.0061	0.43	0.0070	0.49	
White Turnip—another year:—						
" Bulb" (about 1 inch in diameter)	91.6	0.0066	0.46	0.0073	0.51	
Fine roots	86.4	0.0075	0.52	0.0089	0.62	
Swede Turnip—						
" Bulb" (about 3 inches in diameter)	89.6	0.0041	0.29	0.0053	0.37	
Fine roots	85.1	0.0054	0.38	0.0063	0.44	
Field Cabbage—						
Thick roots	82.1	0.0047	0.33	0.0059	0.41	
Fine roots	82.8	0.0084	0.59	0.0101	0.71	
Garden Cabbage	70.0	0.0100	0.70	0.0143	1.00	
Brussels Sprouts	70.0	0.0073	0.51	0.0104	0.73	
" "	73.7	0.0081	0.57	0.0142	0.78	
Broccoli	67.4	0.0103	0.72	0.0153	1.07	
" "	67.8	0.0080	0.66	0.0122	0.85	
Collards	73.4	0.0064	0.45	0.0087	0.61	
" "	72.0	0.0091	0.64	0.0126	0.88	
Rape	82.2	0.0053	0.37	0.0065	0.43	

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).		"Sap acidity" of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.
CRUCIFERÆ.					
<i>Cochlearia</i> (Horse-radish)	62.0	0.0126	0.88	0.0203	1.42
<i>Alyssum</i>	70.6	0.0140	0.98	0.0197	1.38
"	71.4	0.0143	1.00	0.0200	1.40
<i>Cheiranthus</i> (Wall Flower)	69.5	0.0086	0.60	0.0123	0.86
"	67.0	0.0111	0.78	0.0166	1.16
<i>Matthiola</i> (Stock)	78.5	0.0084	0.59	0.0109	0.76
"	83.3	0.0084	0.59	0.0102	0.71
<i>Lunaria</i> (Honesty)	83.9	0.0120	0.84	0.0143	1.00
CARYOPHYLLACEÆ.					
<i>Lychnis</i> (Scarlet)	71.1	0.0096	0.67	0.0124	0.87
"	76.3	0.0135	0.94	0.0163	1.14
<i>Dianthus barbatus</i> (Sweet William)	75.8	0.0083	0.58	0.0109	0.76
"	74.7	0.0086	0.60	0.0114	0.80
TROPEOLACEÆ.					
<i>Tropæolum</i> (Nasturtium)	82.1	0.0067	0.47	0.0081	0.57
LEGUMINOSÆ.					
<i>Trifolium incarnatum</i> (pot grown)	65.1	0.0119	0.83	0.0183	1.28
<i>T. repens</i> (White Clover) (pot grown)	84.0	0.0050	0.35	0.0060	0.42
" (field grown)	69.5	0.0143	1.00	0.0204	1.43
<i>T. pratense</i> (Red Clover) (pot grown)	79.6	0.0065	0.45	0.0080	0.56
" (field grown)	70.5	0.0157	1.10	0.0222	1.53

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).		" Sap acidity " of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.
LEGUMINOSÆ.					
<i>Pisum</i> (Garden Pea) (pot grown)	89.6	0.0043	0.30	0.0049	0.34
<i>Faba</i> (Broad Bean) (pot grown)	93.1	0.0072	0.50	0.0077	0.54
" " (field grown)	70.0	0.0072	0.50	0.0102	0.71
" " (field grown)	79.5	0.0127	0.89	0.0159	1.11
ROSACÆ.					
<i>Geum</i>	66.7	0.0527	3.69	0.0790	5.53
"	70.7	0.0429	3.00	0.0606	4.24
<i>Fragaria</i> (Strawberry)	78.1	0.0219	1.53	0.0280	1.96
"	81.7	0.0217	1.52	0.0266	1.86
ONAGRACÆ.					
<i>Echinochloa</i> (Evening Primrose)	73.3	0.0220	1.54	0.0300	2.10
"	78.2	0.0220	1.54	0.0282	1.97
UMBELLIFERÆ.					
<i>Pastinaca</i> (Parsnip)	73.4	0.0072	0.50	0.0972	0.68
<i>Daucus</i> (Carrot)	90.2	0.0040	0.28	0.0047	0.33
<i>Petroselinum</i> (Parsley)	83.9	0.0077	0.54	0.0092	0.64
"	83.0	0.0072	0.50	0.0087	0.60
<i>Apium</i> (Celery)	84.7	0.0133	0.93	0.0458	1.10
ARALIACÆ.					
<i>Hedera</i> (Ivy)	64.7	0.0098	0.68	0.0150	1.05
"	69.1	0.0069	0.48	0.0100	0.70

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).		" Sap acidity " of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.
DIPSACEÆ.					
<i>Scabiosa</i> (Scabious).....	82.3	0.0052	0.36	0.0063	0.44
"	83.7	0.0050	0.35	0.0063	0.44
COMPOSITEÆ.					
<i>Helianthus</i> (Artichoke).....	74.0	0.0080	0.56	0.0109	0.76
"	77.1	0.0085	0.59	0.0109	0.76
<i>Cichorium</i> (Endive).....	79.8	0.0062	0.43	0.0077	0.54
"	79.6	0.0053	0.37	0.0066	0.46
CAMPANULACEÆ.					
<i>Campanula</i> (Large Garden)	76.7	0.0075	0.52	0.0097	0.68
"	77.9	0.0062	0.43	0.0079	0.55
BORAGINACEÆ.					
<i>Mysotis</i> (Forget-me-not).....	81.3	0.0116	0.81	0.0143	1.00
SOLANACEÆ.					
<i>Solanum tuberosum</i> (Potato)	87.1	0.0041	0.29	0.0049	0.34
SOPHULARIACEÆ.					
<i>Ferunica</i> (Speedwell).....	71.3	0.0119	0.83	0.0167	1.16
<i>Digitalis</i> (Foxglove)	78.4	0.0053	0.37	0.0067	0.47
"	74.4	0.0061	0.43	0.0082	0.57

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).		" Sap acidity " of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.
PRIMULACEÆ.					
<i>Primula</i> (Polyanthus)	73.5	0.0077	0.54	0.0104	0.73
"	76.6	0.0069	0.48	0.0090	0.63
PLUMBAGINEÆ.					
<i>Amelia</i> (Thrift)	66.8	0.0230	1.61	0.0834	2.34
"	67.5	0.0196	1.37	0.0290	2.03
(CHENOPODIACEÆ.)					
<i>Spinacea</i> (Winter Spinach)	87.4	0.0089	0.62	0.0100	0.70
<i>Beta</i> —					
Sugar Beet.....	84.8	0.0059	0.41	0.0069	0.48
Red Chili Beet	82.8	0.0071	0.50	0.0086	0.60
Yellow Chili Beet.....	94.6	0.0053	0.37	0.0056	0.39
Red Mangold (pot grown)	84.3	0.0083	0.58	0.0099	0.69
Orange Tankard Mangold (pot grown)	86.6	0.0076	0.53	0.0087	0.61
" " " (field grown) —					
" " " (about 2 inches in diameter).....	86.0	0.0031	0.22	0.0036	0.25
Fine roots	81.4	0.0054	0.38	0.0066	0.46
LILIACEÆ.					
<i>Allium porrum</i> (Leek).....	91.3	0.0027	0.19	0.0030	0.21
"	92.3	0.0023	0.16	0.0024	0.17
<i>A. cepa</i> (Onion)	91.0	0.0059	0.41	0.0064	0.45
"	90.0	0.0080	0.56	0.0089	0.62

Plant.	Moisture per cent. in roots.	Acidity per cent. in roots (in moist state).		"Sap acidity" of roots.	
		In terms of hydrogen.	In terms of crystallised citric acid.	In terms of hydrogen.	In terms of crystallised citric acid.
<i>GRAMINEÆ.</i>					
<i>Alopecurus pratensis</i> (Fox-tail)	64.3	0.0049	0.34	0.0077	0.54
<i>Phleum pratense</i> (Timothy) (pot grown)	57.3	0.0071	0.50	0.0126	0.88
" " (field grown)	63.6	0.0073	0.51	0.0114	0.80
<i>Poa pratensis</i> (Smooth Meadow Grass)	59.0	0.0037	0.26	0.0063	0.44
<i>Poa trivialis</i> (Rough Meadow Grass)	56.2	0.0069	0.48	0.0121	0.85
<i>Dactylis glomerata</i> (Cock's-foot)	58.9	0.0069	0.48	0.0116	0.81
<i>Cynosurus cristatus</i> (Dog's-tail)	65.1	0.0049	0.34	0.0075	0.52
<i>Festuca heterophylla</i>	59.1	0.0076	0.53	0.0126	0.88
<i>F. ovina</i> (Sheep's Fescue)	62.3	0.0040	0.28	0.0066	0.46
<i>F. pratensis</i> (Meadow Fescue)	52.1	0.0079	0.55	0.0152	1.06
<i>F. elaterii</i> (Tall Fescue) (pot grown)	81.0	0.0032	0.22	0.0040	0.28
<i>Avena</i> (Oats)	66.3	0.0061	0.43	0.0093	0.65
<i>Avena flavescens</i> (Yellow Oat Grass)	67.9	0.0084	0.59	0.0123	0.86
<i>Hordeum distichum</i> (Barley)	70.3	0.0039	0.27	0.0054	0.38
<i>Triticum</i> (Wheat), "Rivets"	50.1	0.0041	0.29	0.0083	0.58
" " Red Square Head,	67.4	0.0049	0.34	0.0073	0.51
<i>Lolium perenne</i> (Perennial Rye Grass) (pot grown) ..	61.6	0.0043	0.30	0.0070	0.49
" " (field grown) ..	71.5	0.0036	0.25	0.0050	0.35
<i>Lolium italicum</i> (Italian Rye Grass) (pot grown) ..	69.9	0.0040	0.28	0.0056	0.39
" " " (field grown) ..	66.2	0.0059	0.41	0.0090	0.63

There are recorded in the foregoing tables about 100 root acidity determinations, the plants being taken from 20 different natural orders. It will have been noticed that the variations are wide even in plants of the same order and even of the same species.

The average "sap acidity" of the roots of the 100 plants is—

Expressed as hydrogen	0·0122
Expressed as crystallised citric acid..	0·8540

If we take, however, the average acidity of the plants in each order examined (since the number of plants examined in each order varied very much), and then average these averages, the average "sap acidity" for the roots of the 20 orders is—

Expressed as hydrogen.....	0·013
Expressed as crystallised citric acid ..	0·910

Of course either mode of averaging is, for very obvious reasons, objectionable, as the manipulation of figures is often liable to be. The average figure—whichever mode of averaging be taken—differs widely from some of the individual figures. The average of the whole, however (0·91 per cent., reckoned as citric acid), represents very nearly the averages found in each case for the plants included in *Ranunculaceæ*, *Cruciferæ*, *Caryophyllaceæ*, *Leguminosæ*, *Onagraceæ*, *Araliaceæ*, and *Boraginaceæ*, which averages vary between the limits of 0·81 per cent. and 1·12 per cent.

Of the remaining orders, we have *Tropæolaceæ*, *Primulaceæ*, *Umbelliferæ*, *Compositæ*, *Campanulaceæ*, *Chenopodiaceæ*, and *Gramineæ*, ranging from 0·53 per cent. to 0·68 per cent. *Dipsaceæ* and *Solanaceæ* (single species only) fall much below the average (0·44 per cent. and 0·34 per cent.), and so do the *Liliaceæ* (0·36 per cent.), though one of the only two species comprising the four liliaceous plants examined gave higher results. On the other hand, the plants examined in *Rosaceæ* and *Plumbagineæ* gave exceeding high results checked in each case by operating on two distinct plants of each species chosen.

Obviously these determinations, numerous and laborious as they have been, can only be regarded as being in the nature of a tentative and preliminary enquiry of a very crude kind if criticised from the botanical or physiological standpoint. But they appear to be sufficient to indicate that the ratio of the soluble free acid in the roots of plants to the moisture contained in them—which is here called sap-acidity—probably generally falls within, and not very far within, 1 per cent., calculated as crystallised citric acid.

Citric acid is chosen to express the acidity partly on account of its being an organic acid, and in that sense kindred to other root sap

acids; partly because it is the acid generally used by those who have attempted to determine available phosphoric acid in manures by means of weak acid, in particular by Tollens, Stutzer, A. Thomson, and P. Wagner; and partly because it is at hand in every agricultural laboratory in a state of purity, and therefore a convenient acid.

On the whole, these sap-acidity determinations, however desultory and imperfect in a scientific sense, seemed to confirm the wisdom of Stutzer in adopting (Tollens had suggested various strengths) a 1 per cent. solution of citric acid as a standard test of the availability of phosphates in manures, though he appears to have lighted on that strength by experimental enquiry based on quite other grounds.

EXPERIMENTS ON ROTHAMSTED BARLEY SOILS.

Since the choice of a solvent for use in soil analyses must in the end be empirical, both as regards its form and its strength, it seemed now worth while to make some effort to test the expediency of adopting a 1 per cent. citric acid solution. Such a solution appears to yield instructive information in the case of manures, and it approximates fairly closely to the average acidity of root sap. It remained, however, to see how far its solvent action on the constituents of the soil might afford a real measure of the soil's present fertility so far as such fertility is affected by the quantity present of available mineral elements of plant food.

In order to do this, it was necessary, clearly, to operate on soils about whose history and whose fertility very exact information was attainable, and the one spot to which an agricultural chemist in England or elsewhere would naturally turn for such a purpose at once suggested itself as a source of material whereon to work.

By the kind permission of Sir John Lawes, and with the advice and personal assistance of Sir Henry Gilbert, the author was fortunate in being allowed to draw a complete set of samples of soil from the world-famed Hoos Field at Rothamsted, on which barley has been grown for 40 years in succession, and on which each plot has been year after year subjected to some one kind of unvarying manurial treatment. A precise record having been preserved, not only of the manures applied to each plot, but also of its yield of grain and straw year by year, a study of a summary of the field's history is sufficient to show which plots are languishing for phosphoric acid, which for potash, which for nitrogen, and which, in varying degree, for all. After so many years of treatment, the knowledge of the manures used almost suffices to predict the crop of an average season; while the yield of crop would, on the other hand, almost suffice to indicate how it has been manured—so closely do the two factors—the *a priori* one of treatment and the *a posteriori*

one of yield—independently point, when properly studied, to the same degree of fertility. Any mode of soil analysis that would furnish a third scale of indications pointing to the same conclusions might almost be accepted as a provisionally satisfactory method of soil analysis—regarding the mineral elements of fertility, with which alone we are at present concerned. Whatever might be the result of the proposed experiments, it could scarcely be doubted that they would bring to light some points of interest—an anticipation that will be seen to have been fully realised.

The samples were drawn in the autumn of 1889. A square sampling iron, such as has been described in papers from Rothamsted, was used. It is so made that it draws a fair sample of the soil to a depth of 9 inches. To sample each plot, samples were drawn in this way from several places and mixed together on a sheet. 20 lbs. of the moist earth, including stones and pebbles, were then weighed out from the mixture, bagged, and sent to the author's laboratory in London. 22 out of the total 29 plots in Hoos Field were thus sampled.

The sample in each case was allowed to become sufficiently air-dried to allow of its being crumbled and sifted. The stones—flints, pebbles, &c.—that would not pass through a $\frac{1}{4}$ -inch sieve were rejected, and the moisture in the air-dried soil was determined by drying a fair sample of it at 100° C. The analytical determinations of total phosphoric acid and potash were made on the dry soil. For all the solubility experiments, however, the *air-dried* soil was used, a quantity being taken which in each case corresponded to a given weight of actually dry soil; for it was considered that to completely dry the soil before weighing it out for the solubility experiments might be to risk, by dehydration, the production of some change in the composition or constitution of the phosphoric acid or potash compounds existing in the soil, and possibly therefrom the bringing about of some artificial modification of their solubility.

The percentage results obtained have been also calculated out as pounds per acre. In these calculations the author has availed himself of data kindly supplied to him by Sir Henry Gilbert, as to the acreage weights of fine soil on the experimental plots. These are—

	Weight per acre of dry soil (excluding stones retained by $\frac{1}{4}$ -inch sieve).
First 9 inches for Series O, A, AA, and AAS (mean of 16 plots and 56 samples)	2,527,879 lbs.
For Series C (mean of 4 plots and 16 samples)	2,361,461 lbs.
For 7 ¹ (mean of 3 samples)	2,486,870 lbs.
For 7 ² (mean of 3 samples)	2,084,567 lbs.

Perhaps a few words may be said as to the analytical methods adopted.

The total phosphoric acid was determined in each case in 10 grams of the dried soil and also in 25 grams, the mean of the two results being taken. The numbers obtained in each case were, however, all but identical, the difference in the duplicate percentages being in most cases only a small one in the third place of decimals.

The soil was incinerated and digested with hydrochloric acid, and evaporated to dryness, redigested with acid, filtered, and washed. The filtrate and washings were concentrated to a small bulk, and treated, in the cold, with excess of a solution of ammonium molybdate in nitric acid. After standing 48 hours, the liquor was decanted through a filter, the precipitate washed several times by decantation, first with dilute acid, then with pure water in very small doses, and finally transferred to the filter and washed free from excess of acid. The ammonium phosphomolybdate was then dissolved in ammonia, evaporated to dryness in a platinum capsule, and dried to constancy in a water-oven. The residue contains 3.5 per cent. of its weight of phosphoric acid. This is the method of O. Hehner (*Analyst*, 1879), and for determining small quantities of phosphoric acid such as occur in soils or in solutions of iron and steel, is very much to be preferred to the old-fashioned method of conversion into magnesium-ammonium phosphate. The solubility of the yellow precipitate in the small quantity of wash water used is in most cases negligible. As a matter of fact, the quantity of wash water used in these analyses was found capable of dissolving only 0.005 gram of precipitate, of which only 0.00017 is phosphoric acid, making an error of 0.0017 per cent. on the soil if 10 grams be used, or of only 0.0006 if 25 grams be used. In the citric acid experiments, to be presently described, the solution from 50 grams of soil was used, when the error due to solubility of precipitate shrinks to 0.0003 per cent. The correction for this solubility was, however, made in each case.

It may be observed that the method of Hehner is not applicable if the molybdic solution be added to a hot liquid, since, in that case, some molybdic acid is sure to crystallise out with the yellow precipitate. Moderate and careful warming to about 35° C. hastens precipitation, but it is preferable, when speed is not a special object, to precipitate cold, and leave the beaker standing at the laboratory temperature over night, or longer if the quantity to be determined is very minute.

To determine potash, 10 grams of fine, dry soil were treated with 10 c.c. of hydrochloric acid and evaporated to dryness on the water-bath, the residue taken up with another 10 c.c. of acid, warmed, diluted with water, boiled, filtered, and washed. The filtrate and

washings were concentrated and gently incinerated to get rid of organic matter, and the residue redissolved in hydrochloric acid, and evaporated slowly down with a considerable quantity of platinum chloride. If the evaporation be conducted *slowly*, the platinum-potassium chloride settles out well, despite the iron, aluminium, and calcium salts, and is easily washed with some more platinum chloride solution, followed by alcohol. The application of this (Tatlock's) modification of the platinum chloride process to solutions containing comparatively minute quantities of potash amid an overwhelming excess of iron, aluminium, and calcium salts is probably new to many chemists. It works admirably, and obviates the necessity for removing iron, aluminium, calcium, magnesium, &c., with the necessary use of ammonia, and the tedious processes of concentration and final volatilisation of the ammonium salts; but, of course, the process cannot be employed if soda also is to be determined. It should be observed that the filtrates from several determinations were collected and very exhaustively examined for any possible trace of unprecipitated potash, but none could be detected.

The potash soluble in hydrochloric acid having been thus determined, the undissolved siliceous matter was incinerated, weighed, and finely ground in an agate mortar. A weighed portion of it was then mixed with a large bulk of pure calcium carbonate and a little ammonium chloride and heated, beginning with a low temperature, rising slowly to bright redness. The mass was then boiled with water, washed, incinerated, re-ground, mixed with some more ammonium chloride, and again heated, boiled, and washed out. The process was repeated once again, and the filtrates from all the treatments concentrated, the calcium being removed as carbonate, and the potash determined in the filtrate, after evaporation and incineration at a low temperature, by means of platinum chloride.

It was found, in repetition analyses, impossible to get constant figures for potash soluble in hydrochloric acid, for even a difference in the time taken to evaporate to dryness with acid was found to affect the result. But all the figures stated under this head were obtained by working under similar conditions, and they are such as are obtained in ordinary soil analysis.

The determinations of solubility in citric acid solution were made as follows:—A weight of air-dried soil corresponding to 200 grams of completely dry soil was placed in a Winchester quart bottle with 2 litres of distilled water in which were dissolved 20 grams of pure citric acid. (Winchester quarts which had been used for the storage of strong acids were chosen in order to eliminate the possibility of dissolving potash, &c., from the glass. The bottles were rinsed many times, allowed to rest full of water for some days, and again rinsed.)

The soil was allowed to remain in contact with the 1 per cent. citric acid solution for seven days, being, except on one day, shaken up a great many times each day, whenever, that is to say, the soil had settled well down. The bottles rested, however, at night. Altogether the shaking up, which was not violent, but only sufficient to break up the cake of mud which formed each time the soil settled down, may have been performed on each sample about 400 times. The temperature ranged between 10° and 19° C., and averaged about 15° C. The experiments being made in winter, it was practically impossible to keep a constant temperature in the laboratory, and the bottles were too large and too numerous to be placed in any ordinary constant temperature closet. On the whole, the conditions throughout the 22 experiments may be said to have been fairly even.

After seven days' treatment as above, the solutions were filtered; 500 c.c., *i.e.*, the solution from 50 grams of soil, were used for each determination. In each case the solution was evaporated to dryness in a platinum basin, and gently incinerated at a low temperature. The residue was dissolved in pure hydrochloric acid, evaporated to dryness, redissolved, and filtered. In the filtrate the phosphoric acid or potash, as the case might be, was determined by the methods already described, and, as the actual precipitate weighed represented 50 grams of soil, the multiplication of any experimental error in converting into percentages was minimised.

The methods of sampling, of analysis, and of experiment, having been sufficiently described, the results may now be recorded and discussed.

For the better study of these, however, it is necessary to prefix a descriptive list of the plots of soil represented, showing fully the manurial treatment that each had received during the 38 years of continuous barley growing, the average yield in grain and straw for the first half of that period, for the second half and for the whole period, and the yield in the year (1890) following that in which the soils were sampled. These data are transcribed from the annual statement of experimental results issued from Rothamsted.

Barley Plots in Hoos Field, Rotterdamsted.

Manurial treatment.	Produce per acre.							
	Dressed grain.			Straw.				
	Average 1st 19 years.	Average 2nd 19 years.	Average whole 38 years.	Yield in 1890.	Average 1st 19 years.	Average 2nd 19 years.	Average whole 38 years.	Yield in 1890.
1 O. Unmanured continuously.....	bushels. 20 $\frac{1}{2}$	bushels. 13 $\frac{1}{2}$	bushels. 16 $\frac{1}{2}$	bushels. 13	cwts. 11 $\frac{1}{2}$	cwts. 7	cwts. 9 $\frac{3}{8}$	cwts. 6 $\frac{1}{2}$
2 O. 3 $\frac{1}{2}$ cwts. superphosphate	25 $\frac{5}{8}$	18	21 $\frac{1}{4}$	16 $\frac{1}{2}$	13 $\frac{3}{8}$	8 $\frac{1}{2}$	10 $\frac{7}{8}$	7 $\frac{1}{2}$
3 O. 200 lbs. sulphate of potash, 100 lbs. sulphate of soda, 100 lbs. sulphate of magnesia	22 $\frac{5}{8}$	14	18 $\frac{1}{2}$	9 $\frac{3}{4}$	12 $\frac{3}{8}$	7 $\frac{1}{2}$	9 $\frac{3}{4}$	4 $\frac{1}{2}$
4 O. 3 $\frac{1}{2}$ cwts. superphosphate, and potash, soda, and magnesia as above.....	27 $\frac{5}{8}$	17 $\frac{1}{2}$	22 $\frac{1}{2}$	17 $\frac{3}{4}$	14 $\frac{3}{8}$	8 $\frac{3}{4}$	11 $\frac{5}{8}$	7
1 A. 200 lbs. ammonia salts	32 $\frac{1}{4}$	26	29 $\frac{1}{4}$	24 $\frac{1}{2}$	18 $\frac{3}{8}$	13 $\frac{1}{2}$	16 $\frac{1}{2}$	12 $\frac{3}{4}$
2 A. 200 lbs. ammonia salts and 3 $\frac{1}{2}$ cwts. superphosphate.....	47 $\frac{1}{4}$	38 $\frac{1}{2}$	42 $\frac{3}{8}$	33 $\frac{1}{2}$	27 $\frac{5}{8}$	20 $\frac{3}{8}$	24	16 $\frac{1}{2}$
3 A. 200 lbs. ammonia salts, and potash, soda, and magnesia salts as on 3 O	34 $\frac{7}{8}$	28 $\frac{3}{8}$	31 $\frac{3}{4}$	23 $\frac{1}{2}$	20 $\frac{1}{2}$	15 $\frac{1}{4}$	18 $\frac{1}{2}$	13 $\frac{1}{2}$
4 A. 200 lbs. ammonia salts, and superphosphate, potash, soda, and magnesia salts as on 4 O.....	46 $\frac{1}{4}$	40 $\frac{1}{2}$	43 $\frac{3}{8}$	46 $\frac{3}{8}$	28 $\frac{1}{4}$	23 $\frac{1}{2}$	25 $\frac{7}{8}$	23 $\frac{1}{2}$
1 A.A. 275 lbs. nitrate of soda	36 $\frac{7}{8}$	28 $\frac{1}{4}$	32 $\frac{1}{4}$	29 $\frac{1}{2}$	21 $\frac{1}{2}$	16 $\frac{1}{4}$	19 $\frac{1}{2}$	14 $\frac{1}{2}$
2 A.A. 275 lbs. nitrate of soda and 3 $\frac{1}{2}$ cwts. superphosphate	49 $\frac{3}{8}$	42	45 $\frac{3}{4}$	47 $\frac{1}{2}$	30 $\frac{1}{2}$	23 $\frac{1}{2}$	27	22 $\frac{1}{2}$
3 A.A. 275 lbs. nitrate of soda, and potash, soda, and magnesia salts as on 3 O.....	37 $\frac{1}{2}$	29 $\frac{7}{8}$	33 $\frac{3}{8}$	28	23 $\frac{3}{4}$	18 $\frac{3}{8}$	21	15 $\frac{1}{2}$
4 A.A. 275 lbs. nitrate of soda, and superphosphate, potash, soda, and magnesia salts as on 4 O	50	41 $\frac{1}{2}$	45 $\frac{1}{2}$	43 $\frac{1}{2}$	32 $\frac{3}{8}$	24 $\frac{1}{4}$	28 $\frac{3}{8}$	23 $\frac{7}{8}$

Barley Plots in Hoos Field, Rothamstel—continued.

Manurial treatment.	Produce per acre.							
	Dressed grain.			Straw.				
	Average 1st 19 years.	Average 2nd 19 years.	Average whole 38 years.	Yield in 1890.	Average 1st 19 years.	Average 2nd 19 years.	Average whole 38 years.	Yield in 1890.
	bushels.	bushels.	bushels.	bushels.	cwts.	cwts.	cwts.	cwts.
1 AAS. 275 lbs. nitrate of soda and 400 lbs. silicate of soda	35½	35½	35½	31¾	20¾	19¾	20¾	15¾
2 AAS. 275 lbs. nitrate of soda, 400 lbs. silicate of soda, and 3½ cwts. superphosphate	48½	44	45	46¼	28½	25	26	22¾
3 AAS. 275 lbs. nitrate of soda, 400 lbs. silicate of soda, potash, soda, and magnesia salts as on 3 O	41¾	37½	38½	36½	24½	21¾	22¼	19½
4 AAS. 275 lbs. nitrate of soda, 400 lbs. silicate of soda and superphosphate, and potash, soda, and magnesia salts as on 4 O	50¼	44¾	46¼	46¾	30½	28¼	28¾	22½
1 C. 1000 lbs. rape-cake	45¾	37¾	41¾	36	26¾	20½	23¾	18½
2 C. 1000 lbs. rape-cake, and 3½ cwts. superphosphate	47	39¾	43½	37¼	28¾	21¾	25½	17¾
3 C. 1000 lbs. rape-cake, and potash, soda, and magnesia salts as on 3 O	43½	36	39¾	31½	26¾	20¾	23¾	16½
4 C. 1000 lbs. rape-cake, and superphosphate, potash, soda, and magnesia salts as on 4 O	47¼	39¾	43½	33½	29¾	22¾	25¾	15¾
7 ¹ . Farm-yard manure, 14 tons for 20 years, but un-	48¼	30½	39¾	22¾	28¼	16¾	22¾	11¼
matured since 1871	48	49¼	48¾	53	27¼	29¾	28¼	29¾
7 ² . Farm-yard manure, 14 tons every year								

The following tables show the results of the determinations of total phosphoric acid, and also of the portion of phosphoric acid dissolved by the 1 per cent. solution of citric acid, expressed as percentages of the "fine," dry soil, and also as (estimated) lbs. per acre:—

Phosphoric Acid Determinations in Samples of Barley Soils from Hoos Field, Rothamsted.

Manure applied every year since 1852 (for quantities see pages 143 and 144).	Percentage of P_2O_5 in fine soil, calculated on dry state.	
	Total P_2O_5 .	P_2O_5 dissolved by 1 per cent. solution of citric acid.
1 O. No manure	0·099	0·0055
2 O. Superphosphate.....	0·182	0·0463
3 O. Potash, &c. (no phosphates).....	0·121	0·0100
4 O. Superphosphate, potash, &c.....	0·189	0·0538
1 A. Ammonia salts.....	0·097	0·0060
2 A. Ditto and superphosphate.....	0·173	0·0425
3 A. Ditto, and potash, &c. (no phosphate).....	0·102	0·0084
4 A. Ditto, superphosphate, and potash, &c.....	0·182	0·0500
1 AA. Nitrate of soda.....	0·104	0·0067
2 AA. Ditto and superphosphate.....	0·165	0·0350
3 AA. Ditto and potash, &c. (no phosphates).....	0·104	0·0082
4 AA. Ditto, superphosphate, and potash, &c.....	0·179	0·0475
1 AAS. Nitrate of soda and silicate of soda.....	0·106	0·0074
2 AAS. Ditto, ditto, and superphosphate.....	0·180	0·0475
3 AAS. Ditto, ditto, and potash, &c. (no phosphates).....	0·105	0·0112
4 AAS. Ditto, ditto, superphosphate, and potash, &c.....	0·169	0·0479
1 C. Rape-cake.....	0·158	0·0187
2 C. Ditto and superphosphate.....	0·229	0·0636
3 C. Ditto and potash, &c. (no phosphates).....	0·152	0·0214
4 C. Ditto, superphosphate and potash, &c.....	0·203	0·0563
7 ¹ . Farm-yard manure for 20 years, unmanured for last 18 years.....	0·134	0·0206
7 ² . Farm-yard manure for 38 years.....	0·176	0·0447

Phosphoric Acid.

Percentage results calculated into lbs. per acre, on the assumption that the samples drawn fairly represented the soil to a depth of 9 inches.

Manure applied every year since 1852 (for quantities see pages 143 and 144).	Total phosphoric acid.	<i>Phosphoric acid soluble in 1 per cent. solution of citric acid.</i>
	lbs. per acre.	lbs. per acre.
1 O. No manure	2503	139
2 O. Superphosphate.....	4601	1170
3 O. Potash, &c. (no phosphates).....	3059	253
4 O. Superphosphate, potash, &c.....	4778	1360
1 A. Ammonia salts.....	2452	152
2 A. Ditto and superphosphate	4373	1073
3 A. Ditto and potash, &c. (no phosphates)	2579	205
4 A. Ditto, superphosphate, and potash, &c.	4602	1264
1 AA. Nitrate of soda.....	2629	170
2 AA. Ditto and superphosphate.....	4171	909
3 AA. Ditto and potash, &c. (no phos- phates)	2629	207
4 AA. Ditto, superphosphate, and pot- ash, &c.....	4525	1201
1 AAS. Nitrate of soda and silicate of soda.....	2680	150
2 AAS. Ditto, ditto, and superphosphate	4550	1201
3 AAS. Ditto, ditto, and potash, &c. (no phosphates)	2654	283
4 AAS. Ditto, ditto, superphosphate, and potash, &c.....	4272	1211
1 C. Rape-cake.....	3731	442
2 C. Ditto and superphosphate	5408	1503
3 C. Ditto and potash, &c. (no phos- phates)	3590	505
4 C. Ditto, superphosphate, and potash, &c.....	4794	1330
7 ¹ . Farm-yard manure for 20 years, un- manured last 18 years	3332	512
7 ² . Farm-yard manure for 38 years.....	3669	932

Those closely interested in the subject will scarcely need any guidance for the study of these tables. Almost every one of the analytical figures possesses an interest read in conjunction with the history and yield of its own plot, and correlated with the data, historical and analytical, of other plots.

Although, however, the reader having sufficient interest and suffi-

cient patience to thus study the figures in detail will need no commentative guidance, some of the results may be summarised for the sake of those who care only to learn the main conclusions, if any, to which the investigation tends.

In the next table are four averages deduced each from the analyses of four plots, viz.: 1(O, A, AA, AAS), 3(O, A, AA, AAS), 4(O, A, AA, AAS), and 2(O, A, AA, AAS).

DYER: AVAILABLE "MINERAL"

	1(O, A, AA, AAS), 4 plots. 3 manured with nitro- gen. No MINERALS.	3(O, A, AA, AAS), 4 plots. 3 manured with nitro- gen; all with potash, soda, and magnesia. No PHOSPHATES.	4(O, A, AA, AAS), 4 plots. 3 manured with nitro- gen; all with potash, soda, and magnesia, and with PHOS- PHATES.	2(O, A, AA, AAS), 4 plots. 3 manured with nitro- gen; all WITH PHOS- PHATES. No potash, &c.
Average.				
Total phosphoric acid per cent.	0.102	0.108	0.180	0.175
Phosphoric acid soluble in 1 per cent. citric acid solution per cent.	0.0063	0.0094	0.0498	0.0428
Total phosphoric acid estimated in lbs. per acre.....	2566 lbs.	2730 lbs.	4544 lbs.	4124 lbs.
Phosphoric acid soluble in 1 per cent. citric acid solution estimated in lbs. per acre....	160 lbs.	237 lbs.	1259 lbs.	1089 lbs.
Barley yield, average per annum for 38 years aw ditto, ditto	28½ bushels 16¼ cwts.	30½ bushels 17¾ cwts.	39½ bushels 25¾ cwts.	38½ bushels 21½ cwts.
Barley yield in 1890.	24½ bushels	24½ bushels	38½ bushels	36 bushels
Straw yield in 1890	12½ cwts.	13½ cwts.	19¼ cwts.	17¾ cwts.

It will be seen that the average percentage of total phosphoric acid in the eight plots that received no phosphates is 0.106 per cent., while on the phosphatically manured plots it is 0.178 per cent. There is here, of course, a difference that is actually great, as might be expected; seeing that during the 38 years of experiment, nearly 500 lbs. of phosphoric acid per acre must have been removed from the former plots, without any replacement by manuring, while the latter, though yielding not far short of 800 lbs. of phosphoric acid, had during the same time received nearly 2500 lbs. of phosphoric acid as manure. Roughly speaking, the average difference to be expected between the total phosphoric acid left in the phosphated and non-phosphated soils would be somewhere about 0.08 per cent., the actual average difference found by analysis being 0.072.

But the difference between 0.105 per cent. and 0.178 per cent., great as it is, would have told us practically nothing apart from the known history and yield of the plots. The difference between 2500 lbs. of total phosphoric acid and 4500 lbs. of total phosphoric acid, per acre, appears to be immaterial as a measure of present fertility for a crop that only requires 20 lbs. per annum for its actual sustenance.

The average percentage, as we have seen, of *total* phosphoric acid in the eight plots receiving no phosphates was 0.106; in the eight plots receiving phosphates, 0.178. These numbers are nearly in the ratio 1 : 1.7.

Now, however, let us consider the percentages of phosphoric acid soluble in the 1 per cent. solution of citric acid.

We find that the average percentage thus found in the eight plots receiving no phosphates was 0.0078; in the eight soils that received phosphates it was 0.0463. *These percentages are in the ratio of nearly 1 : 6.* The difference in the percentages of phosphoric acid *soluble in dilute citric acid* is thus comparatively *overwhelming*.

Further, if we compare the four plots that have received neither phosphoric acid nor potash with those that have received potash, soda, and magnesia salts, without phosphoric acid, we find that, although the total phosphoric acid is practically identical in the two sets of plots, yet the four plots treated with alkaline salts have half as much again of citric acid soluble phosphate as the others—in fact 77 lbs. more per acre. Their fertility is also shown to have been greater, and it appears not impossible that this may have been in some degree due to the solvent chemical action of the soluble alkaline salts on the phosphates of the soil.

Again, there is a considerable difference between the average citric acid soluble phosphoric acid of the four completely manured plots and that of those which received phosphates without alkalis. The

former have 170 lbs. per acre more of such soluble phosphoric acid than have the latter, although their fertility, both on the average of years and in the last yield recorded, is higher. It would almost appear as though the presence of the alkaline salts here again exercised a solvent action.

This apparent solvent action of potash and soda (? and magnesia) salts, indicated by the presence of more citric acid soluble phosphoric acid, is suggested not only by the average results, but by detailed examination of each of the sets of plots from which the foregoing summary was averaged.

Unfortunately complete mineral analyses have not been made of the crops grown on all the plots, but on two of them, viz., Plots 2 A and 4 A, complete ash analyses have been made of the whole of the grain and straw grown in the course of 40 years. Sir Henry Gilbert has been good enough to supply the author with the results of these analyses, from which the actual gain or loss per acre of mineral constituents can be calculated.

The crops on Plots 1 A and 1 AA have also been analysed, but only for the last 20 years. On these two plots the total mineral losses per acre during the earlier period of experiment can only be estimated. It is true that as far as potash is concerned, such retrospective estimates are of little value, but the phosphoric acid can be computed from already existing figures, with a fair approach to certainty, as the percentage of phosphoric acid found in grain and in straw is far less variable, and less dependent on soil and manuring than that of potash.

The following table, based in the case of Plot 1 A on 20 years crop analyses, and in the other plots on a complete series of analyses, is particularly interesting, as affording an actual quantitative illustration of facts which have been already considered, but only in the averages of many plots, and by the aid of rough estimates:—

PLANT FOOD IN SOILS.

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	Plot 1 A. Ammonia salts only.	Plot 2 A. Ammonia salts and superphosphate.	Plot 4 A. Ammonium salts, superphosphate, potash, soda, and magnesia.
Total phosphoric acid	0·097	0·173	0·182
Phosphoric acid soluble in 1 per cent. citric acid solution ..	0·0060	0·0425	0·0500
Total phosphoric acid, lbs. per acre	2452	4373	4602
Phosphoric acid soluble in 1 per cent. citric acid solution, lbs. per acre	152	1073	1264
Barley yield per acre in 38 years	1106 bushels	1625 bushels	1647 bushels
Straw yield per acre in 38 years	610 cwt.	912 cwt.	980 cwt.
Barley average annual yield per acre from 1886 to 1890. . .	21½ bushels	324 bushels	367½ bushels
Straw, do., do.	11¼ cwt.	17 cwt.	20¼ cwt.
Estimated removal of phosphoric acid in 38 years' crops, per acre	424 lbs.	794 lbs.	852 lbs.
Phosphoric acid added in manure in 38 years, per acre. . . .	—	2428 lbs.	2428 lbs.
Estimated loss or gain of phosphoric acid per acre	-424 lbs.	+ 1634 lbs.	+ 1576 lbs.
Expected difference in phosphoric acid between phosphate plots and non-phosphate plot	—	2058 lbs.	2000 lbs.
Difference in total phosphoric acid found by analysis.	—	(= 0·081 per cent.)	(= 0·079 per cent.)
Ditto, ditto in citric acid soluble phosphoric acid	—	1921 lbs.	2150 lbs.
	—	(= 0·076 per cent.)	(= 0·085 per cent.)
	—	921 lbs.	1112 lbs.
	—	(= 0·036 per cent.)	(= 0·044 per cent.)

Sir Henry Gilbert has also been good enough to supply the author with samples of soil from Plot 2 A, drawn in 1882, and samples from 4 A, drawn in 1868 and in 1882. These include not only samples of the surface soil (top 9 inches), but also samples of the second and third depths of 9 inches each. No samples of the subsoil were drawn in 1889. These samples have been analysed, with the following results (p. 153), the results of the 1889 samples being here repeated for comparison.

The total phosphoric acid in the 1882 sample of Plot 2 A is higher than would have been expected, the difference of 0.003 per cent. between it and the 1889 sample representing an accumulation between 1882 and 1889 of only 76 lbs. per acre, whereas the estimated accumulation during that time should amount to 378 lbs. of phosphoric acid per acre. But if the phosphoric acid soluble in 1 per cent. citric acid solution in the two samples be compared, it will be found that there is an increase of 0.01 per cent., representing no less than 253 lbs. per acre.

The figures for Plot 4 A are even more interesting. The difference between the total phosphoric acid found in the 1868 sample and that found in the 1889 sample is 0.035 per cent., or 885 lbs. per acre. The estimated accumulation of phosphoric acid on the plot is about 950 lbs. per acre. Curiously enough the 1882 sample seems, as in the case of Plot 2 A, to be unduly rich in total phosphoric acid, for the total phosphoric acid figures indicate an accumulation of 859 lbs. between 1868 and 1882, and of only 25 lbs. between 1882 and 1889, the estimated accumulations being 600 lbs. between 1868 and 1882, and 350 lbs. between 1882 and 1889.

The citric acid soluble results, however, are more consistent. Between 1868 and 1882 the citric acid soluble phosphoric acid rises from 0.0231 to 0.0334, a rise of 0.0103 or 260 lbs. per acre; while between 1882 and 1889 it rises from 0.0334 to 0.0500, a rise of 0.0166 or 420 lbs. per acre. Between 1868 and 1889 the weak citric acid solution accounts for 680 lbs. out of the accumulation of 958 lbs. estimated from analyses of crops and the composition of the manures.

The subsoil analyses do not appear to suggest that the cropping or manuring have much affected the subsoil below 9 inches from the surface. From the fact that so little citric acid soluble phosphoric acid is found in the subsoils, even on these very abundantly phosphated soils, it would appear that the superphosphate applied does not, to any appreciable extent, sink or accumulate in the subsoil.

But to return to the analyses of the more recent samples.

No reference has yet been made to the rape-cake plots, 1, 2, 3, and 4 C.

PLANT FOOD IN SOILS.

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	Plot 2 A. Ammonia salts and superphosphate.			Plot 4 A. Ammonia salts, superphosphate, and potash salts, &c.		
	1-9 in.	10-18 in.	19-27 in.	1-9 in.	10-18 in.	19-27 in.
1868.						
Total phosphoric acid.....	—	—	—	0·147	0·129	0·129
Phosphoric acid soluble in 1 per cent. solution of citric acid.....	—	—	—	0·0231	0·0023	0·0014
1882.						
Total phosphoric acid.....	0·170	0·131	0·126	0·181	0·125	0·122
Phosphoric acid soluble in 1 per cent. solution of citric acid.....	0·0328	0·0015	0·0010	0·0334	0·0015	0·0014
1889.						
Total phosphoric acid.....	0·173	—	—	0·182	—	—
Phosphoric acid soluble in 1 per cent. solution of citric acid.....	0·0425	—	—	0·0500	—	—

These, as might be expected from their treatment, are far richer in phosphoric acid than the corresponding plots of the other series, though the comparative richness is brought out far more strikingly in the citric acid soluble proportions than in the total percentages.

In the case of the two farm-yard manure plots we have respectively 0.134 per cent. and 0.176 per cent. of total phosphoric acid. Not the most experienced chemist could venture, with no information but these two numbers to guide him, to form any reliable opinion of the comparative phosphoric acid fertility of the two soils; and yet one, after 20 years of dunging, has been left for nearly 20 years unmanured, while the other has been dunged on year by year until to-day. When, however, we compare the *citric acid soluble* phosphoric acid, we find that *the one plot is rather more than twice as rich as the other. Its present fertility, too* (though this of course depends also on other constituents than phosphoric acid), *is rather more than twice as great as that of the other.*

SUGGESTED CONCLUSION AS TO PHOSPHORIC ACID.

From a careful consideration of the whole of the results, it would perhaps not be unreasonable to suggest that, *when a soil is found to contain as little as about 0.01 per cent. of phosphoric acid soluble in a 1 per cent. solution of citric acid, it would be justifiable to assume that it stands in immediate need of phosphatic manure.*

POTASH RESULTS.

The next tables show the results of the potash determinations, expressed as percentages, as in the case of the phosphoric acid results, and also in the form of estimated lbs. per acre corresponding to those percentages.

Like the phosphoric acid results, they are interesting to examine, the differences between the potash found in the plots manured with potash and in those not so manured being, however, even more striking if we regard the proportions soluble in citric acid.

Potash Determinations in Samples of Barley Soils from Hoos Field, Rothamsted.

Manure applied every year since 1852 (for quantities see pages 143 and 144).	Percentages in fine soil calculated on dry state.		
	Total potash yielded by acid and subsequent lime "fusion" of the undissolved siliceous matter.	Potash dissolved by HCl only.	Potash dissolved by 1 per cent. solution of citric acid.
1 O. No manure.....	1·448	0·183	0·0036
2 O. Superphosphate.....	1·500	0·204	0·0065
3 O. Potash, &c. (no phosphates)....	1·695	0·318	0·0366
4 O. Superphosphates, potash, &c. ...	1·718	0·300	0·0340
1 A. Ammonia salts.....	1·418	0·267	0·0020
2 A. " " and superphosphate.....	1·439	0·248	0·0023
3 A. " " and potash, &c. (no phosphate)	1·568	0·257	0·0407
4 A. " " superphosphate, and potash, &c.	1·713	0·326	0·0298
1 AA. Nitrate of soda.....	1·293	0·136	0·0050
2 AA. " " and superphosphate.....	1·353	0·142	0·0038
3 AA. " " and potash, &c. (no phosphates)	1·396	0·239	0·0350
4 AA. " " superphosphate and potash, &c.	1·390	0·210	0·0305
1 AAS. Nitrate of soda and silicate of soda.....	1·423	0·193	0·0042
2 AAS. " " and superphosphate.....	1·531	0·188	0·0035
3 AAS. " " and potash, &c. (no phosphates)	1·574	0·230	0·0454
4 AAS. " " superphosphate and potash, &c.	1·572	0·250	0·0270
1 C. Rape-cake.....	1·384	0·170	0·0079
2 C. " and superphosphate....	1·363	0·194	0·0079
3 C. " and potash, &c. (no phosphates).....	1·504	0·219	0·0351
4 C. " superphosphate and potash, &c.	1·605	0·238	0·0304
7 ¹ . Farm-yard manure for 20 years (unmanured for 18 years).....	1·603	0·159	0·0135
7 ² . Farm-yard manure for 38 years...	1·601	0·167	0·0321

Potash.

Percentage results calculated into lbs. per acre, on the assumption that the samples drawn fairly represented the soil to a depth of 9 inches.

Manure applied every year since 1852 (for quantities see pages 143 and 144).	Total potash.	Potash dissolved by HCl.	Potash dissolved by a 1 per cent. solution of citric acid.
	lbs. per acre.		
1 O. No manure.....	36,604	4626	91
2 O. Superphosphate.....	37,918	5157	165
3 O. Potash, &c. (no phosphates).....	42,848	8039	925
4 O. Superphosphate, potash, &c.....	43,429	7584	859
1 A. Ammonia salts.....	35,845	6750	50
2 A. Ditto and superphosphate.....	36,376	6269	57
3 A. Ditto and potash, &c. (no phosphates).....	39,637	6497	1029
4 A. Ditto, superphosphate, and potash, &c.....	43,301	8242	753
1 AA. Nitrate of soda.....	32,686	3438	126
2 AA. Ditto and superphosphate.....	34,203	3589	96
3 AA. Ditto and potash, &c. (no phosphates).....	35,290	6041	884
4 AA. Ditto, superphosphate, and potash, &c.....	35,138	5309	771
1 AAS. Nitrate of soda and silicate of soda.....	35,973	4879	106
2 AAS. Ditto, ditto, and superphosphate.....	38,701	4752	89
3 AAS. Ditto, ditto, and potash, &c. (no phosphates).....	39,789	5814	1147
4 AAS. Ditto, ditto, superphosphate and potash, &c.....	39,738	6320	683
1 C. Rape-cake.....	32,683	4014	187
2 C. Ditto and superphosphate.....	32,187	4581	187
3 C. Ditto and potash, &c. (no phosphates).....	35,517	5172	829
4 C. Ditto, superphosphate, and potash, &c.....	37,902	5620	718
7 ¹ . Farm-yard manure for 20 years, unmanured, last 18 years.....	39,864	3954	336
7 ² . Farm-yard manure for 38 years.....	33,374	3481	669

For brevity's sake, 16 of the plots, arranged in comparable groups, have been, as in the case of the phosphoric acid results, averaged.

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Average.	1(O, A, AA, AAS), 4 plots.	2(O, A, AA, AAS), 4 plots.	3(O, A, AA, AAS), 4 plots.	4(O, A, AA, AAS), 4 plots.
Total potash per cent.	1.396 per cent.	1.456 per cent.	1.558 per cent.	1.598 per cent.
Potash soluble in HCl per cent.	0.195 "	0.196 "	0.261 "	0.272 "
Potash soluble in 1 per cent. citric acid solution per cent.	0.0037 "	0.0040 "	0.0394 "	0.0303 "
Total potash estimated in lbs. per acre.	35,277 lbs.	36,800 lbs.	39,391 lbs.	40,401 lbs.
Potash soluble in HCl estimated in lbs. per acre.	4,924 lbs.	4,942 lbs.	6,598 lbs.	6,864 lbs.
Potash soluble in 1 per cent. citric acid solution estimated in lbs. per acre.	93 lbs.	102 lbs.	996 lbs.	767 lbs.
Average barley yield 38 years.	28½ bushels	38½ bushels	30½ bushels	39½ bushels
" straw " "	16½ cwts.	21½ cwts.	17½ cwts.	23½ cwts.
Barley yield in 1890	24½ bushels	36 bushels	24½ bushels	38½ bushels
Straw " "	12½ cwts.	17½ cwts.	13½ cwts.	19½ cwts.

The total potash determinations, as might be expected, are devoid of comparative significance, apart from *a priori* knowledge. The total potash now existing in the eight non-potash plots averages 1.426 per cent.; in the potash plots 1.578 per cent. These numbers are in the ratio 1 : 1.07. The hydrochloric acid soluble potash averages on the eight non-potash plots 0.195, and on the eight potash plots 0.266. These numbers are in the ratio 1 : 1.36, the difference again being of little or no significance, apart from *a priori* knowledge, as any index of comparative practical poverty or richness in potash.

Now, however, let us turn to the *citric acid soluble* percentages. The eight non-potash plots average 0.0038 per cent., while the eight potash plots average 0.0348. These numbers are in the ratio 1 : 9, the difference being, as in the case of the phosphoric acid, comparatively *overwhelming*.

The difference between the citric acid soluble potash in the four potash-manured plots that have had no phosphates and that in the four potash-manured plots that have been also manured with phosphates is striking and interesting. The crops on the former, being gradually starved for want of phosphoric acid, have dwindled down to 24 $\frac{3}{8}$ bushels of barley and 13 $\frac{1}{8}$ cwts. of straw. The plots fed with phosphoric acid in addition to potash (and nitrogen) have so kept up, that the crops in 1890 still averaged 38 $\frac{3}{8}$ bushels of grain and 19 $\frac{1}{4}$ cwts. of straw. Consequently, these latter plots have removed more potash in the course of 39 years than the former. This quantity of potash, being unremoved by crops, will have accumulated in the soil. On the four plots in which it has so accumulated the average quantity of citric acid soluble potash is 996 lbs. per acre; on the other four plots it is 767 lbs. Thus there is a difference of 229 lbs. of citric acid soluble potash.

On the rape-cake plots, which are not included in the average results just considered, we have, as would naturally be expected, a much larger quantity of citric acid soluble potash on the non-potash plots than on the corresponding plots in the various series receiving no rape-cake, rape-cake itself containing an appreciable quantity of potash. Here again, too, the plot that has received potash without superphosphate is richer in citric acid soluble potash than that which has had superphosphate in addition to rape-cake and potash, to the extent of 89 lbs. per acre. The latter plot has yielded larger crops, which will have removed from the soil much more potash than those produced on the latter. Much of the difference appears as accumulated citric acid soluble potash.

In the two farm-yard manure plots, one of which was dunged for nearly 20 years and unmanured for nearly 20 years, while the other

has been dunged every year throughout the whole time, the percentages of potash are respectively 1·603 and 1·601. Duplicate samples of the same soil might well differ to such an extent as that, or even two analyses of the same soil as ordinarily carried out. The respective hydrochloric acid soluble percentages 0·159 and 0·167, obtained by the ordinary mode of analysis, are also to be regarded as virtually identical. Certainly they convey no indication of difference in fertility or condition. But when we examine again the *citric acid soluble* percentages, we find respectively 0·0135 per cent. and 0·0321 per cent. The continuously dunged plot is more than *twice as rich as the other*, closely corresponding to the differences indicated also in the citric acid soluble phosphoric acid. The comparative present fertility of the two plots, as has been already pointed out, endorses the indications thus furnished, for the *one yields now more than twice as much produce as the other*.

A further examination of the figures conveys more interesting information.

If we turn back to the table indicating the treatment and yield of each plot (pp. 143 and 144), and look down each group of plots, we see that in the O group, where no nitrogen is applied, Plots 1 and 2 yield small crops. There is no strain on the natural potash resources of the soil; and we find that these two plots are about twice and three times as rich in citric acid soluble potash as are the corresponding plots of the next (ammonia salts) group.

In this (ammonia salts) group we get valuable information. The yield of grain, but more particularly of straw, on the Plots 2A and 4A shows that the former is now suffering from potash starvation. On analysis its soil is shown to contain *only 0·0023 per cent. of citric acid soluble potash*.

On comparing the yields of grain and straw from Plots 2AA and 4AA, correspondingly manured, except that the nitrate of soda is used as a source of nitrogen instead of ammonia salts, we do not find anything like the same appreciable indications of potash starvation in the plot that has had no potash. On turning to the analytical results, we see that this plot has 0·0038 per cent. of citric acid soluble potash—*nearly twice as much as the corresponding ammonia plot*. It seems not improbable that the constant dressings of nitrate of soda have here acted as a solvent of the natural potash of the soil.

The same thing, though not to quite the same extent, is noticeable on comparing the corresponding Plots 2AAS and 4AAS, which have been treated with nitrate and silicate of soda, where the citric acid soluble potash is 0·0035, just half as much again as in the corresponding ammonia plot.

The ash analyses of the Plots 2A and 4A supplied to the author by

Sir Henry Gilbert, and already referred to under phosphoric acid, enable the following table to be drawn up.

The results of these calculations are very interesting, showing that of the estimated accumulation of 3027 lbs. of potash per acre on Plot 4A, 1973 lbs.—*i.e.*, about two-thirds of the total estimated accumulation—is actually found as potash soluble in hydrochloric acid, while 696 lbs., or about one-fourth, exists in a form soluble in weak citric acid solutions.

	Plot 2A. Ammonia salts and superphosphate.	Plot 4A. Ammonia salts, superphosphate, potash, soda, and magnesia.
Total potash	1·439	1·713
Potash soluble in HCl	0·248	0·326
Potash soluble in 1 per cent. solution of citric acid	0·0023	0·0298
Total potash, lbs. per acre	36,376 lbs.	43,301 lbs.
Potash soluble in HCl, lbs. per acre ...	6,269 "	8,242 "
Potash soluble in 1 per cent. solution of citric acid	57 "	753 "
Barley yield in 38 years	1625 bushels	1647 bushels
Straw " " "	912 cwts.	980 cwts.
Barley " (yearly average) 1886 to 1890	32½ bushels	36½ bushels.
Straw " " "	17 cwts.	20½ cwts.
Estimated removal of potash in 38 years' crops per acre	984 lbs.	2057 lbs.
Potash added in manure in 38 years per acre	—	4100 "
Estimated loss or gain of potash per acre	-984 lbs.	+2043 "
Expected difference in potash per acre between the 2 plots	3027 lbs. (=0·120 per cent. on dry soil)	
Difference found by analysis in potash soluble in hydrochloric acid	1973 lbs. (=0·078 per cent.)	
Ditto, ditto citric acid soluble potash ...	696 lbs. (=0·0275 per cent.)	

The surface and subsoil samples of Plots 2A and 4A drawn in 1868 and 1882, the phosphoric acid contents of which have been already discussed, have also been examined as regards their potash contents. The figures obtained from the different samples are less consistent than the phosphoric acid figures, but it must be remembered that the stock of natural mineral potash in these soils is vast, and evidently unevenly distributed, so that errors of sampling are necessarily greater than when we regard phosphoric acid.

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	Plot 2A. (Ammonia salts and superphosphate.)			Plot 4A. (Ammonia salts, superphosphate, potash salts, &c.)		
	1-9 inches.	10-18 inches.	19-27 inches.	1-9 inches.	10-18 inches.	19-27 inches.
1868.						
Total potash.....	—	—	—	1·539	1·484	1·518
Potash soluble in hydrochloric acid....	—	—	—	0·194	0·239	0·290
Potash soluble in 1 per cent. solution of citric acid.....	—	—	—	0·0217	0·0038	0·0031
1882.						
Total potash.....	1·456	1·614	1·685	1·647	1·628	1·612
Potash soluble in hydrochloric acid....	0·170	0·303	0·336	0·228	0·254	0·296
Potash soluble in 1 per cent. solution of citric acid.....	0·0036	0·0031	0·0024	0·0202	0·0038	0·0030
1880.						
Total potash.....	1·439	—	—	1·713	—	—
Potash soluble in hydrochloric acid....	0·248	—	—	0·326	—	—
Potash soluble in 1 per cent. solution of citric acid.....	0·0023	—	—	0·0298	—	—

Potash is, no doubt, one of the constituents of soil most likely to be modified and rendered available by the action of winter, weathering, frost, rain, &c. The 1889 samples of soil were all drawn in autumn, just after the barley crop had withdrawn its yearly share of available potash, and before the winter had done its work in preparing for next year's crop; so that it is difficult—more difficult than in the case of phosphoric acid—to draw from the figures any fairly plausible suggestion as to what percentage limit of citric acid soluble potash should be regarded as marking the non-necessity of special potash applications. *Probably this limit lies below 0.005 per cent.*

There seems good reason to suppose that the use of nitrate of soda (and possibly, to some extent, of superphosphate) helps to bring about by its solvent action on a part of the main stock in the soil a yearly supply of available potash. Soda salts generally were found by Voelcker in laboratory experiments to dissolve or liberate potash from soil.

In two sets of field experiments on cabbages, carried out by the author in Sussex and Essex, potash salts, as an addition to phosphatic manure and nitrate of soda, produced an abundant increase; but the substitution of common salt for potash salts on other plots answered just as well, probably owing to the decomposing action of the salt on the compound silicates of potash existing in the soil.

The soil economy of potash is probably more complicated than that of phosphoric acid and needs a good deal of farther investigation.

"AVAILABLE" PHOSPHORIC ACID IN MANURES.

After what has been said incidentally in the former part of this paper, it is not necessary to say much more by way of preface to some experiments (confirmatory of the views of Stutzer) now to be recorded. They appear to demonstrate, in more detail than the published figures of Stutzer, the uselessness of ammonium citrate as a means of quantitatively measuring the practical value of commercial phosphates, and, on the other hand, to further establish the value for such a purpose of a weak solution of citric acid.

In the following experiments with ammonium citrate, 200 c.c. of the solution rendered distinctly ammoniacal were shaken up with 2 grams of the manure or material to be tested, in a stoppered bottle, and allowed to stand, with occasional shaking, for three days, at a temperature of 10° C. to 18° C.

The figures indicate the quantity of phosphoric acid dissolved by the citrate for every 100 parts of phosphoric acid present.

Ammonium Citrate Experiments.

Strength of ammoniacal ammonium citrate solution	10 per cent.	20 per cent.	30 per cent.	40 per cent.	50 per cent.
	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .
Canadian apatite	1·55	0·76	0·89	1·28	1·88
Spanish phosphate	1·73	1·46	1·66	1·89	2·45
Aruba phosphate	1·58	2·87	3·58	2·52	2·56
Belgian phosphate	0·86	1·12	2·06	3·21	3·17
Somme phosphate	1·55	1·71	2·28	—	2·55
Another Somme phosphate	0·94	1·35	1·96	2·55	3·23
South Carolina phosphate	3·71	4·45	5·16	3·37	3·76
Another deposit of the same	3·70	3·94	3·45	3·79	4·09
Cambridge coprolites	4·02	4·25	3·72	4·02	8·27
Raw Redonda (aluminium) phosphate	54·92	61·76	60·29	56·68	59·20
Calcined ditto, ditto	78·88	84·74	78·46	73·86	—
Bone meal	15·62	25·42	36·66	38·71	38·71
Boiled bone meal	8·44	11·75	15·25	18·31	18·55
Steamed bone flour	10·73	13·81	16·83	18·38	—
Basic slag or cinder	21·86	40·58	51·32	66·44	47·51
Peruvian guano (Pabellon de Pica)	48·29	49·71	55·49	55·99	58·48
" " (Punta de Lobos)	10·61	14·43	19·55	16·81	16·00
" " (Lobos de Afuera)	15·46	19·72	22·41	24·40	23·43
" " (Huanillos)	19·43	22·73	27·35	29·25	33·46
Fish guano	29·07	37·72	42·85	48·33	62·24

In the citric acid experiments from 0·5 to 1·0 gram of the manure or material was placed in a bottle with 200 c.c. of the solvent, and allowed to stand, with occasional shaking, for three days.

Citric Acid Experiments.

Strength of citric acid in solution.....	0·25 per cent. Solvent $\frac{400}{1}$ Material = $\frac{1}{1}$	0·50 per cent. Solvent $\frac{200}{1}$ Material = $\frac{1}{1}$	1·0 per cent. Solvent $\frac{200}{1}$ Material = $\frac{1}{1}$
	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .	Per cent. of total P ₂ O ₅ .
Canadian apatite.....	12·59	11·85	15·81
Spanish phosphate.....	9·31	7·34	10·73
Aruba phosphate.....	26·06	20·82	29·99
*Belgian phosphate.....	1·54	1·75	3·08
Somme phosphate.....	22·93	23·24	30·36
Another ditto, ditto.....	16·31	16·69	30·51
South Carolina phosphate	29·62	25·87	38·06
Another deposit of same..	29·09	26·82	34·46
Cambridge coprolites....	30·18	22·21	33·31
Raw Redonda phosphate.	7·12	8·49	9·21
Calcined ditto, ditto.....	8·36	10·74	16·06
Bone meal.....	80·80	91·17	100·00
Steamed bone flour.....	65·06	71·52	89·66
Basic slag or cinder.....	47·44	57·79	72·84
Peruvian guano:—			
Pabellon de Pica....	98·14	91·29	97·50
Punta de Lobos....	66·19	61·06	76·67
Lobos de Afuera....	72·31	74·42	87·23
Huanillos.....	73·94	70·84	74·16
Fish guano.....	100·00	89·07	91·46

The ammonium citrate results appear to assign comparatively no value to ground mineral calcium phosphates. As a matter of fact we know that finely ground mineral phosphates do afford an available, if not an economical, source of plant food, their value being determined mainly by fineness of grinding and specific hardness.

A 1 per cent. solution of citric acid, on the other hand, does assign a value—and a graduated value—to them. Such a solution dissolved only (in round numbers) 11 per cent. of the phosphate in Spanish phosphate, and 16 per cent. of that in Canadian apatite, showing a low degree of availability. Softer phosphates—Sommes, Carolinas, and coprolites—give from 30 to 38 per cent. of their total phosphoric acid, indicating a greater availability, which accords well with practical experience; while ammonium citrate, on the other hand, comparatively speaking, shows scarcely any solubility. Bone meal shows from 90 to 100 per cent. of its phosphoric acid soluble in 1 per cent. solution of citric acid, while the maximum solubility in bones

* In this case, no doubt, the neutralisation of the acid by carbonate of lime diminished the solubility.

to strong ammonium citrate only rose to 38, and sank as low as 8 when only a 10 per cent. solution of citrate was used. Bone meal is generally looked upon as one of the most available forms of undissolved phosphatic manure, and the citric acid test gives results which clearly accord with experience. Basic cinder, or slag, which yielded 67 per cent. of its phosphoric acid to a 50 per cent. solution of ammonium citrate, yielded nearly 73 per cent. to a 1 per cent. citric acid solution. Various forms of Peruvian guano gave up from 74 to 97 per cent. of their phosphoric acid to the citric acid solution, but only from 23 to 67 per cent. to the strongest ammonium citrate solution. Fish guano yielded $91\frac{1}{2}$ per cent. of its phosphoric acid to 1 per cent. citric acid solution (and 100 per cent. to a larger proportionate bulk of weaker solution), while 62 was the highest proportion yielded to the strongest ammonium citrate.

In all these experiments the materials were finely ground—more finely a good deal than in Stutzer's experiments—and consequently the solubilities here obtained are higher, though the conclusions are in the same direction.

P. Wagner (*Chem. Zeitung*, 1886, 10) objected to the suggestions of Tollens and Stutzer, to make a 1 per cent. solution of citric acid the analytical test for "available" phosphate, on the ground that it did not attack phosphate of iron and alumina, whereas ammonium citrate does. This contention is borne out by a comparison of the results just recorded for Redonda (aluminium) phosphate. This, particularly when calcined, is freely soluble in ammonium citrate solution—to the extent of nearly 85 per cent. of its phosphoric acid—while citric acid only indicates a solubility of 16 per cent. Wagner suggests a combination of the two tests, viz., the use of a solution containing per litre 150 grams of citric acid neutralised with ammonia and 10 grams of citric acid in the free state.

This suggestion appears to be objectionable, because the object is to ascertain, if we can, what proportion of the phosphate is readily available as plant food; and if the use of citric acid has any meaning at all, it lies in an attempted imitation of the acidity of the root sap of plants.

That strongly alkaline ammonium citrate estimates the quantity of "precipitated," "reverted," or "retrograde" phosphate may be approximately true, though the experience of the present author is at variance with that of Lloyd (*Chem. Soc. Trans.*, 1882, 308), that "an ammoniacal solution of ammonium citrate, no matter what may be its strength, whilst capable of dissolving precipitated phosphate of lime, does not act either upon mineral phosphates or upon bone ash, and *only to a very slight extent upon raw bones.*" The experiments described, however, in the present

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paper were made with a much larger proportion of solvent to material than was used in Lloyd's experiments and possibly on material more finely ground.

What it is desirable to determine is *readily available* phosphate; whether "reverted" or not is of no consequence.

Phosphoric acid soluble in water is beyond all doubt much more valuable weight for weight than is any other form, however available, since it is immediately diffusible. Many of the pot experiments made to determine the relative availability of different forms of phosphate are, no doubt, to some extent misleading, for in such experiments the manure is often thoroughly incorporated by hand with the soil. In actual farming the manure is drilled or broadcasted and finally harrowed over, or at once buried by the plough. For its further incorporation with the soil it is dependent upon the action of rain. The property of solubility is, therefore, of great value as a means of diffusion, although in any soil but a pure sand the soluble phosphoric acid must be precipitated or fixed long before most of it functions as actual plant food.

"Soluble" phosphate will, therefore, probably continue to command a higher price than undissolved phosphate, however "assimilable" the latter may be, for the reason that it goes farther as an immediate dressing. But the "insoluble" phosphates, as the undissolved phosphates are usually called in England, must be of variable value according to their fineness and softness, conditions of hydration, &c., and to class them all together is clearly unreasonable, however convenient to the analyst or however in accordance with English commercial usage.

The use of ammonium citrate (the reagent ordinarily employed as a means of diagnosing the condition of "insoluble" phosphates), being clearly based upon wrong principles, should, however, be abandoned, and the method of Tollens and Stutzer adopted in its place.

CONCLUSION.

A 1 per cent. citric acid solution appears, then, to give indications fairly bearing out the manurial properties of phosphatic materials as recognised by experience in the field; it approximates fairly well to the average strength of the natural solvent (root-sap) used by the plant itself; and, tested by the results it gives on soils of known history and condition, it appears likely to afford a not unreliable means of gauging, as regards the available "mineral" constituents, the probable fertility of the soil itself.

The author has already acknowledged the kindness of Messrs.

Sutton and Sons, of Reading, in providing him with pure cultivations of the various grasses used for determination of sap acidity, and he would here also acknowledge the valuable help rendered to him in the laboratory work by his former pupil and assistant, Mr. F. H. Perry Coste, B.Sc., and by his present assistants, Mr. James Nimmo, F.I.C., Mr. E. H. Roberts, and Mr. C. H. Allan Bennett.

[*Note*.—It has been very properly pointed out to the author that in the case of soils containing large quantities of calcium carbonate, an additional quantity of citric acid, corresponding to the quantity of calcium carbonate, might reasonably be added to the solution of citric acid.—B. D.]
