

# NEW TRENDS IN THE STUDY OF PLANT AVAILABLE PHOSPHATE

## Part I — THE USE OF RADIOACTIVE PHOSPHORUS

By G. H. WOOD

### Introduction

Most of the methods currently used for the estimation of plant available phosphate in soils are to a greater or lesser extent arbitrary, involving the use of extractants which often have a drastic effect on the chemical equilibrium of the soil.

Schofield<sup>1</sup> in 1955 pointed out that to assess the availability of phosphate in soil to plants, it was not only necessary to know the quantity of phosphate which could be regarded as available, but also its chemical potential (or free energy) and the rate of decrease of this potential with phosphate withdrawal. This is analogous to the assessment of the availability of water in the soil, which requires the measurement not only of the amount of water present, but also its potential or the tension with which it is held by the soil (pF) and the rate of increase of this potential with the removal of water.

The use of radioactive phosphorus (P-32) has demonstrated that there exists in the soil a pool of "labile" or "exchangeable" phosphate from which plants can draw their phosphate requirements. This "labile" pool can only be measured by means of P-32, and is a distinct fraction of the total inorganic phosphorus present in the soil.

The quantity of phosphate in the "labile" pool can be increased by adding phosphate to the soil and allowing the soil and the added phosphate to come to equilibrium. The phosphate potential is thereby changed, the extent of this change indicating the capacity<sup>2</sup> of the soil to supply phosphate to plants.

### The Equilibrium Phosphate Potential

Schofield<sup>1</sup> contended that quite general considerations pointed to the potential of mono-calcium phos-

phate ( $\frac{1}{2}pCa + pH_2PO_4$ ) as the function most likely to give a numerical index of the condition in the soil which mainly controls the availability of phosphate. Its evaluation is independent of arbitrary methods or procedures.

The equilibrium mono-calcium phosphate potential of a soil is measured<sup>3, 4</sup> by shaking aliquots of the soil with 0.01M-CaCl<sub>2</sub> solutions of increasing H<sub>2</sub>PO<sub>4</sub>-ion concentration, plotting the *change in phosphate content of the solution per gram of soil* ( $\Delta P$ ) against the final mono-calcium phosphate potential, and interpolating at  $\Delta P = 0$ .

The result should be independent of the duration of shaking and the soil/solution ratio, if the soil is at equilibrium and the suspension aerated during shaking.

If the soil is not at equilibrium, as is the case with soil in the field, short shaking periods will measure sites in the soil of low potential (i.e. high phosphate concentration). With longer shaking periods, these sites equilibrate with sites of high potential and the potential of the solution rises until complete equilibrium is achieved. Hence this method also permits the extent of "disequilibrium" to be measured. Microbial activity may invalidate results from the longer shakings.

### Preliminary Results

Some preliminary equilibrium phosphate potential measurements on several Natal Sugar Belt soils of variable phosphate content are given in Table 1, together with the amount of phosphate extracted by 0.02N-H<sub>2</sub>SO<sub>4</sub> and the pH, Ca, Mg and clay contents. All shaking was carried out in stoppered bottles without aeration, using an end-over-end shaker revolving at 30 r.p.m.

TABLE 1

Soil No.	Series	Derivation	P (ppm)	Equilibrium $\frac{1}{2}pCa + pH_2PO_4$	Shaking time (hrs.)	Ca (ppm)	Mg (ppm)	pH	Clay %
1	Cartref	T.M.S. (ord)	4	7.325	21.8	150	79	5.15	9
2	Cartref	T.M.S. (ord)	15	7.225	22.4	130	48	5.05	8
3	Cartref	T.M.S. (ord)	50	6.468	23.1	210	42	4.35	8
4	Fernwood	Recent Sands (Grey)	75	6.675	48.0	320	44	5.50	6
5	Clansthal	Recent Sands (Red)	271	4.340	0.5	460	63	6.10	4
5	Clansthal	Recent Sands (Red)	271	5.095	52.0	460	63	6.10	4

Soils 1, 2 and 3 are from a 3 x 3 x 3 fertilizer trial with phosphate applied at the rate of 0, 100 and 200 lbs. P<sub>2</sub>O<sub>5</sub> respectively.

The Q/I type curves ( $\Delta P$  versus  $\frac{1}{2} pCa + pH_2PO_4$ ) from which the values of the equilibrium phosphate potentials were obtained are shown in figure 1.

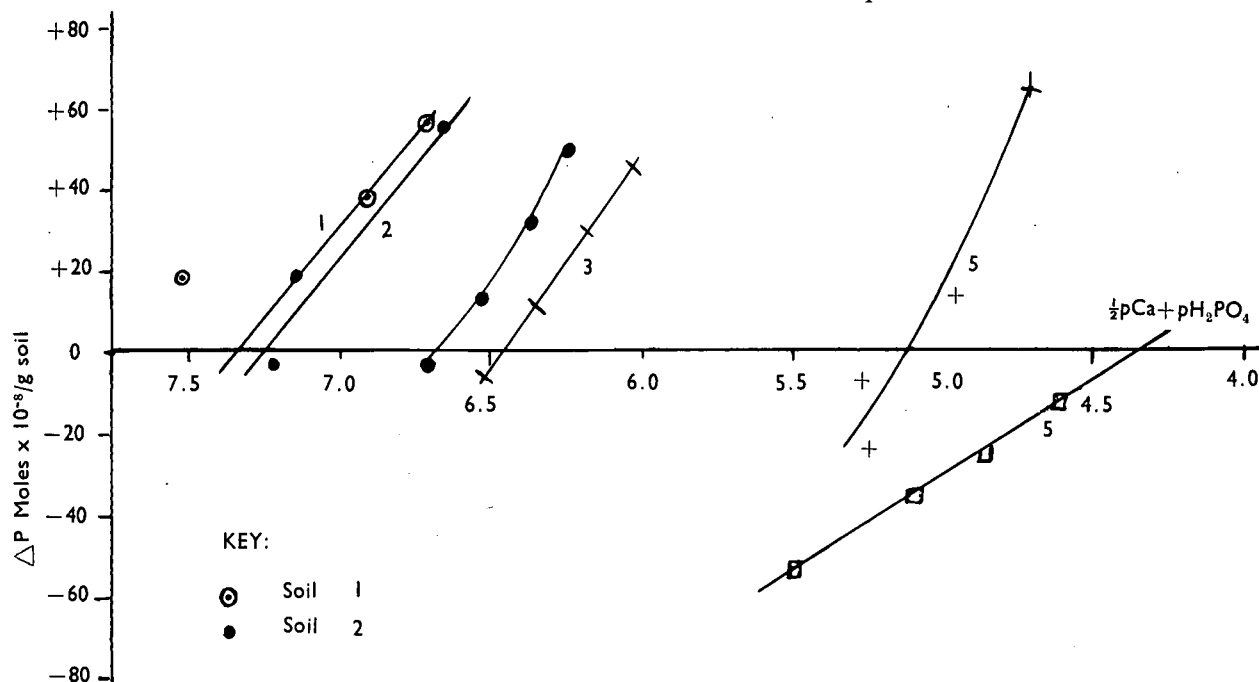


Fig. 1 —Q/I CURVES FOR EVALUATION OF EQUILIBRIUM PHOSPHATE POTENTIAL

They are of interest in that the slopes provide information on the ability of the labile pool of phosphate to maintain the potential of the soil solution. The variation of slope with time of shaking provides information on the nature and history of the labile pool.<sup>3</sup>

As stated earlier, a low equilibrium potential indicates a high concentration of phosphate in the soil solution and consequently less work is required by the plant roots for its absorption. Similarly, plant roots can absorb soil water more easily as its pF decreases.

The results in Table 1 show that soil 5 is not at equilibrium and has sites of very low phosphate potential, as shown by shaking for only 30 minutes. The overall potential of this soil (52 hours shaking) is considerably higher, although much lower than that of the other soils studied. If allowance is made for the difference in shaking times, correlation with the 0.02N-H<sub>2</sub>SO<sub>4</sub> extractable P is excellent.

#### Labile Phosphate

There are two distinct techniques for measuring this fraction of the soil phosphate. Theoretically they should both give the same numerical results.

##### (a) L-value

In this method, developed by Larsen,<sup>5</sup> plants are grown in a soil intimately mixed with phosphate labelled with P-32. At harvest the plants, whose function here is simply to sample the phosphate in the labile pool, are analysed for P-32 and total phosphate. The L-value is obtained from the equation:

$$L = X \left( \frac{S_f}{S_p} - 1 \right)$$

where X = the amount of phosphate added to the soil  
 $S_f$  = the specific activity of the added phosphate  
 $S_p$  = the specific activity of the plant phosphate  
 $S_f/S_p$  = the extent of dilution of the added P by the labile pool.

A correction has to be made for the phosphate content of the seed.

##### (b) E-value<sup>6</sup>

When a soil is shaken with a P-32 labelled orthophosphate solution an initial rapid exchange reaction between the added P-32 and P-31 in the soil is followed by a slower process. This causes a drop in the specific activity of the solution until equilibrium is reached. Three fractions of labile phosphate have been distinguished according to their associated rates of isotopic exchange, namely "rapid", "medium" and "slow", and the amounts of phosphate in each can be measured. The E-value is given by the equation:

$$E = x \left( \frac{S_i}{S_\infty} - 1 \right)$$

where x = the amount of phosphate initially present in the solution

$S_i$  = the initial specific activity of the solution

$S_\infty$  = the specific activity at equilibrium

A prerequisite of the E-value technique is that the soil should be in equilibrium with the solution, particularly with regard to phosphate, before the P-32 is added, so that no change in the phosphate potential occurs during measurement.

In order to start the E-value determination with a solution of the correct potential, it is first necessary to measure the equilibrium phosphate potential.

It is intended to use both the above methods in phosphate studies on Natal Sugar Belt soils.

### Discussion

In contrast with normal chemical methods of assessment of available phosphate, these relatively new techniques have a sound theoretical basis and bring order into the study of soil phosphorus.

The information that can be obtained about the phosphate status of soils by their use can be summarised as follows:

- (i) The overall phosphate potential using long shaking times.
- (ii) The variation of potential within a field soil, by varying the duration of shaking.
- (iii) Q/I curves giving information on the ability of the labile pool to maintain the potential of the soil solution; also on the nature and history of the labile pool.
- (iv) The total quantity of phosphate in the labile pool, together with the amount of phosphate in the fractions which can be characterized by "rapid", "medium" or "slow" exchange.
- (v) The rate of change of phosphate potential with change in the size of the labile pool, indicating the capacity of the soil to supply phosphate for plant growth.

These methods, although simple in principle, do not lend themselves to routine fertilizer advisory work. Therefore it is planned to evaluate existing methods in the light of these new developments, with a view to improving fertilizer advice.

The Electrical Extraction method discussed in Part II of this paper<sup>8</sup> lends itself more readily to routine work and hence it would be of much value to compare results obtained by this technique with that of the equilibrium phosphate potential to see if a close correlation exists between them.

### Summary

Two new complementary methods for the assessment of plant available phosphate in soils are discussed, namely the equilibrium phosphate potential and isotopically exchangeable (or labile) phosphate. They are both based on sound theoretical principles and the interrelationship between them gives a measure of the capacity of the soil to supply phosphate to plants.

Their value in evaluating existing and proposed routine methods of analysis is discussed, with a view to improvements in fertilizer advisory work.

### Acknowledgments

The author wishes to thank Dr. M. E. Sumner, Department of Soil Science, University of Natal, for his help and interest in this work.

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## Part II — ELECTRICAL EXTRACTION

By R. T. BISHOP

**Introduction**

In recent years the purely chemical approach to soil science (as for mineral assay) has been replaced by an electro-chemical one. Although there is little doubt that the new approach, as described by Beckett,<sup>2</sup> is sounder than the existing techniques for determining plant available nutrients, it is unpractical for routine fertilizer advisory work. The advisory chemist is therefore faced with the option of continuing with artificial extractions involving empirical solutions, ratio's of soil to solution, time of shaking etc., or of trying to comply with the new concepts. An attempt to adopt a more realistic approach of estimating plant available nutrients in the soil is outlined below.

**Extraction of cations and anions by electro-dialysis**

Under normal field conditions two components exert electrokinetic forces on an ion in the outer diffuse cloud surrounding the soil colloid. These components are (i) the colloidal particle itself and (ii) the root hairs. The respective potentials between these two components and the ion will depend on its location. The distance between the ion and the colloid surface is influenced by the concentration of the soil solution.<sup>4</sup> This distance increases with dilution and the resulting drop in potential renders the ion more available to the plant root.

The results of a growth analysis experiment<sup>1</sup> showed conclusively that optimum concentrations of nutrients

in the above ground portions of the sugarcane plant only occurred when, or soon after, the soil reached field capacity. It is therefore concluded that ions are most readily available to plants at this soil moisture content.

The approximate moisture content at field capacity of a soil from an N, P, K factorial experiment was determined. This amount of water was then added to soil samples from each plot. The soils were equilibrated in an end-over-end shaker and the solutions extracted in a pressure membrane extractor at two atmospheres. The concentrations of P and K in the extracted solutions, compared with those from normal chemical extractions are presented in Table 1.

While concentrations of K in the suction extraction revealed fertilizer treatment, no detectable P was present.

The only factor overlooked in the above extraction is the role played by the plant root. In an attempt to simulate the forces exerted by the plant root the soil was subjected to electro-dialysis, the apparatus used being shown in Figure 1.

Soil samples from a second N, P, K factorial experiment were moistened to field capacity and a current of 67 volts applied across the electrodes for one hour. The concentrations of P and K determined in the boric acid surrounding the respective electrodes are presented in Table 2.

TABLE 1

Concentrations of P and K removed at 2 atmospheres and by chemical extractions

Level	Extraction		Level	Extraction	
	0.02N H <sub>2</sub> SO <sub>4</sub> (ppm P in soil)	2 atms. suction		N amm. acetate (ppm K in soil)	2 atms. suction (ppm K in soln)
P <sub>0</sub>	5	Nil	K <sub>0</sub>	46	61
P <sub>1</sub>	9	Nil	K <sub>1</sub>	72	73
P <sub>2</sub>	18	Nil	K <sub>2</sub>	112	133

TABLE 2

Concentrations of P and K removed by electro-dialysis and chemical extractions

Level	Extraction		Level	Extraction	
	0.02 N H <sub>2</sub> SO <sub>4</sub> (Klett reading on final soln.)	Electro- dialysis (Klett reading)		N amm. acetate (ppm in soil)	Electro- dialysis (ppm in soln.)
P <sub>0</sub>	16	18	K <sub>0</sub>	42	42
P <sub>1</sub>	52	88	K <sub>1</sub>	55	45
P <sub>2</sub>	89	131	K <sub>2</sub>	69	54

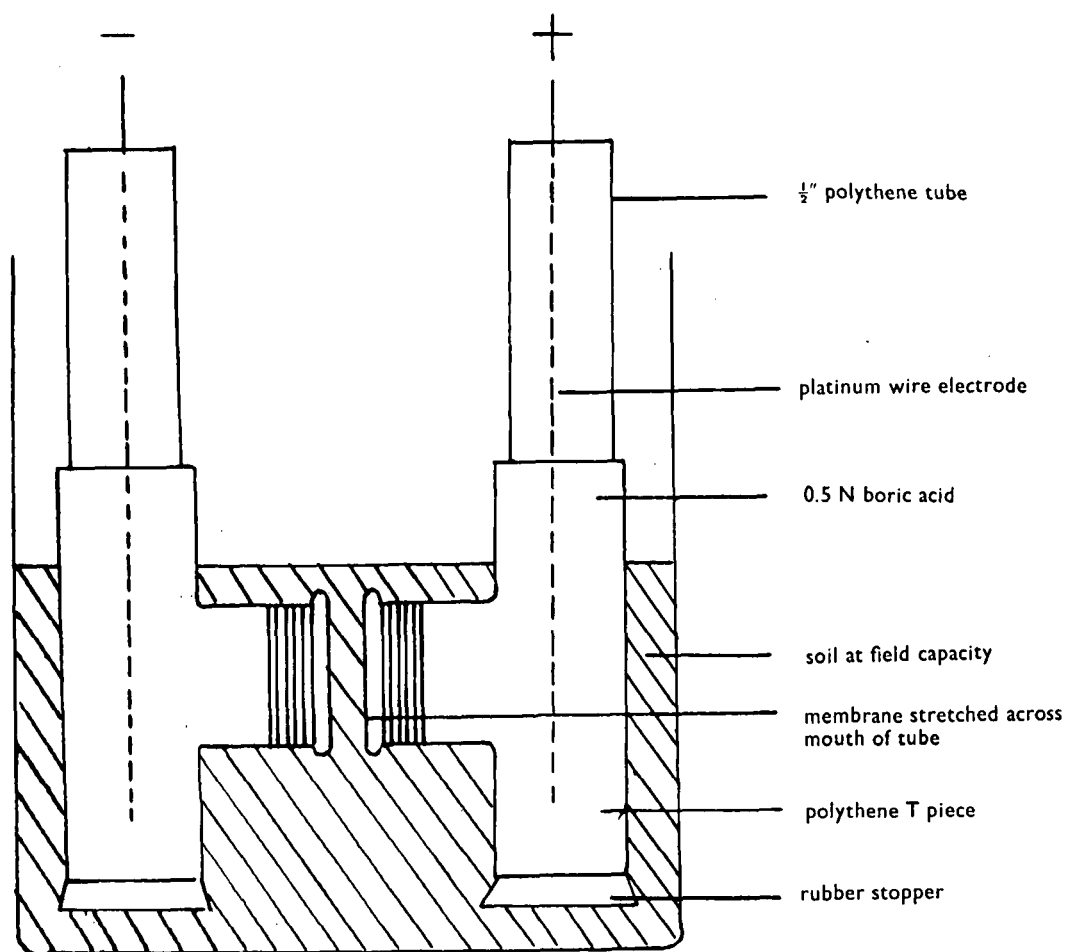


Fig. 1 — APPARATUS USED FOR ELECTRODIALYSIS OF SOILS

The electrolytic method successfully detected differences in P and K fertilizer applications.

Since it was not known what volume of soil contributed to the observed results, values could not be expressed on a quantitative basis. A modification of the above apparatus now being tested is shown in Figure 2.

The modified apparatus has the following advantages:

- (i) the weight of soil being extracted can be determined,
- (ii) the larger surface area of soil exposed ensures more efficient extraction,
- (iii) the thin layer of soil requires a smaller potential across it (reducing any heating effects) thus allowing more units to be operated from the same power supply,
- (iv) the taps below the acid containers increase the efficiency in removal of solution.

### Applications of electro dialysis

#### A — Practical

- (i) Extraction of ions by electro dialysis can possibly replace the routine chemical methods used for the determination of plant available nutrients. The main advantages would appear to be as follows:
  - (a) the only empirical factor introduced is the voltage applied,
  - (b) anions and cations are extracted simultaneously,
  - (c) no shaking or filtering is necessary,
  - (d) no dilution is required before determining nutrient concentrations.
- (ii) A quantitative measure of plant available trace elements in the soil may be possible.
- (iii) The presence of toxic amounts of ions e.g. aluminium may be detectable.

#### B — Theoretical

If the power supply can be made sufficiently sensitive to allow measurements in the millivolt range the following may be feasible:

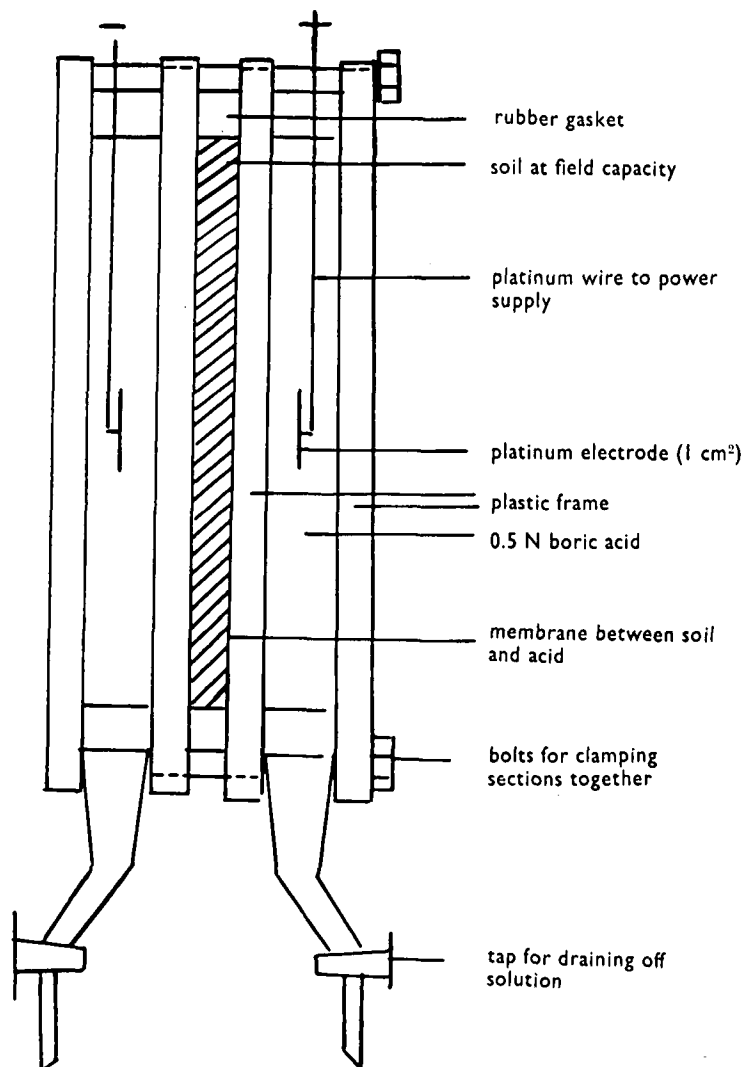


Fig. 2a—PROPOSED APPARATUS FOR ELECTRODIALYSIS OF SOILS (Side view)

- (i) the testing of Bolt's<sup>3</sup> theory that the ratio of divalent ions to monovalent ions in the soil solution increases as the soil dries out,
- (ii) more rapid measurement of Beckett's<sup>2</sup> Q/I type curves. The quantities of P extracted by electro-dialysis will be correlated with the P potentials as measured by G. H. Wood in section (1) of this paper. Similar correlations will be made with the K potentials,
- (iii) determination of the force exerted on ions by plant roots.

It should be emphasised that the above applications are purely speculative at this stage.

#### Summary

An extraction by electro-dialysis of soils has been found to reflect P and K fertilizer treatments. The possibilities of using this technique for routine and research determinations is considered.

#### Acknowledgments

Professor E. R. Orchard, Department of Soil Science, who is Responsible Officer for the author's M.Sc. degree of which the data published will form a part.

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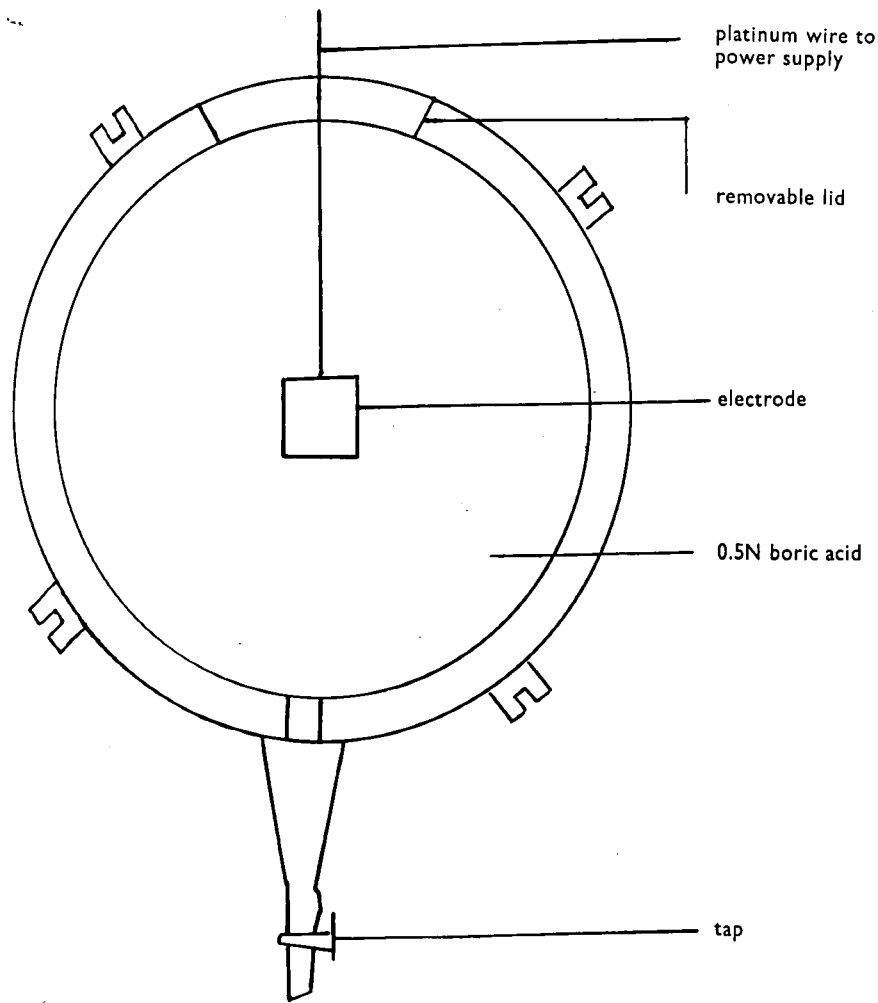


Fig. 2b — PROPOSED APPARATUS FOR ELECTRODIALYSIS OF SOILS (front view)

**Mr. R. A. Wood:** Referring to Mr. G. H. Wood's, and also to Mr. Bishop's paper, we are pleased to be able to say that research of this nature will shortly be occupying us at the Experiment Station. If it is going to be possible to satisfactorily predict the levels of P and K in the very wide range of soils existing in the sugar belt, then this will be a very worthwhile venture. The approach to the question of soil analysis must be flexible, however, as all the authors have made clear to us today.

**Mr. G. R. Thompson:** The theory developed by Schofield and Beckett on the Q/I relation of plant nutrients, is undoubtedly based upon sound theoretical principles. However, on reading the literature on this subject, one finds that these methods have been applied to only a few British soils, mainly the Upper and Lower Greensand soils.

I feel the work presented by Mr. G. H. Wood is a step in the right direction in that he has taken the lead in introducing these methods into this country.

Furthermore, a wider application of these methods to a larger number of soils would possibly more than justify the further use of these methods. In this respect one must be careful in expressing the correct potential of different soils, e.g. an aluminium potential in relation to a phosphate potential and a sodium potential in relation to a phosphate potential could possibly be used when dealing with very acid or alkaline soils.

However sound a method may be in theory, it may have limitations in its practical application. In this respect much research could be done on improving laboratory techniques for the purpose of routine work.