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CHEMICAL ANALYSIS OF SOILS.

BY G. E. PATRICK.

There is hardly a subject upon which the opinions of chemists differ more widely than upon that of the utility of soil analysis, as a means of judging of the present crop-producing power of soils, or of ascertaining in what particular element or elements their store of available plant-food most needs replenishing in order to restore or increase fertility. This difference of opinion is not because any one questions the efficiency of chemical analysis in determining the total amount of the several plant-food elements present in the soil. That is easily done. The difficulty lies in determining how much of this total amount is in such condition, or combination, as to be readily available to the growing plant. This the chemist is as yet unable to do with certainty.

It is not my intention to imply that there is a hard and fast line separating these two groups, the available and the unavailable plant-food materials of the soil; for as regards the mineral matters, at least, availability is a matter of degree; and moreover, certain stores of plant-food, in one and the same soil, seem more available to the one class of plants than to another. Nevertheless the distinction, as ordinarily made, is entirely valid; the debatable ground is narrow; on one side of it are the compounds readily soluble in the root juices of all plants—the distinctly available; on the other side are the great stores of food material in forms nearly insoluble in the root-sap of all the higher plants—the unavailable.

Evidently some means of distinguishing between these two groups is much to be desired, to enable the chemist to ascertain with certainty the needs of any particular soil in respect to readily available plant-food; and the hope of finding such a means has been the motive of a number of researches in recent years.

The solvent that for many years has been employed for extracting the soluble portions of soils, is hydrochloric acid,

sometimes dilute, but more frequently quite strong (twenty-three to twenty-five per cent), sometimes hot, sometimes cold, acting for periods ranging from one to forty-eight hours*.

Now hydrochloric acid of this strength, or anything approaching it, is a much more powerful solvent than is the root-sap of plants. It is not surprising, therefore, that the results obtained by chemical analysis have not been found reliable measures of the relative amounts of the different plant-foods existing in readily assimilable form in the soils analyzed, except possibly in the case of new (virgin) or nearly new soils, where a large "total" of any element may be assumed to indicate a large supply of that element in available form, and *vice versa*. (Hilgard.)

Since the sap of plant roots is mildly acid with vegetable acids it seems reasonable, not to say evident, that in our attempts to discriminate between the available and the unavailable constituents of the soil we should imitate nature by employing weak solutions of some kind of vegetable or organic acid. But what acid, and how weak the solution? These are questions that at present need answering. Some work has, however, been done on these lines.

In 1872 H. von Liebig† reported some work on the soils of the Rothamsted wheat plots, in which he used "dilute" nitric and acetic acids as solvents; but the extent of dilution was in neither case stated. Each plot had received annually the same treatment as to manuring—the treatment recorded below—for nearly thirty years. All had been cropped continuously with **wheat**. The soil samples examined represented the first and second depths of nine inches each for each plot. Results were as follows:

* Of sp. gr. 1.115 (=23.4 per cent strength) for thirty-six hours at the boiling point of water. (Ass'n of Official Agricultural Chemists, 1893).

Of 25 per cent strength, at ordinary temperature for forty-eight hours; or of 10 per cent strength at temperature of boiling water for three hours. (Ass'n of Agr. Expt. Stations of Germany, 1890).

Of sp. gr. 1.15 (=30.3 per cent strength), at boiling temperature for one hour. Wahnschaffe, Brant's translation, 1891).

Of about 15 per cent strength, on water bath for five hours. (Fresenius.)

† Quoted in Jour. Ch. Society, London, 1894, p. 117.

TABLE I.

SOILS.	Potash sol- uble in dilute acetic acid	Phosphoric acid soluble in dilute ni- tric acid.
	Percent.	Percent.
No. 3. Continuously unmanured—		
1st 9 inches.....	.015	.075
2d 9 inches.....	.018	.047
No. 10 A. Ammonium Salts only—		
1st 9 inches.....	.013	.076
2d 9 inches.....	.019	.047
No. 5 A. Mixed mineral manures without nitrogen—		
1st 9 inches.....	.038	.108
2d 9 inches.....	.022	.058
No. 7 A. Mixed minerals and ammonium salts—		
1st 9 inches.....	.039	.126
2d 9 inches.....	.018	.061
No. 2. Farm yard manure—		
1st 9 inches.....	.041	.093
2d 9 inches.....	.056	.065

These results are striking, especially those for potash soluble in dilute acetic acid. The surface soils that had annually received supplies of available potash (in the mineral and barn-yard manures) showed two to three times as much potash soluble in acetic acid as did the soils not thus reinforced; while the subsoils showed much smaller differences. Unfortunately the amounts soluble in strong HCl were not reported in the abstract to which I have access, if determined at all.

In 1881, Deherain* observed that in the neighborhood of Grignon, France, where phosphatic manures had but little or no effect, the soil contained no more than an average amount of phosphoric acid, and yet gave up to acetic acid from one-fourth to one-half of the total amount present. Later, having followed up his studies in the use of acetic acid as a means of distinguishing 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." These last would, of course, have yielded very considerable quantities to strong hydrochloric acid, by the usual mode of analysis.

In 1882, A. Vogelf† suggested that if a sample of soil tested with acetic acid yields no indications of phosphoric acid, its

*Quoted in Jour. Chem. Soc., London, 1894, p. 119.

†Loc. cit. quoted from Bied. Centr., p. 852. 1882.

percentage of phosphates should be regarded as abnormally low.

In 1884, Stutzer* endorsed the suggestion previously made by Tollens, of using a dilute solution of citric acid in place of the usual ammonium citrate solution, in estimating the available phosphoric acid of fertilizers; claiming that thereby the actual manurial value was much better approximated than by the old method. He adopted and recommended a one per cent solution of citric acid.

Later A. Thomson† endorsed Stutzer's recommendation. "Neither Stutzer nor Thomson, however, appeared 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 (one per cent), showed a fair correspondence with the comparative efficacy accredited by practical experience to the fertilizers examined." Their suggestions related to the testing of fertilizers, not soils.

In March of the present year Bernard Dyer‡ published the results of an extended investigation in which he applied to soils the method recommended by Stutzer for application to phosphatic fertilizers. The soils with which he worked were those of the famous experimental barley plots at the Rothamsted Experiment Station, England.

In order to decide intelligently upon the strength of the citric acid solution to be used in the work, Dyer first made approximate determinations of the acidity of the root-sap of a large number of plants, belonging to twenty different natural orders, and including most of the ordinary agricultural plants, garden vegetables, as well as field crops. From about 100 determinations he obtained an average acidity of a trifle less than one per cent, calculated as crystallized citric acid. The average for 100 plants was .85 per cent. Averaged first by orders, the average of these averages was .91 per cent. Speaking of these sap-acidity determinations, Dyer says: "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 criticized from the botanical or physiological standpoint. But they appear to be sufficient to indicate that the ratio of the soluble free acid in

*Chem. Ind., Feb., 1884. Quoted in Jour. Ch. Soc., 1894, p. 121.

†Chem. Ind., 1885. Quoted in Jour. Ch. Soc., 1894, p. 122.

‡Jour. Chem. Society, London, March, 1894.

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, one per cent, calculated as crystalized 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 the available phosphoric acid in manures by means of weak acid, in particular by Tollens, Stutzer, A. Thompson, and L. 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 one per cent solution of citric acid as a standard test of the availability of phosphates in manures, though he appeared to have lighted on that strength by experimental enquiry based on quite other grounds.”

The several plots of soils which Dyer examined by the method indicated, had each received the same fertilization continuously for thirty-eight years—some phosphatic, some potassic and some mixed; all had been cropped continuously with barley. The soils were sampled to a depth of nine inches. Two hundred grammes of the air dried soil were treated with 2,000 c. c. of the one per cent solution of citric acid, and left in contact therewith for seven days, with frequent shaking. For comparison with the citric acid results, determinations of potash and phosphoric acid soluble in strong hydrochloric acid were also made. The averages for phosphoric acid were as follows:

Percentage of total phosphoric acid—soluble in strong HCl.—in the eight plots receiving no phosphates, was .106; in the eight plots receiving phosphates, .178. These numbers are nearly in the ratio 1 : 1.7. Percentage of phosphoric acid dissolved by citric acid from the eight plots receiving no phosphates, was .00078; from the eight plots receiving phosphates .0463. These figures are in the ratio of nearly 1:6. “The difference in the percentages of the phosphoric acid soluble in dilute citric acid is thus comparatively overwhelming.”

Striking as these results are, those obtained in the potash determinations are even more so. The average percentage of HCl-soluble potash in the eight plots receiving no potash, was .195; in the eight plots receiving potash, .266. These figures

are in the ratio 1 : 1.36. The average percentage of potash dissolved by citric acid from the eight plots receiving no potash was .0038; while from the eight plots that had received potash, it was .0348. These figures are in the ratio 1 : 9. Again, an "overwhelming" difference.

The results of Dyer's work upon the Rothamsted soils, the treatment of which had been such as would naturally cause wide differences in the amounts of available plant food present, suggested the desirability of trying his method upon soils whose treatment had been that of ordinary agricultural practice. Therefore I resolved to try the method upon some samples of Iowa soils that I had in process of analysis last spring for the state geological survey; and I also resolved to apply the method to the nitrogen of the soils, as well as to the phosphoric acid and potash.

Correspondents in different parts of the state had each sent me two samples of soil, one representing the "best" and the other the "poorest" soil occurring over any considerable area in his vicinity. Each sample was (or according to directions was to be) a composite sample from five different spots in the field or area which it was intended to represent. The directions were that every sample should be taken to a depth of exactly nine inches. The methods of Dyer were followed except in some details of the determinations, where the official methods of the Association of Agricultural Chemists were preferred.

With these explanations the table of results will be intelligible. (Table II.) The total nitrogen, also potash and phosphoric acid soluble in hot HCl (*i. e.*, by the Association method) have been determined on eight samples, and for comparison these results are included in the table.

TABLE II.
PERCENTAGE IN AIR-DRIED SOILS.

SAMPLES.	PHOSPHORIC ACID P ₂ O ₅		POTASH K ₂ O		NITROGEN.	
	Soluble in HCl	Soluble in citric acid	Soluble in HCl	Soluble in citric acid	Total.	Soluble in citric acid
A } Best20	.0118	.27	.0039	.179	.0032
A } Poorest15	.0235	.33	.0060	.301	.0150
B } Best18	.0196	.33	.0139	.278
B } Poorest13	.0133	.26	.0095	.154	.0028
C } Best16	.0146	.34	.0092	.236	.0087
C } Poorest15	.0091	.34	.0058	.109	.0031
D } Best16	.0192	.38	.0117	.245	.0109
D } Poorest22	.0131	.30	.0056	.225	.0075
E } Best037601290075
E } Poorest007000270029
F } Best056201120092
F } Poorest052000460176
G } Best051702090134
G } Poorest028101410118
H } Best014100560124
H } Poorest013200280124
I } Best013900480115
I } Poorest008300360039

It will be noticed in the results on the first four pair of samples where the old and new methods of analysis can be compared, that as a rule the differences shown between the best and the poorest soils are relatively much greater by the new than by the old method. Usually the differences are in the same direction, by the two methods; but there appear to be exceptions to this, namely, in respect to the phosphoric acid of samples A and D. Such a condition might reasonably be expected in comparing a soil originally more fertile, but much worn, with one originally less fertile, but little worn. In the cases here recorded I can not state the history of the soils.

It will also be noticed, in comparing the figures obtained by the new method for each pair of soils, that in every case there is a wide difference in regard to at least one of the three plant nutrients reported upon—the three in which a soil is most likely to be deficient. These wide differences probably, in most of the cases, reveal the causes of the observed differences in fertility; I say, probably, because the work here reported is purely chemical, and little account has been taken of the mechanical condition, or physical constitution, of the soils—a factor second only to chemical composition in determining fertility. Physical

condition or constitution, rather than chemical, seems to be the controlling factor in the case of the "poorest" of the first two soils of the list—marked A. This soil contains decidedly more citric acid-soluble $P_2 O_5$, $K_2 O$, and N, than does its mate marked "best"; also more of these elements soluble in HCl, except $P_2 O_5$ —and respecting this the difference is only slight.

In order to find the explanation in this case—the only exceptional one in the list—I made inquiry of the sender (Mr. J. O. Overholt, of Havelock, Pocahontas county) to which he replied: "The sample marked 'poorest,' is soil that needs tile drainage, and on wet years is difficult to farm. The one marked 'best' is high land, and is productive every year, wet or dry." These facts explain the apparent anomaly, and forcibly illustrate the necessity of considering the physical as well as the chemical constitution of soils, in studying the conditions affecting fertility.

The tentative conclusions to which Dyer was led by his work on the Rothamsted soils are as follows: "It would perhaps not be unreasonable to suggest that, when a soil is found to contain as little as about .01 per cent of phosphoric acid soluble in a one per cent solution of citric acid, it would be justifiable to assume that it stands in immediate need of phosphatic manure." Concerning potash he says it is difficult "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 .005 per cent." How far below he does not venture an opinion. Nor can we draw any more definite conclusion from the results on the Iowa soils. So far as they bear witness, however, they seem to justify Dyer's tentative conclusions. Evidently it will require much careful work—chemical work correlated with field observations—to fix the exact limits below which the several elements may, with certainty, be declared deficient for the purposes of immediate crop production; and doubtless any such limits will have to be qualified by conditions as to the physical constitution of the soil.

Although much remains to be done in the future along this or some similar line of research, before the desired end will be attained, sufficient has already been learned to justify the opinion that the citric acid method of soil analysis, as proposed by Dyer, is a distinct advance upon the method commonly in use for ascertaining deficiencies in available phosphoric acid.

and potash. With reference to available nitrogen its adaptability cannot be pronounced upon without further research.

The acknowledgements of the writer are due to Mr. O. H. Pagelsen and Mr. D. B. Bisbee, for their assistance in the above recorded work.

NITROGEN COMPOUNDS OF THE SOIL.

BY D. B. BISBEE.

(Abstract.)

In examining for ammonia a soil-extract, prepared by digesting soil for three days in dilute HCl, the author noticed that Schloesing's method (distilling the extract with excess of MgO) gave a continuous separation of ammonia, amounting in this case to .0024 per cent. Another portion of the extract was filtered after the addition of MgO and before boiling. In it the separation of ammonia ceased after boiling a comparatively short time, and the total separated was .0017 per cent. The evident inference is that "part of the amides in Schloesing's extract can be precipitated by magnesia; and, by the second method 'results are obtained which are much nearer the truth in respect to the ammonia of the soil than by the original Schloesing's method.'"

Kjeldahl's process for determining the total nitrogen in a soil-extract consists in boiling the extract with H_2SO_4 and salicylic acid till colorless, adding HgO and $KMnO_4$, and distilling with NaOH. The same results were obtained by reducing the nitrates, preferably with a zinc-copper couple, and distilling with a strong excess of alkaline permanganate.

From experiments with citric acid it was found that "a one per cent solution of citric acid dissolves a part of the nitrogen of the soil as amides and none as ammonia. If ammonia is in the soil citric acid either does not dissolve it or else converts it into amide-like bodies. These amides dissolved in citric acid are volatile at least in part. The volatile part is converted into ammonia by long boiling with dilute HCl, or by boiling a short time with alkaline permanganate."