THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID AND POTASH IN CALCAREOUS SOILS.

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THE citric acid method for determining the "available" phosphoric acid and potash in soils has proved of great service in the interpretation of soil analyses. It breaks down, however, as a discriminating agent if applied to a calcareous soil strictly according to the standard method of Dyer (*Journ. Chem. Soc.*, 1894, 141).

In the course of our study of the cultivated soils of Jamaica we have found the citric acid method of great service, and it has given us data which have, as a rule, been corroborated by manurial experiments in the field.

We have found with bananas, for instance, that soils containing over 0.01 per cent. of phosphoric acid soluble in 1 per cent. citric acid solution do not require phosphatic fertilizers.

In some cases we have had to deal with isolated soils in an alluvial series of low content of carbonates which are abnormally rich in calcium carbonate. Such soils give markedly low results for "available" phosphoric acid and potash by the Dyer process, although in practice it has been ascertained that they are not in need of assistance from fertilizers providing these ingredients.

To ignore the "available" results, and base judgment upon the "total" phosphoric acid and potash only, replaces the analyst in the unsatisfactory position rendered necessary by obsolete methods of soil analysis, and deprives him of a most valuable guide in drawing practical conclusions from the results of a soil analysis.

Under these circumstances, it was thought desirable to follow the practice advocated by Hilgard of neutralizing the carbonates in the soil before subjecting it to the solvent action of the standard citric acid solution.

For California soils under arid conditions and marked by an exceptional depth of root-range Hilgard employs a 2 per cent. solution of citric acid, as giving results more in harmony with local experience as to the requirements of these soils in phosphoric acid and potash. In Jamaica the 1 per cent. solution has given us results that appear to warrant a critical judgment as to the mineral requirements of a soil. Our experience of tropical soils has borne out in a gratifying manner the main conclusions arrived at by Hall and Plymen in their comparative study of dilute solvents as to the discriminating value of citric acid (*Journ. Chem. Soc.*, 1902, 117).

Some illustrations of the masking effect of carbonates upon the determination of available phosphoric acid and potash by the Dyer method, and of the effect of neutralizing the carbonates as a preliminary to the citric acid extraction, are here given.

The agricultural results obtained on these soils agree with those obtained by the modified process, whereas the ordinary method yields results that are absolutely misleading.

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SOIL A.

Details.—Alluvial soil. Medium texture. Very fertile, growing bananas without manure.

			Per Cent.
Soluble in HCl	...	...	$\left\{ \begin{array}{l} \text{CaCO}_3 \\ \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 14.15
			... 0.244
			... 0.507
Soluble in 1 per cent. citric acid (Dyer's method)	...	...	$\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 0.0017
			... 0.0019
Soluble in 1 per cent. citric acid after neutralization of carbonates	...	...	$\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 0.0128
			... 0.0040

SOIL B.

Details.—Alluvial soil. Has grown sugar-cane for one hundred years and bananas for sixteen years without manure. Bananas do not yet respond at all to fertilizers.

			Per Cent.
Soluble in HCl	...	...	$\left\{ \begin{array}{l} \text{CaCO}_3 \\ \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 26.92
			... 0.122
			... 0.745
Soluble in 1 per cent. citric acid	...	...	$\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 0.0008
			... 0.0048
Soluble in 1 per cent. free citric acid after neutralization of carbonates	...	...	$\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 0.0450
			... 0.0050

SOIL C.

Details.—Adjacent to B, but not calcareous. The soils closely correspond in the class of fruit produced.

			Per Cent.
Soluble in HCl	...	...	$\left\{ \begin{array}{l} \text{CaCO}_3 \\ \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 1.83
			... 0.204
			... 0.458
Soluble in 1 per cent. citric acid; no allowance for carbonates	...	...	$\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \\ \text{K}_2\text{O} \end{array} \right.$... 0.0287
			... 0.0088

All workers in this field are aware that the Dyer citric acid method cannot be applied to a calcareous soil, and yet doubts have been raised as to the justification of neutralizing carbonates as a preliminary to the extraction with 1 per cent. of free citric acid. The solvent action of the liberated carbonic acid and of the neutral citrate itself have been urged as insuperable objections to this modification of Dyer's method.

We hoped, if such were the case, to arrive at a factor whereby we could correct results obtained in this way, and reduce them to the same standard as those obtained with soils of moderate content of carbonates. The following experiments were therefore carried out :

Three soils deficient in carbonates which we had previously analysed, and the productive capacity of which were known to us from field experiments, were

selected. An addition of 30 grammes of pure carbonate of lime was made to every 100 grammes of the soils taken for analysis. This was then neutralized (*a*) with oxalic acid, (*b*) with citric acid. Finally, the usual extraction with 1 per cent. solution of citric acid was carried out. It was considered that if the neutral citrate exerted an additive solvent action the insoluble oxalate of lime would avoid this source of error.

The results obtained are set out in tabular form :

	Normal Soil.	Carbonated Soil + Oxalic Acid.	Carbonated Soil + Citric Acid.
<i>Soil No. 1.—Sandy alluvial ; irrigated.</i>			
Soluble in HCl $\left\{ \begin{array}{l} \text{K}_2\text{O} \dots \\ \text{P}_2\text{O}_5 \dots \\ \text{CaCO}_3 \dots \end{array} \right.$	0.339 0.387 Trace.	— — —	— — —
Soluble in 1 per cent. citric acid $\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \dots \\ \text{K}_2\text{O} \dots \end{array} \right.$	0.0432 0.0049	0.0432 0.0043	0.0432 0.0047
<i>Soil No. 2.—Red soil from limestone.</i>			
Soluble in HCl $\left\{ \begin{array}{l} \text{K}_2\text{O} \dots \\ \text{P}_2\text{O}_5 \dots \\ \text{CaCO}_3 \dots \end{array} \right.$	0.547 0.247 Trace.	— — —	— — —
Soluble in 1 per cent. citric acid $\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \dots \\ \text{K}_2\text{O} \dots \end{array} \right.$	0.0109 0.0054	0.0109 0.0077	0.0109 0.0064
<i>Soil No. 3.—Alluvial ; light ; high fertility.</i>			
Soluble in HCl $\left\{ \begin{array}{l} \text{K}_2\text{O} \dots \\ \text{P}_2\text{O}_5 \dots \\ \text{CaCO}_3 \dots \end{array} \right.$	0.573 0.168 0.296	— — —	— — —
Soluble in 1 per cent. citric acid $\left\{ \begin{array}{l} \text{P}_2\text{O}_5 \dots \\ \text{K}_2\text{O} \dots \end{array} \right.$	0.0440 0.0210	— —	0.0440 0.0230

It will be observed that the phosphoric acid in each case remains *absolutely constant*, whether carbonates were added and neutralized or not. This is true of oxalic as of citric acid employed for the neutralization.

The figures for phosphoric acid are so uniform as to suggest some apology. We have, however, evolved a modified process for phosphoric acid in soils that yields remarkably uniform results.

As regards potash, the figures indicate that in two cases the carbonic acid has exerted an additional solvent action. Our experience in Jamaica leads us to doubt whether citric acid is an adequate detective solvent for all forms of potash in a soil available for present consumption by plants.

Under tropical conditions, with a liberal rainfall or irrigation, it would appear that many soils containing a low proportion of potash soluble in 1 per cent. citric acid (0.005 and less) may yet actually be supplied adequately for the needs of such a crop as sugar-cane or bananas.

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