

T H E S I S

THE USE OF ELECTRODIALYSIS
IN SOIL PHOSPHORUS STUDIES

Submitted by

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In partial fulfillment of the requirements

for the Degree of Master of Science

Colorado Agricultural College

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THE USE OF ELECTRODIALYSIS IN SOIL PHOSPHORUS STUDIES

(By James B. Goodwin)

INTRODUCTION

An accurate, practical laboratory method for measuring available plant nutrients in the soil is highly desirable. Many methods, both chemical and biological, have been advanced for this purpose but all of them have limitations. Electrodialysis has been proposed by several investigators as a method for studying soil fertility.

The electrical conductance of solutions of electrolytes involves the actual movement of matter. These carriers of current were termed "ions" by Faraday (25)¹. The ions which moved toward the cathode he called "cations" and those which moved toward the anode he called "anions." Faraday's studies led to his universal law that for a definite amount of current transferred, definite quantities of matter were deposited at both the cathode and anode, which are proportional to their chemical equivalents. Faraday's quantitative law is one of the most exact in physical chemistry.

¹Reference by number (in parenthesis) is to "Literature Cited."

There are certain qualitative predictions which may be made by applying the above principle to a colloidal soil separated from the cathode and anode by means of suitable membranes. If a direct current is passed through this system, a process known as electrodialysis, only those ions to which the membranes are permeable will conduct the current between the poles. Hence, electrodialysis offers a comparatively rapid means of separating crystalloids from colloids.

The quantitative removal of the readily soluble, or available, phosphate ions from a soil suspension by means of electrodialysis involves a very complex system. The importance of the interaction of each variable on all of the other variable factors affecting electrodialyzable phosphorus cannot be over-emphasized.

An intelligent interpretation of the amount of phosphorus removed from arid and semi-arid soils would be impossible without controlling the temperature and pH change of the soil suspension being electrodialyzed, the total soluble salt content, types of salts, and hydration of ions, or at least a knowledge of the manner in which these variable factors change during the process of electrodialysis.

Effect of Salts

Two soils having exactly the same available phosphorus content but having either different total salt contents or

different kinds of salts, or both, will not deliver equal amounts of phosphorus in the anode chamber for one faraday of current transferred. From Ohm's law, $I = \frac{E}{R}$, it is evident that the RI drop across the electro dialysis cell is a function of the resistance offered by the soil suspension. Therefore, if the above mentioned soils were electro dialyzed under equal and constant potential for the same period of time, all other factors being equal, the amount of phosphorus removed from the two soils would be more nearly equal. In other words, the same tendency (potential) exists for the phosphate ions to carry a part of the current in both soils.

Effect of Type of Membrane

Bradfield (9), Bradfield and Bradfield (12), Komagata (38), and Löddesöl (41) have studied the effects of positively and negatively charged membranes on the rate of ion removal from pure solutions and soil suspensions. Like charges repel and unlike charges attract. Their results show that this fact is a measurable quantity for membrane permeability to ions. From the work of Michaelis (47), (48) on membrane permeability to electrolytes and electro-endosmosis, the effect of ion hydration is very much elucidated. He states that differences in ionic mobilities are magnified enormously when passing through a membrane. This is probably due to the friction caused by the number of water molecules which each ion drags through the capillary canals of the membrane.

He further states that a change in pH may increase the friction due to the bound charge on the capillary walls and thus retard or increases the velocity of the passing ion. There is a large difference in the hydrodynamic radii of ions, as has been shown by Jenny (35).

Effect of Temperature

Any temperature change in the soil suspension will result in a whole series of changes in the system. External factors (room temperature, etc.) remaining constant, temperature variation will be a result of the current transferred. Increased temperature decreases the viscosity of the dispersing medium, alters the hydration of the ions, affects the solubility and ionization of the compounds present, including solid phase phosphates, and changes to some extent the permeability of the membranes. Due to the heterogeneity of most soils, it is difficult to obtain any two samples which, upon electrodialysis under constant potential, will maintain the same temperature or will vary in temperature to the same degree. It is almost impossible to maintain a constant temperature even with a cooling system.

Effect of pH

Continued electrodialysis results in a gradual decrease in pH of the soil suspension due to an increase in hydrogen ion saturation of the non-diffusible soil material. If the membranes

are not equally permeable to their respective ions, there will be a tendency for rapid pH change until most of the readily soluble salts are removed. As a result, the solubilities of all compounds present are altered, conductivity changes and temperature fluctuates. Consequently, the transport numbers are different for every ion and again there is no way of knowing what part of the current is being transferred by the phosphate ions.

Freundlich and Loeb (24) by the use of various membrane combinations and a sodium chloride solution, show that the pH can be increased, decreased, or held practically constant. The ionization of the phosphates is a function of the pH but the pH range involved during electrodialysis should not affect the mobility of the phosphate ions unless there is a difference in hydration between H_2PO_4^- , HPO_4^{--} , and PO_4^{---} . Buehrer (14) has shown there is very little difference between the mobility of H_2PO_4^- and HPO_4^{--} . The effect of pH change on membrane permeability already has been mentioned.

The equation which Heymann (28) derives, for the amount of current carried by a pure solution of an electrolyte, expresses quite adequately the relationship of these variables and is as follows:

$$J = q \cdot e \cdot 10^{-5} \alpha (u + v) \cdot c$$

where

- J = current in amperes
 α = degree of dissociation
 c = concentration
 u and v = relative ion mobilities and
 $E = \frac{e}{l}$ where e = potential in volts between
the electrodes and l = distance between
the electrodes.

REVIEW OF LITERATURE

Cameron and Bell (16), in 1905, used an electrical current for removing the bases and hydrolyzed products of minerals. König, Hasenbäumer and Hassler (39), in 1911, used this principle in studying soil colloids. They believed that it furnished a reliable method for determining the easily soluble plant nutrients in soils.

Mattson (44) has stimulated recent interest in electrodialysis by using it to purify soil samples for cataphoresis experiments. Since Mattson's application of electrodialysis to the study of soil exchangeable bases, it has been used by many investigators for this purpose (11), (18), (50), (59), (60). It has been used for the pretreatment of soil samples for mechanical analysis (11), (44), (56), for measuring the translocation of calcium in soils

(61), and for other purposes (1), (5), (23), (26), (30), (34), (36), (45).

Yegarov (62), in 1905, observed that after an electrical current had been passed through a soil the citric acid soluble phosphorus was increased almost 100 percent, while the nitric nitrogen was decreased. Rost (53) attached little value to electro dialysis as a method for determining plant available phosphorus. Taranov (58), Kottgen and Diehl (40), Di Gleria (19), Harper (27) and Brewer and Rankin (15) have compared electro dialysis with other methods, especially the Neubauer, for measuring the availability of mineral nutrients. They report varying degrees of agreement between the methods. Harper (27) found very close agreement between electro dialyzable phosphorus, dilute acid soluble phosphorus and plant response to phosphate fertilizers. Neither the pH values nor the lime contents of the soils he used is given but it is probable that they were non-calcareous, judging from the close agreement obtained between field response to phosphate fertilizers and dilute acid soluble phosphorus. McGeorge (46), after studying some of the calcareous soils of Arizona as well as soils from other parts of the United States, believes that the determination of available phosphorus by electro dialysis presents much that is promising provided certain limitations are recognized, namely:

1. Soluble phosphate is lower in sandy soils
but the plant's ability to obtain phosphorus
is greater.

2. There is a great difference between the degree of phosphate dissociation in calcareous and non-calcareous soils.

He concludes, "1. The process of electrodialysis is an excellent means of dissolving the active or available forms of phosphate from calcareous soils with least interference from the calcium carbonate present," and "4. The method is sufficiently delicate to measure the increase in phosphate content of the soil following an ordinary application of phosphate fertilizer."

The soils of Arizona are probably very similar to those of Colorado, especially in their alkalinity, soluble salt content, lime content, and total phosphorus content. For this reason, the method of electrodialysis, as proposed by McGeorge, for measuring phosphate availability should be as applicable to Colorado soils as to the soils of Arizona.

A chemical analysis of the soils used by these investigators is not included in these articles and this omission limits the ability of the reader to draw specific conclusions from the electrodialysis data which are given. In many cases, it is probable that the soils used from other states were acid which would minimize certain variables, such as total salt content and lime content, affecting electrodialyzable phosphorus. A phosphorus deficiency in such soils might even indicate a deficiency in total phosphorus

which usually is not the case in western calcareous soils. The accuracy with which the electro-dialyzed phosphorus results could be repeated has not been discussed by most investigators, except for such statements as "duplicate analyses agreed fairly well." The data of many of the investigators show that much more rapid methods for estimating available phosphorus agree with field response to phosphate fertilization almost as well as their method of electro-dialysis. Their data are not sufficient to determine whether the differences between the various methods used are statistically significant or due merely to chance.

MATERIALS AND METHODS

Soils Used

The soil samples used in this investigation have been collected from many parts of the state. These samples were secured from the untreated plots of fields to which treble superphosphate had been applied. The response of the crop being grown (usually alfalfa, sugar beets, or truck crops) to the phosphate fertilizer was determined by observation. Only fields producing large crops and showing no apparent increase due to the fertilizer treatment, were used for the soils high in available phosphorus according to field trials. Similarly, only fields which were producing poor crops and to which the application of treble superphosphate increased

the crop yield sufficiently to be very evident by observation, were used for the soils low in available phosphorus. Each sample is the composite of at least 10 borings to a depth of 6 inches from the untreated portion of the fields.

Statistical Analysis of Data

The "analysis of variance" (22) was used to determine the statistical significance of the differences obtained. The principle of the method, as applied to these experiments, may be given briefly. The summation of variability of each electro dialysis determination (sum of squares) is divided into various known causes, leaving a remainder attributed to uncontrolled or unknown causes. The standard error (standard deviation) is calculated from the remainder sum of squares. The variance ($S.E.^2$) due to any particular cause is found by dividing the sum of squares by the proper degrees of freedom. The significance of the results so obtained is determined from the tables of distribution of "Z" as given by Fisher (23). If the obtained "Z" value is equal to, or greater than, the expected 5 percent point, the odds are at least 19 to 1 that the differences are significant; similarly with a "Z" value equal to, or exceeding, the 1 percent point, the odds are at least 99 to 1 for significance.

In this paper the 5 percent point (corresponding to 2 S.E.) is taken as the minimum level of significance. Comparisons also are made on the basis of the 1 percent point. The "difference for

significance" as given in the tables is twice the standard error of a difference. The standard error of a difference is obtained by multiplying the standard error of the mean by $\sqrt{2}$.

The estimation of covariance was made by means of the correlation coefficient, Fisher's "t" test (22) being used to determine the significance of the association. The level of significance used in this investigation was the 1 percent point. Hence, an obtained "t" value which is as great as, or greater than, the expected gives odds of at least 99 to 1 that the correlation is significant.

Preliminary Studies

It seemed advisable to determine the practical importance of some of the factors which, theoretically, should affect electrodialyzable phosphorus. The soils of Colorado are so widely different in soluble salt contents and lime contents that the variability due to these factors should be near a maximum.

The several types of electro dialysis cells, which have been used so far, are discussed in detail by their designers (4), (8), (10), (21), (31), (42), (43), (51), (54). Each investigator has designed or modified a cell to fit his requirements. The apparatus used in this investigation is the Bradfield three-compartment type, similar to the electro dialysis cell described as No. 4461

in the Arthur H. Thomas Company's catalog. However, the center compartment was slightly modified in order to permit the recording of temperatures and pH determinations as well as the stirring of the soil suspension. A 250 cc. pyrex beaker, with the top and bottom removed and four holes drilled as close together as possible in the side, served as the center compartment. Direct current was obtained from a motor generator set with a field rheostat and sufficient resistance in the circuit to give a potential from 5 to 300 volts. A voltmeter and a wide range ammeter remained in the circuit at all times.

The procedure used by McGeorge (46) was followed as closely as possible with the above described equipment. The constant amperage as used by McGeorge was reduced to 0.1 amperes because of heating. However, it was found impossible to maintain accurately a constant current throughout a period of nine hours or more. To overcome this difficulty, two electrodialysis cells were connected in series which necessitated the same current passing through both units. Thus the results of the two cells for any one run are comparable providing there are no differences within the cells. To determine any cell variation, the same soil was placed in both cells for several runs. The results are given in Table 1. The different runs are not comparable. A collodion hemoglobin membrane was used on the anode side and a parchment paper membrane on the cathode side. Humfeld and Alben (33) have studied various electrode combinations.

Table 1. - Results with Cells in Series*

Run No.	Soil No.	Field Response to P	Total Soluble Salts	Carbon-ates ex-pressed as CaCO ₃	p.p.m.	pct.	pH	Textural grade	K ₂ CO ₃ Sol-uble P	Time Eleo-trolyzed hrs.	Ca-CO ₃ added gm.	NaOH 0.1 N cc.	HCl 0.1 N cc.	P Eleo-trolyzed mgm.	Av. Temp. °C
1	R51A	Little	410	0.30	7.40	Loam	61	6	None	0.70	3.35	0.144	22.0		
	R51A	Little	410	0.30	7.40	Loam	61	6	None	0.70	3.35	0.144	22.0		
22	129A	None	595	1.70	8.45	C.Loam	69	28	None	2.85	13.55	0.653	25.7		
	129A	None	595	1.70	8.45	C.Loam	69	28	None	3.20	15.65	0.650	25.7		
3	R51A	Little	410	0.30	7.40	Loam	61	9	None	1.30	7.70	0.696	25.0		
	R51A	Little	410	0.30	7.40	Loam	61	9	0.5	2.10	3.20	0.120	24.0		
4	99A	None	345	0.30	8.40	Sand	133	9	1.0	4.05	9.80	0.162	24.0		
	99A	None	345	0.30	8.40	Sand	133	9	2.0	4.05	9.90	0.163	24.1		
5	125A	None	400	0.50	8.30	C.Loam	119	9	0.2	5.05	19.15	0.267	25.0		
	125A	None	400	0.50	8.30	C.Loam	119	9	0.7	4.95	18.35	0.176	25.0		
6	97A	None	55	0.45	8.60	Sand	61	11	None	1.60	7.45	0.960	22.8		
	102A	None	3300	0.90	8.30	Sand	133	11	None	7.55	8.35	0.162	22.0		
7	R63A	Great	600	7.40	8.30	C.Loam	42	7	None	1.60	9.85	0.190	22.4		
	127A	None	1960	7.30	8.15	C.Loam	84	7	None	3.25	9.45	0.148	22.0		
8	R68A	Great	1950	1.50	7.70	F.S.Loam	42	45	None	15.55	26.60	0.574	22.3		
	101A	None	335	0.30	8.70	Loam	137	45	None	4.10	17.90	3.044	22.3		
9	102A	None	3300	0.90	8.30	Sand	133	10	None	12.15	15.25	0.311	23.2		
	111A	Great	700	2.80	8.30	F.S.Loam	42	10	None	2.35	15.30	0.500	23.4		

potential of approximately 180 volts.

*A potential of approximately 180 volts.

There, no doubt, is a difference in conductivity of the different electrodes which affects their efficiency but so long as the electrode does not give up ions to the surrounding solution, there should be no particular disadvantage to any one of the several types which these authors discussed. A platinum anode and a nickel cathode, as supplied with the cells, were used throughout this investigation. A 5-gram soil sample was used in order to facilitate stirring and to decrease heating. A small motor stirrer was used to keep the soil in suspension. To the center compartment were added 180 cc. of distilled water and to both the anode and cathode chambers were added 100 cc. of distilled water.

The dialysates were analyzed for phosphorus by the Denigès colorimetric method as modified by Hockensmith, Gardner, and Goodwin (29). The other ions were far below the concentrations which Chapman (17) shows interfere with the blue colored formation. The dialysates were removed from both cells at the same time within each run, but the intervals vary between runs as well as the total time of electrodialysis. This was done for the purpose of determining the most suitable procedure.

From runs 1 and 2 (Table 1), it can be seen that the results of the two cells are comparable. Hence, the data obtained from the two cells of the same run may be compared, i.e., if a different soil is placed in each cell, any difference in electrodialyzable phosphorus should be due to the soil variation rather than to

the method of electrodialysis. In runs 3, 4 and 5, the effect of adding CaCO_3 to the soil suspension in the center compartment for different soils was studied. In run 3, the addition of 0.3 grams of CaCO_3 has reduced the phosphorus electrodialyzed from 0.696 milligrams to 0.120 milligrams. In run 4, the addition of 1.0 and 2.0 grams of CaCO_3 to cells 1 and 2, respectively, shows no significant difference, probably because sufficient CaCO_3 was added to furnish a solid phase of CaCO_3 in both cells. In run 5 with soil 125-A, the addition of 0.2 and 0.7 grams of CaCO_3 to cells 1 and 2, respectively, shows a difference in electrodialyzable phosphorus.

It has been shown theoretically that any variation in salt content should affect the amount of phosphorus electrodialyzed. In run 6, neither soil responded to phosphate fertilizers under field conditions. Soil 97-A is very low in soluble salts and contains less than one-half as much K_2CO_3^2 soluble phosphorus as soil 102-A which has a large amount of soluble salts. Both soils are sandy. The phosphorus electrodialyzed is in the reverse magnitude of that obtained with the K_2CO_3 extractant but the soil with the lower soluble salt content yielded more electrodialyzable phosphorus. In run 7, electrodialyzable phosphorus does not agree with either field results or K_2CO_3 soluble phosphorus. The CaCO_3

²The K_2CO_3 method has given the closest agreement with field response to phosphate fertilizers of any method so far used in this laboratory on Colorado soils (29).

content of these soils is much higher than any of the soils so far electrodialyzed. Again the salt content may account for the difference. The results of run 8 agree with K_2CO_3 soluble phosphorus and field trials. It should be noted that the salt content, including the percent lime, of the two soils favors these results. In run 9 electrodialyzable phosphorus does not agree with either field response or K_2CO_3 soluble phosphorus, but the salt content may again account for these differences. It is probable that the $CaCO_3$ contents of both soils in this run are sufficient to give a solid phase.

These data indicate that electrodialyzable phosphorus in soils obeys the laws of physical chemistry, as would be expected. Hence, the electrodialysis of Colorado's highly variable soils with a constant current appears to be of little value. With the exception of the Arizona work (46), investigators have used soils which were probably acid. Acid soils are usually formed under conditions of excessive leaching which means the soluble salt content is probably very low and there is no $CaCO_3$ present. This may account for the favorable results reported by other investigators without any apparent consideration of the variables which might affect the results.

The next part of the investigation was to determine, if possible, some procedure whereby electrodialyzable phosphorus would represent "plant available" phosphorus. It was thought ad-

visable to determine the effect of different salts which usually are found in these soils, temperature and stirring of the soil suspension, membranes used and the potential on electrodialyzable phosphorus.

Effect of Salts and Type of Membrane

The effects of the different salts and types of membranes were determined on salt solutions of 0.04 normality. In the first series of experiments, a collodion hemoglobin-coated anode membrane was used with a parchment paper cathode membrane. In the second series a cellophane anode membrane was used with the parchment paper cathode membrane. The procedure was as follows: 100 cc. of a solution containing approximately 18 parts per million of phosphorus as KH_2PO_4 were pipetted into the center compartment of both cells for every run; 80 cc. of the 0.04 normal salt solution to be studied were added to this. The two cells were run in parallel under a constant potential of 5 volts. The current was so small that the temperature remained practically the same as that of the laboratory and any variation due to temperature can be ignored. The results of the various runs should be comparable in these experiments.

The data are presented graphically in fig. I. With the cellophane membrane, the effects of the different salts vary considerably more than when the collodion hemoglobin membrane is used. The depressing effect of CaCO_3 should be emphasized. This

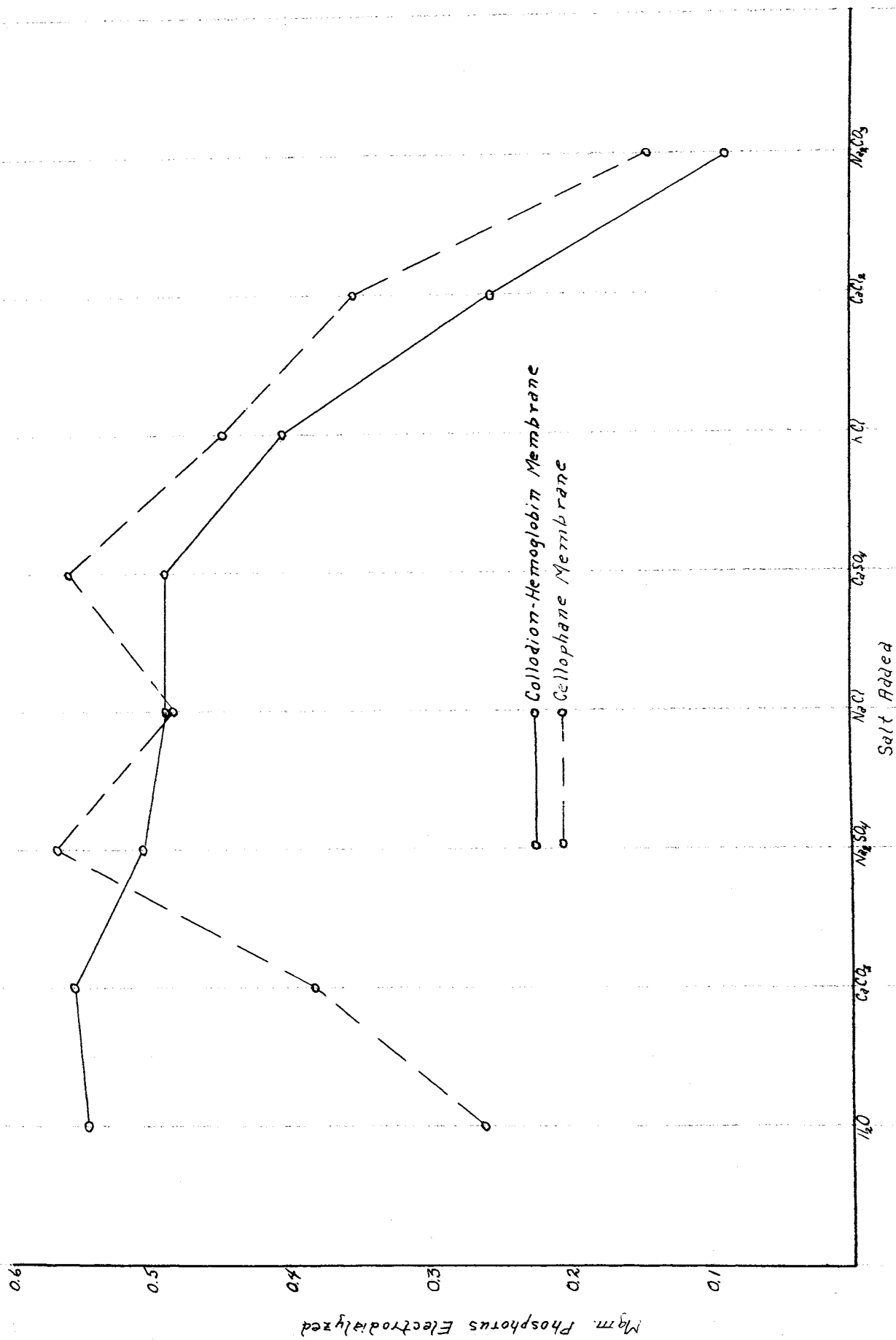


Fig. I Effect of Salts on Electrolysable Phosphorus

makes the cellophane membrane less desirable than the collodion hemoglobin membrane for the electrodialysis of Colorado soils which are usually calcareous. The very slight effects of H_2O , $CaCO_3$, Na_2SO_4 , $NaCl$, and $CaSO_4$, all of which are common salts in Colorado soils, on the collodion hemoglobin membrane should be noted. In the case of Na_2CO_3 , the pH was above 9.6. The decrease in electrodi-
alizable phosphorus when Na_2CO_3 is used might be explained by the high alkalinity which may decrease the permeability of the membrane or retard the ionization of the phosphate compounds.

Each point on the collodion hemoglobin curve in fig. I is the average of triplicate electrodialysis analyses and each point on the cellophane curve is the average of duplicate analyses. The experiment was so performed with the collodion membrane that it was possible to analyze the data statistically. These data and analyses are given in Table 2. From the "Z" value for replications the error is not significant. All of the salts studied except $CaCO_3$ reduced the amount of phosphorus electrodialed significantly when compared with no salt added.

Voltage

The external voltage to be used in electrodialecting soils will vary with the resistance offered by the particular equipment being used and can be determined by experimentation only. The factors to be considered are:

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1. The first step in the process of the investigation is the identification of the subject. This is done by the use of the subject's name, address, and other identifying information. The subject is then located and interviewed. The interview is conducted in a confidential manner and the subject is assured that their information will be kept confidential. The subject is then asked to provide information about their activities and contacts. This information is then used to identify other individuals who may be involved in the investigation. The process is then repeated for each individual identified. The final step in the process is the compilation of the information gathered into a report. This report is then used to identify the individuals involved in the investigation and to determine the nature of their activities. The report is then used to determine the appropriate course of action to be taken.

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biovideobroadcasts are being used for significant treatment and
-helped establish a program for providing similar treatment to other people with
and video recordings of the treatment as well as the video of the person

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Table 2. - Effect of Salts on Electrodialyzable Phosphorus

Salt	P (average of 3 replications) mg.	Deviation from No treatment pct.
H_2O	0.544	0.00
$CaCO_3$	0.555	-2.02
Na_2SO_4	0.508	6.62
$NaCl$	0.489	10.11
$CaSO_4$	0.489	10.11
KCl	0.403	25.92
$CaCl_2$	0.257	52.76
Na_2CO_3	0.088	83.82

$Z = -0.3559$ for replications, 5% pt. = 0.6594, 1% pt. = 0.9570

$Z = 2.9428$ for treatments, 5% pt. = 0.5099, 1% pt. = 0.7287

S. E. of mean = 0.008

Difference for significance = 0.025

S. E. in pct. of mean = 2.07

1. Conductivity of soil suspension - the more current carried the greater the heating. The theoretical effects of increased temperature on electrodiализable phosphorus have already been discussed.
2. Amount of electrodiализable phosphorus contained in the soil.

If a particular current is desired, the external voltage is immaterial so long as there is sufficient resistance to maintain the desired amperage through the soil suspension. As has already been shown, electrodiализis using a constant current is of little value in Colorado soils. The current in the following experiments will be allowed to vary with the soil suspension, holding the RI drop between the electrodes of the cell as nearly constant as possible. The external voltage which was found to be best for the equipment used in this investigation was 130 volts.

Temperature and Stirring of Soil Suspension

The difficulty of maintaining a constant temperature for any period of time is evident with an ever-changing conductivity of the soil suspension being electrodiализed and such wide differences in conductivity between soils. A study of the magnitude of this error and a possible correction were undertaken. Soil 15 was

chosen for this purpose because of the large amount of electro-dialyzable phosphorus it was known to contain and because of its tendency to heat without the use of a water-cooling system which was inserted in the cathode and anode compartments of the cells. The two cells were connected in parallel and a copper coulometer placed in series with each cell to measure the total number of coulombs transferred during electro-dialysis. All experiments were continued for a 9-hour period in which the dialysates were removed each hour for four hours, followed by one 2-hour period, and this followed by one 3-hour period. The soil suspensions were stirred by means of an electric stirrer. A 5-gram soil sample and 180 cc. of distilled water were placed in the center compartment. Collodion hemoglobin-coated anode membranes and parchment paper cathode membranes were used.

The results are given in Table 3. The soil was electro-dialysed twice in cell I and once in cell II in order to study the comparableness of the internal resistance of the two cells which are now in parallel and independent of each other. Runs 1, 2 and 3 give the data for this study. The temperature was held as nearly constant as possible with the cooling system. The approximate average temperature for each 9-hour run is given, which varies about one degree. The total amount of phosphorus actually electro-dialysed varies to the extent of 0.3 milligrams of phosphorus. But the actual coulombs of current transferred vary in the same order which suggested the possibility of a constant ratio between coulombs transfer-

Table 3. - Effect of Temperature and Stirring
On Electrolyzable Phosphorus

Run No.	Sol. No.	Av. Temp. °C	NaOH		HCl		Total P		Cur- rent trans- ferred coul.	P per 1,000 Cell coul.	Remarks
			cc.	cc.	cc.	cc.	Electro- lyzed mg.	mg.			
1	15	25.4	6.7	42.9	1.590	1.501	1.222	I	Check		
2	15	24.4	8.2	37.9	1.290	986	1.309	I	Check		
3	15	25.2	8.4	40.8	1.410	1107	1.273	II	Check		
4	15	25.2	5.9	11.5	0.280	384	0.714	I	Center compartment not stirred		
5	15	25.5	5.5	11.0	0.243	343	0.703	II	Center compartment not stirred		
6	15	42.2	6.6	53.8	2.020	1479	1.366	I	Temperature increased		
7	15	41.1	7.7	41.9	1.460	1140	1.281	II	Temperature increased		
8	15	25.6	7.6	27.2	0.886	692	1.280	I	Electrodes moved 1 cm. from membranes		

red and phosphorus electrodialyzed. These data are given under the column headed "Mgm. P per 1,000 coulombs." The variability between different runs and the two cells has been reduced from 0.3 milligrams to 0.087 milligrams of phosphorus. That is what would be expected if temperature variation did not markedly change the ratio of transport numbers between the phosphate ions and the other ions present.

To further study the effect of temperature variability, in runs 6 and 7 (Table 3), a burner was placed under the cells, both of which were wrapped with asbestos, to increase the temperature. Throughout the 9-hour period of electrodialysis, the temperature was maintained between 40 and 50 degrees C. with an approximate average of 42.2 degrees C. in run 6 and 41.1 degrees C. in run 7. The actual amount of phosphorus electrodialyzed in run 6 has increased considerably when compared with runs 1, 2 and 3. In run 7, the cell had been taken apart and reassembled because of a torn membrane. This may account for no increase in actual phosphorus electrodialyzed when compared with runs 1, 2 and 3. If the data of runs 6 and 7 are based upon 1,000 coulombs transferred, the results check very well with runs 1, 2 and 3.

However, it would be possible to have a soil, containing the proper kinds and amounts of salts, wherein a marked increase or decrease in temperature would change the transport numbers of the various ions. In this case the ratio of phosphorus

electrodialyzed to coulombs transferred would be of little value. For this reason the temperature should be held as nearly constant as possible during the process of electrodialysis.

The effect of the torn membrane in run 7 suggested a possible error due to variation in cell constant. Since it was necessary to take both cells apart periodically to clean them, it would be almost impossible to reassemble the cells with exactly the same internal resistance as before, which is largely due to variation in distance between the electrodes. In run 8, the electrodes were moved 1 centimeter away from the membranes. The phosphorus electrodialyzed has been reduced almost one-half, but when based on 1,000 coulombs transferred the results agree very well with runs 1, 2, 3, 6 and 7. The effect of cell variation on electrodialyzable phosphorus is reduced by comparing the phosphorus electrodialyzed on the basis of coulombs transferred.

The importance of stirring the soil suspension is shown in runs 4 and 5. Only about one-fourth as much phosphorus actually was electrodialyzed and when these data are based on 1,000 coulombs transferred, the results do not agree with those of runs 1, 2, 3, 6, 7 and 8. Conditions are so changed without stirring that the results hardly would be expected to be comparable. By determining the ratio of phosphorus electrodialyzed to coulombs transferred, the effects of slight variation in rate of stirring,

voltage and cell constant on electrodialyzable phosphorus are reduced.

pH Considerations

The impracticability of maintaining a uniform pH change in the soil suspension being electrodialyzed is obvious with a system as variable as these soils. The amount of phosphorus electrodialyzed might be interpreted better if the pH of the soil suspension could be determined at intervals during the period of electrodialysis.

The electrodes to be used for determining the pH of the center compartment must meet certain requirements. Few ions should be liberated from the electrodes because the conductivity of the soil suspension would be altered and thus interfere with subsequent electrodialysis. The equilibrium potential must be reached quickly. The electrode should have considerable mechanical strength.

The quinhydrone electrode, as ordinarily used, would render the soil suspension unfit for subsequent electrodialysis. Bugher (15) describes a quinhydrone electrode covered with a collodion membrane which worked very satisfactorily. However, he states that certain dissolved salts may alter the correct pH value. Considerable time is required to make the electrode and the slow diffusion of quinhydrone through the membrane necessitates replacing the electrode at frequent intervals.

The hydrogen electrode could be used but it is less desirable because of the time required to reach equilibrium. This electrode would require troublesome gas connections which would greatly complicate the electrodialysis.

The glass electrode seemed to fit the requirements for these pH measurements. But, the danger of breaking the glass membrane would be increased because it was desired to make the pH measurements while the soil suspension was being stirred. The extensive electrical equipment and vibration would interfere with the amplifying system necessary with the glass electrode.

Since the electrodes were to be left in the soil suspension only long enough to make the reading, the antimony electrode seemed best suited for the purpose because of its mechanical strength, rapid equilibrium potential and because it does not require the addition of any foreign material. Kolthoff and Hartong (37) and Roberts and Fenwick (52) have shown the applicability of the antimony-antimony trioxide electrode for measuring acidity.

Various forms of the antimony electrode have been used by the different investigators for measuring the pH of the soils (2), (3), (6), (20), (49), (55), (57). Antimony amalgam electrodes were prepared according to Shukoff and Awsejewitsch (55). Considerable "drifting" was observed with this type of electrode. The electro-deposited antimony gradually diffused off which necessitated

the construction of new electrodes at frequent intervals. Stick antimony electrodes prepared according to Parks and Beard (49) were found to give the best results. When checked against the quinhydrone electrode and buffer solutions, the equation of Shukoff and Awsejewitsch (55) closely approached the correct pH value.

$$E = 0.009 + 0.053 \text{ pH}$$

The stick antimony electrode and the saturated calomel half cell with a KCl agar bridge were used in making all of the pH measurements during electrodialysis.

Method of Electrodialysis

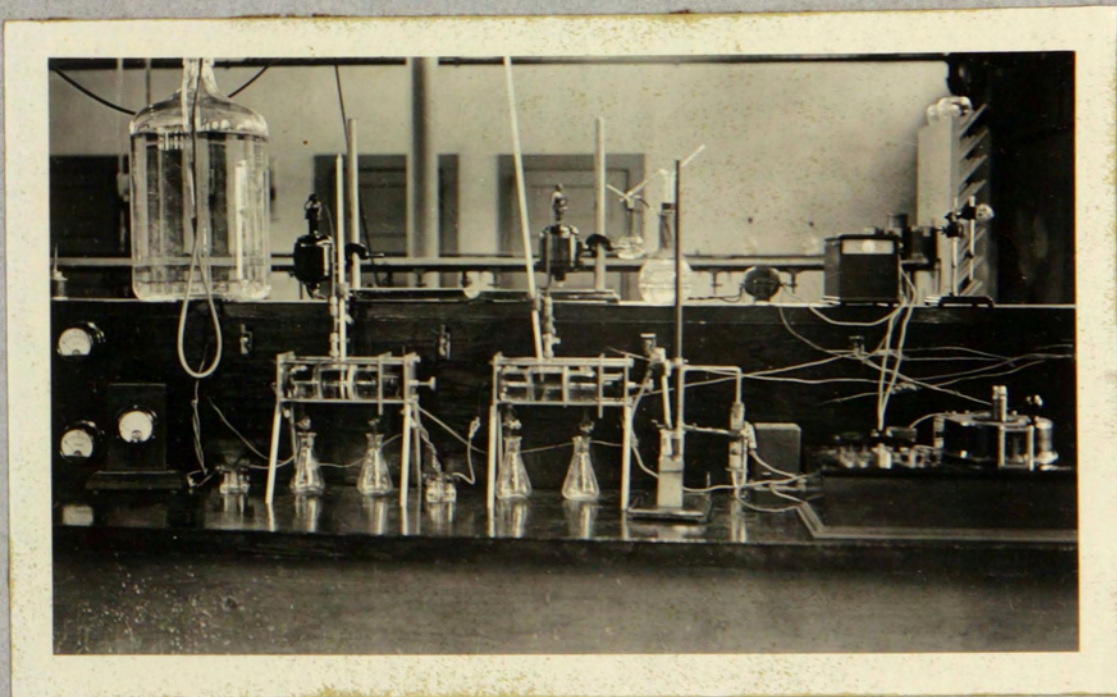
From the preliminary studies, the electrodialysis procedure which appeared to be best fitted for determining plant available phosphorus is as follows: 5 grams of soil and 180 cc. of distilled water were placed in the center compartment of the electrodialysis cell. To the cathode and anode compartments were added 100 cc. of distilled water. A small coil made of glass tubing was inserted in the cathode and anode compartments and connected to the water tap for cooling purposes. The cells were connected in parallel and a copper coulometer placed in series with each cell. Each soil was electrodialyzed for 9 hours under a constant potential of as nearly 180 volts as possible. The dialysates were removed hourly for the first 4 hours, followed by a 2-hour period and this followed by a 3-hour period, making a total of 9 hours of electro-

dialysis. The dialysates were titrated with 0.1 normal HCl and NaOH, using phenolphthalein as the indicator for the anolyte and brom thymol blue as the indicator for the catholyte. The temperature was maintained at as nearly 25 degrees centigrade as possible. The soil suspensions were stirred throughout the period of electrodialysis by means of electric stirrers. A thermometer graduated in 1/10th degree divisions was inserted in the center compartment and clamped there. At the beginning of the 9-hour run and each time the dialysates were removed, the antimony electrode and the KCl agar bridge connected to the calomel half cell were inserted in the center compartment and the potential measured by means of a type "K" potentiometer and a sensitive galvanometer. The potentials were measured while the soil suspension was being stirred. It was necessary to turn off the motor generator in making the pH measurements. Collodion hemoglobin anode membranes, prepared according to Bradfield and Bradfield (12), were used. Parchment paper cathode membranes were used. The cells were taken apart and washed every three runs. New cathode membranes were inserted after each washing. The same collodion hemoglobin membranes were used throughout the remaining investigation.

A milliammeter was connected in series with each cell at the beginning of every run to aid in adjusting the current density in the coulometers to about 0.01 amperes per square centimeter. This is very important in order to obtain a firm deposit of copper which

can be washed with water and then with alcohol, and weighed before oxidation takes place.

At the end of the 9-hour electro dialysis run, each anolyte is analyzed for phosphorus by the Denigés colorimetric method as modified by Hockensmith, et al (29). A simple calculation³ places this quantity of phosphorus on a basis which permits comparison with the data of other electro dialysis runs.



Electro dialysis Apparatus Used in the Investigation

$$\frac{\sum P}{C} \times 1000 = P \text{ per 1,000 coulombs transferred}$$

where $\sum P$ = summation of the phosphorus from each dialysate of a run
C = coulombs transferred during entire time of electro dialysis

EXPERIMENTAL RESULTS

Triplicate electro dialysis analyses were made on each of 45 soil samples to determine the accuracy of the method. The soils were numbered from 1 to 45 and electro dialysed in 3 series. In the first series the soils were electro dialyzed consecutively from 1 to 45. In the second series the number of each soil was placed on a small card and the numbers drawn from a hat after being well mixed. Two soil samples were electro dialysed per day and care was taken to pair different soil samples throughout the three series. The procedure was repeated in determining the order of samples for electro dialysis in the third series. Randomization is necessary for the application of the analyses of variance.

A rather complete chemical analysis also was made on most of the soils studied to aid in interpreting the electro dialysis results. These data, together with the average milligrams of phosphorus electro dialysed per 1,000 coulombs transferred in the 3 replications, are given in Table 4. All of these soils are seen to contain a rather large amount of total phosphorus. There is no correlation between field response to phosphate fertilizers and the total phosphorus content of the soils. The wide variability in soluble salt content is sufficient to explain the little or no correlation between electro dialyzable phosphorus and field response to phosphate fertilizers when a constant current is applied for a definite period of time to each soil. The carbonates, expressed as CaCO_3 , varied

Table 4. - Chemical Analyses of Soils Electrolyzed

Soil No.	Field Response to P	P per 1,000 Coulombs	MgCO ₃ Soluble P	Water Soluble P	Total P ₂ O ₅	Soluble Salts*	Carbonates expressed as CaCO ₃	Organic matter
		mg.	p.p.m.	p.p.m.	pot.	p.p.m.	pot.	pot.
1	Yes	0.253	29	0.01	0.153	5720	2.4	2.3
2	No	0.450	56	0.07	0.193	1980	3.9	2.8
3	Yes	0.152	25	0.01	0.152	1910	13.3	4.1
4	No	4.903	120	0.62	0.155	1650	0.3	2.4
5	Yes	0.499	22	0.01	0.174	6010	1.9	2.4
6	No	0.849	43	0.03	0.145	2340	0.1	2.2
7	Yes	1.853	31	0.07	0.129	1400	0.3	1.9
8	No	0.554	45	0.04	0.209	2520	7.4	2.4
9	Yes	0.430	14	0.01	0.163	1730	7.5	0.9
10	No	0.433	61	0.09	0.193	3530	5.0	2.3
11	Yes	0.365	42	0.03	0.135	6350	0.9	2.0
12	No	1.422	42	0.07	0.129	1350	0.3	1.5
13	Yes	0.543	31	0.01	0.133	3910	3.1	2.7
14	No	2.313	95	0.13	0.171	900	0.1	1.6
15	Yes	1.263	27	0.02	0.223	6190	7.3	2.0
16	No	1.339	51	0.11	0.154	2320	0.6	1.6
17	Yes	0.379	21	0.01	0.129	20730	1.5	1.6
18	No	1.323	53	0.10	0.123	570	0.2	1.7
19	Yes	1.320	14	0.02	0.146	1690	2.6	1.3
20	No	2.075	33	0.06	0.132	1910	0.4	1.6
21	Yes	0.230	13	0.01	0.154	7340	2.1	1.9
22	No	3.262	73	0.19	0.117	560	0.2	1.3
23	Yes	0.755	31	0.01	0.173	2660	1.0	2.2

*The salts were determined electrometrically in a one to thirty-six soil water suspension, so these values are much higher than would be obtained by the usual method of determining soluble salts in soil.

from 0.1 percent to 13.5 percent. There appears to be a rather close agreement between phosphorus electrolyzed per 1,000 coulombs transferred, K_2CO_3 soluble phosphorus, water soluble phosphorus and actual field trials. The significance of these data will be discussed later.

The water soluble phosphorus was determined by the "molybdenum blue" method of Zinzadze (63) (64) and is accurate to about 0.01 part per million of phosphorus. The K_2CO_3 soluble phosphorus was determined by the method of Hockensmith, et al (29).

The complete electrolysis data are given in Table 5. Each value represents the average of the three replications. The statistical analyses of the data are given at the bottom of the table. The obtained "Z" value for replicates in the case of actual phosphorus electrolyzed shows that the differences are highly significant, but when the phosphorus electrolyzed is based upon 1,000 coulombs transferred, the "Z" value indicates that the differences between replicates are not significant. The corresponding standard errors (S. E.) are 13.6 and 3.1 in percent of the general mean. From these facts, it may be concluded that the ratio of phosphorus electrolyzed to coulombs transferred gives a more accurate comparison than does the actual phosphorus electrolyzed.

The statistical analyses of the titratable anions and

Table 5. - Electrodiagnosis Analyses of Soils, Average of Three Analyses

Soil No.	Field Response to P	Total P Electrolyzed mgm.	Current Transferred coulombs	P per 1,000 Coulombs mgm.	AV. Temperature °C	Anions NaOH 0.1 N cc.	Cations HCl 0.1 N cc.	Anions per 1,000 Coulombs cc.	Cations per 1,000 Coulombs cc.
1	Yes	0.151	510	0.258	25.2	5.6	21.2	10.9	41.5
2	No	0.320	715	0.450	25.6	5.8	28.1	5.3	39.3
3	Yes	0.222	1476	0.152	25.1	4.7	43.8	3.6	32.1
4	No	0.858	175	4.906	24.5	1.9	9.1	10.6	52.5
5	Yes	0.262	525	0.499	23.5	5.5	20.6	10.3	39.3
6	No	0.159	189	0.849	24.1	1.4	7.8	7.1	44.0
7	Yes	0.538	286	1.856	23.5	2.3	11.5	7.3	42.1
8	No	0.755	1351	0.554	24.0	4.9	39.5	3.9	30.2
9	Yes	0.424	944	0.480	24.0	3.9	29.2	4.5	31.8
10	No	0.413	851	0.483	24.2	3.7	31.0	4.4	38.6
11	Yes	0.690	796	0.865	24.1	4.4	29.2	5.5	38.8
12	No	0.492	342	1.422	24.6	2.2	10.0	6.5	31.1
13	Yes	0.579	1075	0.543	23.9	4.0	39.7	3.7	37.0
14	No	0.622	222	2.818	24.3	1.6	7.2	8.0	38.3
15	Yes	1.295	1023	1.268	25.4	8.2	37.0	8.5	36.6
16	No	0.313	167	1.869	25.8	1.9	9.4	11.9	57.6
17	Yes	0.380	951	0.379	24.8	17.7	30.2	18.6	31.7
18	No	0.368	201	1.828	24.4	1.7	10.2	9.2	49.3
19	Yes	0.311	235	1.320	24.6	2.3	12.7	10.0	54.8
20	No	0.813	392	2.075	24.5	3.3	11.3	8.4	28.7
21	Yes	0.117	514	0.230	24.1	6.3	19.2	12.4	34.2
22	No	0.423	130	3.262	24.2	1.7	6.2	9.3	37.0
23	Yes	0.241	318	0.755	23.6	2.6	13.0	8.3	42.1
24	No	0.649	234	2.777	25.6	1.6	9.4	7.0	42.8
25	Yes	0.314	641	0.490	24.5	3.4	24.3	5.2	37.7
26	No	0.339	222	1.511	23.2	1.6	9.6	8.0	43.8
27	Yes	0.310	530	0.584	24.0	2.9	21.5	5.5	40.5
28	No	0.498	249	2.004	23.6	1.9	11.2	7.3	45.3

Table 5. - Electrodiagnosis Analyses of Soils, Average of Three Analyses - cont.

Soil No.	Field Response to P	Total P Electrolyzed mg.	Current Transferred coulombs	P per 1,000 Coulombs mg.	AV. Temperature °C	Anions NaOH 0.1 N cc.	Cations HCl 0.1 N cc.	Anions per 1,000 Coulombs cc.	Cations per 1,000 Coulombs cc.
29	Yes	0.274	489	0.562	25.0	2.7	18.8	5.4	56.3
30	No	0.535	221	2.451	24.0	1.5	7.5	6.9	55.7
31	No	0.710	806	0.872	25.8	3.8	27.4	4.8	55.1
32	No	0.825	699	1.184	24.1	3.3	26.3	4.7	57.7
33	Yes	0.982	1512	0.750	24.8	10.4	45.2	8.0	54.5
34	No	2.100	772	2.720	23.9	7.3	29.7	9.5	58.5
35	Yes	0.487	1360	0.553	24.4	4.9	45.6	3.6	53.4
36	No	0.715	1319	0.557	24.8	4.0	43.4	3.1	53.1
37	Yes	0.243	783	0.508	24.7	3.4	29.7	4.3	56.7
38	No	0.522	585	0.895	22.9	3.2	23.0	5.4	59.3
39	Yes	0.579	1422	0.401	25.9	4.9	47.4	3.4	53.3
40	No	0.391	258	1.533	23.8	2.0	10.4	7.5	41.0
41	Yes	0.508	1138	0.270	24.3	4.4	40.3	3.8	55.4
42	No	0.384	840	0.458	24.0	8.7	29.8	5.6	55.5
43	Yes	0.357	639	0.560	23.7	4.4	25.7	6.9	57.0
44	Yes	0.366	775	0.474	23.4	2.9	25.8	3.7	53.0
45	Yes	0.108	590	0.186	23.1	4.4	25.5	7.5	59.8
Z for replicates		= 1.2844		0.5005		1.3928	1.8932	0.4804	1.6625
5% point		= 0.5756		0.5486		0.5786	0.5756	0.5486	0.5756
1% point		= 0.8025		0.7638		0.8025	0.8025	0.7638	0.8025
Z for samples		= 1.6183		3.3655		2.8870	1.8175	1.2406	1.5965
5% point		= 0.2854		0.2654		0.2654	0.2654	0.2654	0.2654
1% point		= 0.3743		0.3746		0.3746	0.3746	0.3746	0.3746
S.E. of mean		= 0.069		0.035		0.25	2.0	0.9	1.2
S.E. in pct. mean		= 13.6		3.1		6.3	8.7	12.4	8.2
D. for significance		= 0.193		0.098		0.70	5.7	2.5	5.5

cations, both the amounts actually electrodialed and based upon 1,000 coulombs transferred, are very interesting. When based upon 1,000 coulombs transferred, the standard error in percent of the general mean for the cations has been reduced from 8.7 to 3.2, while for the anions the standard error has been increased from 6.3 to 12.4 in percent of the general mean. The exact quantitative chemical reactions in either the anode or cathode compartment are very complex, or at least unknown, since the amounts of the various ions participating are unknown. However, in the case of the cations, the chemical reactions resulting to give titratable basicity are more nearly quantitative than the chemical reactions of the anions to give titratable acidity when compared with coulombs transferred. For example, most of the cation reactions are merely replacement reactions, such as :



On the other hand, if chlorine is the anion, upon contact with the positive electrode, chlorine gas may be formed and the titratable acidity has not been increased in proportion to the current transferred. Thus, when the anions electrodialed are based upon 1,000 coulombs transferred, this error is magnified.

It should be noted that the soils with the larger soluble salt contents do not always transfer the greater number of coulombs. In other words, it is not entirely the number of ions

present at any one time which determines the amount of current transferred but also the ability of the soil to yield ions over an extended period of time. The titratable acids and bases are a result of secondary changes. The titratable anions are not as proportional to the primary reactions as are the titratable cations and, of course, Faraday's law applies only to the primary changes.

For clearness, these data have been graphed. Fig. II presents the actual phosphorus electro dialyzed. According to field trials, all of the soils to the left of the perpendicular broken line are deficient in available phosphorus and all of the soils to the right are sufficient in available phosphorus. There are no marked differences between the amounts of phosphorus electro dialyzed from the deficient soils and the sufficient soils. In other words, it would be impossible to pick out those soils which responded to phosphate fertilizers from these electro dialysis data.

The milligrams of phosphorus electro dialyzed based upon 1,000 coulombs transferred, are given in fig. III. The broken perpendicular line again divides the sufficient and deficient soils. The broken horizontal line was drawn arbitrarily to include as many of the deficient soils below it and as many of the sufficient soils above it as possible. In general, these data agree much better with field results than do the data of fig. II. From the "difference for significance" (Table 5) taking 0.800 milligrams

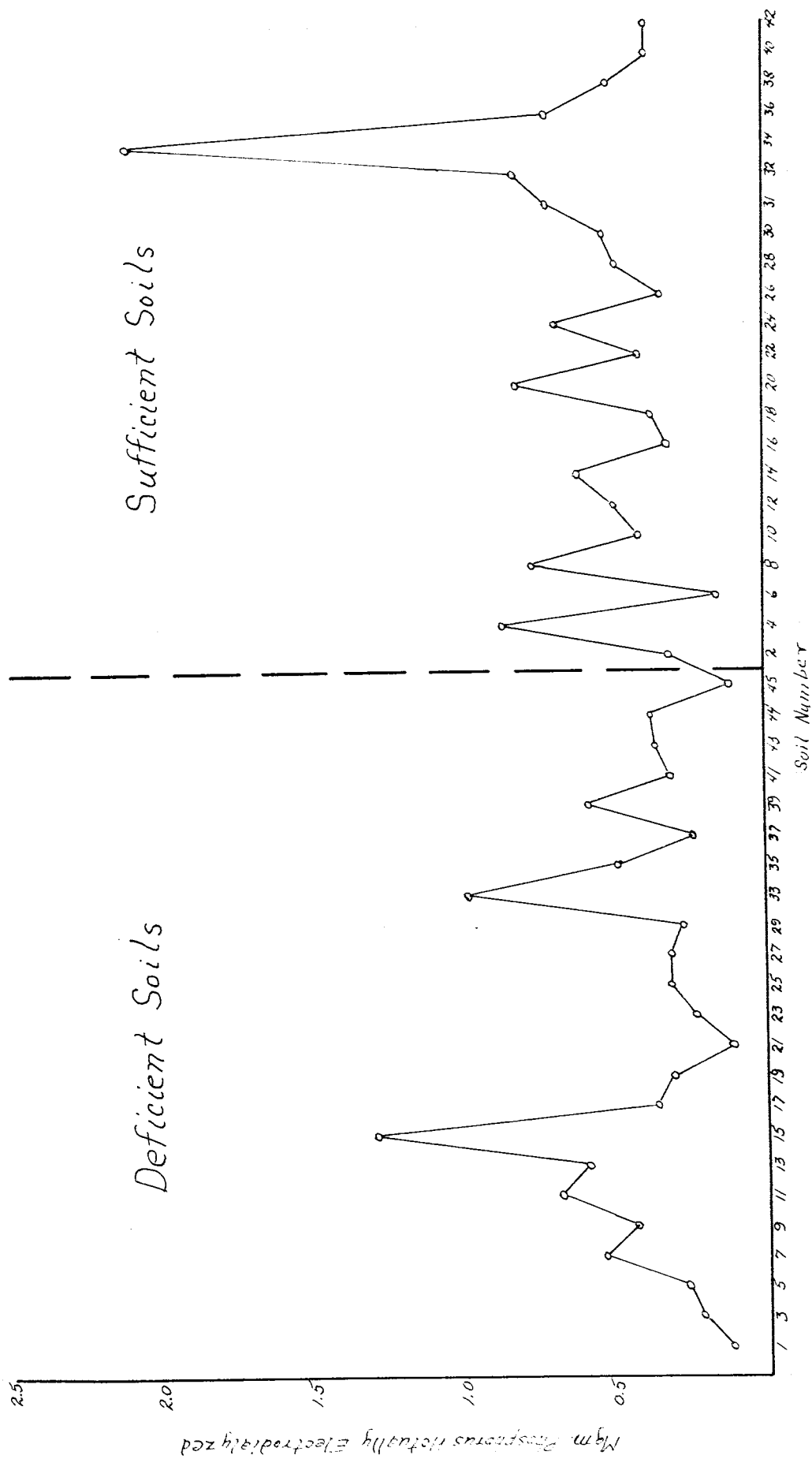


Fig. II Phosphorus Actually Electrolyzed

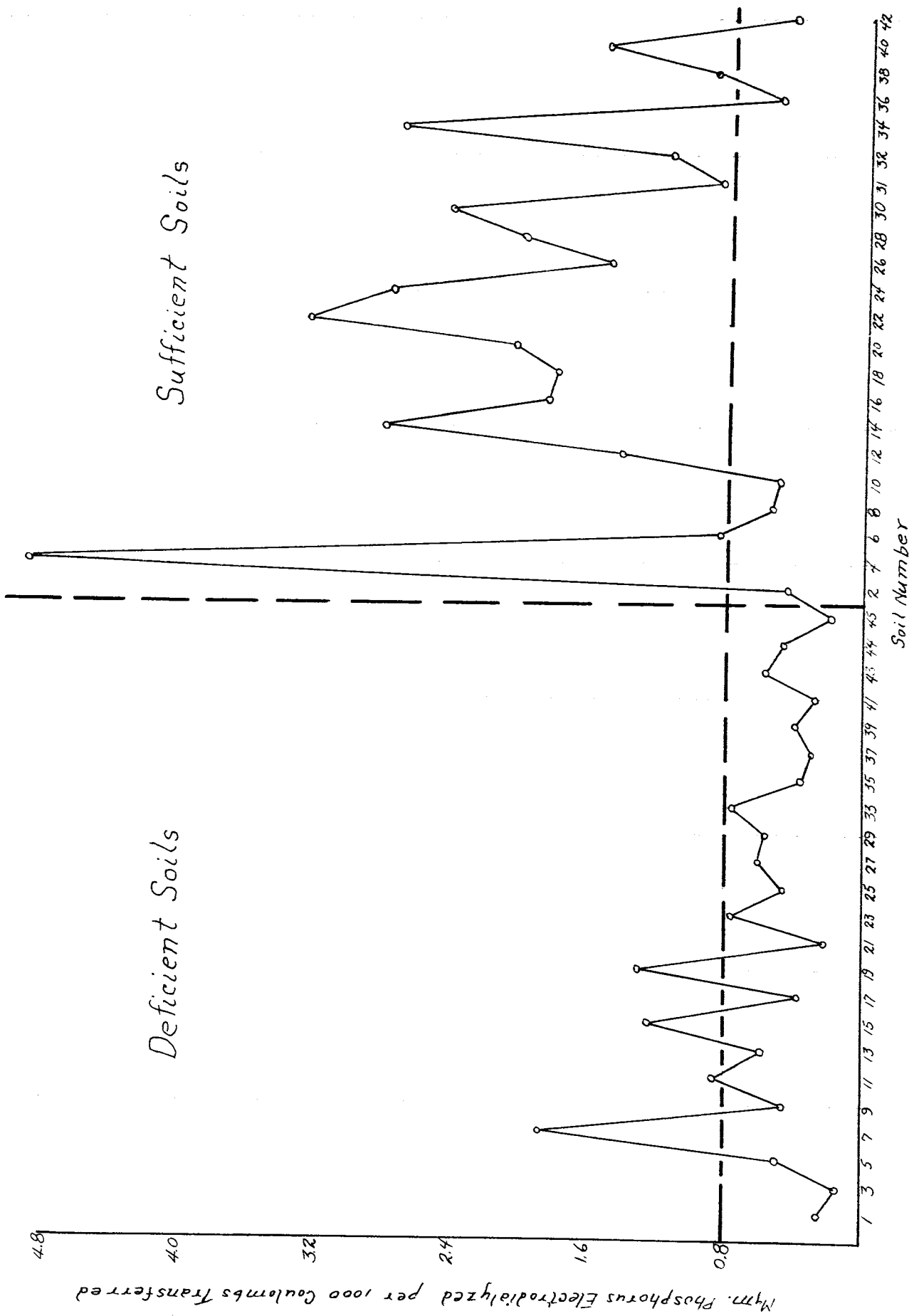


Fig. III Ratio of Phosphorus Electrolyzed to Coulombs Transferred

phosphorus as the dividing line between sufficiency and deficiency, soils 11, 23, 35, 6, 51 and 38 fall in the doubtful class. Soils 7, 15, 19, 2, 8, 10, 36 and 42 do not check with field results. Placing these data in percent, the results are as follows:

13.3 percent in the doubtful class

17.3 percent do not agree with field results

68.9 percent agree with field results

In fig. IV, the water soluble phosphorus has been graphed in the same manner. Sufficient data for a statistical analysis are not available. The method is accurate to about 0.01 part per million of phosphorus. On this basis, then, soils falling closer than 0.01 part per million phosphorus to the line 0.03 part per million phosphorus are doubtful and soils 11, 6 and 52 fall in the doubtful class. Soil 7 does not check with field results. The analysis for soil 45 is lacking because of insufficient soil. These data, on a percentage basis, are as follows:

6.6 percent in the doubtful class

2.3 percent do not agree with field results

90.9 percent agree with field results

Potassium carbonate soluble phosphorus is given in fig. V. Sufficient data for a statistical analysis are lacking here also. Soils 20 and 36 do not check with field results and assuming (29) soils 11, 44, 12 and 38 to be in the doubtful class, the agreement is as follows:

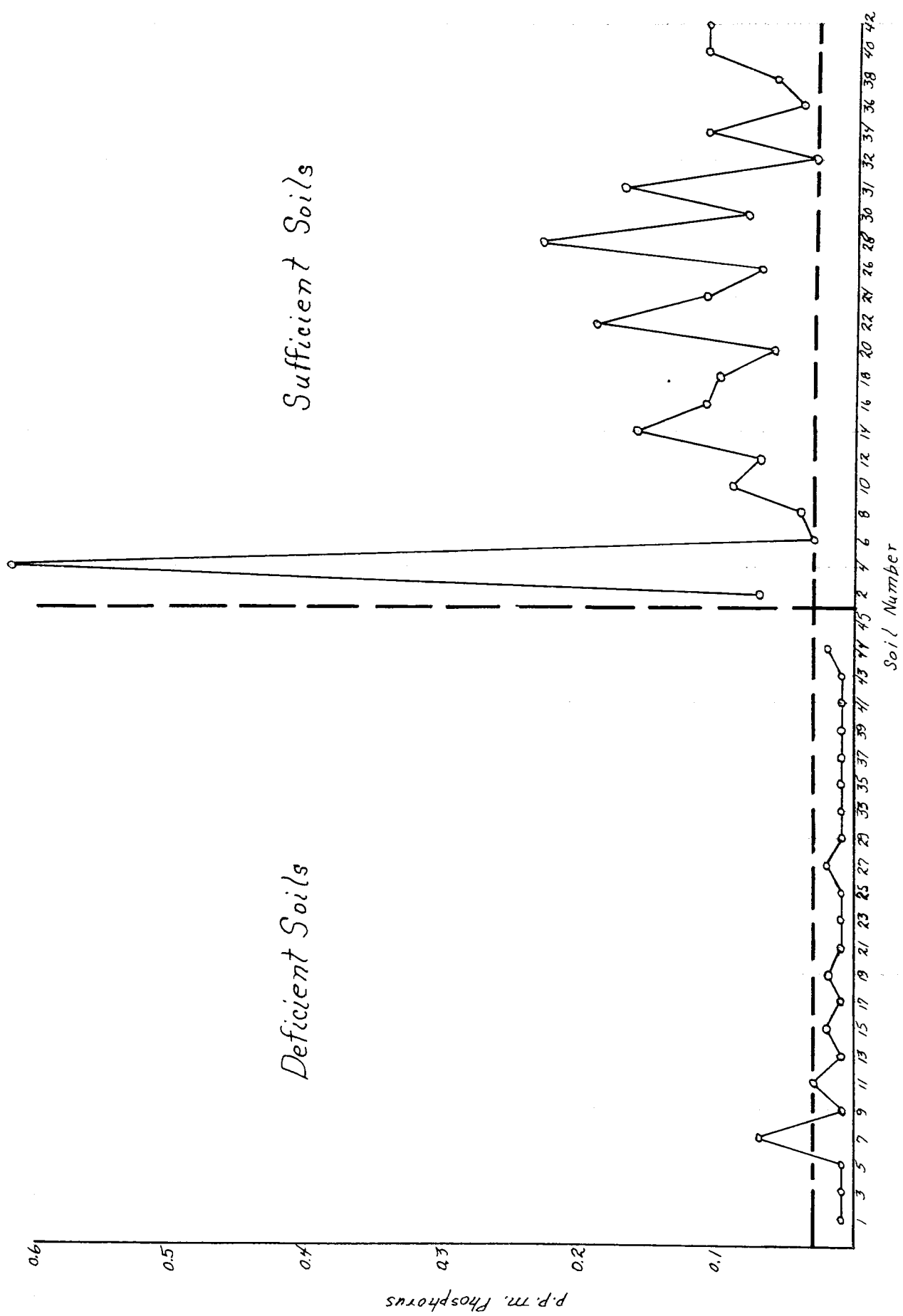


Fig. IV Water Soluble Phosphorus

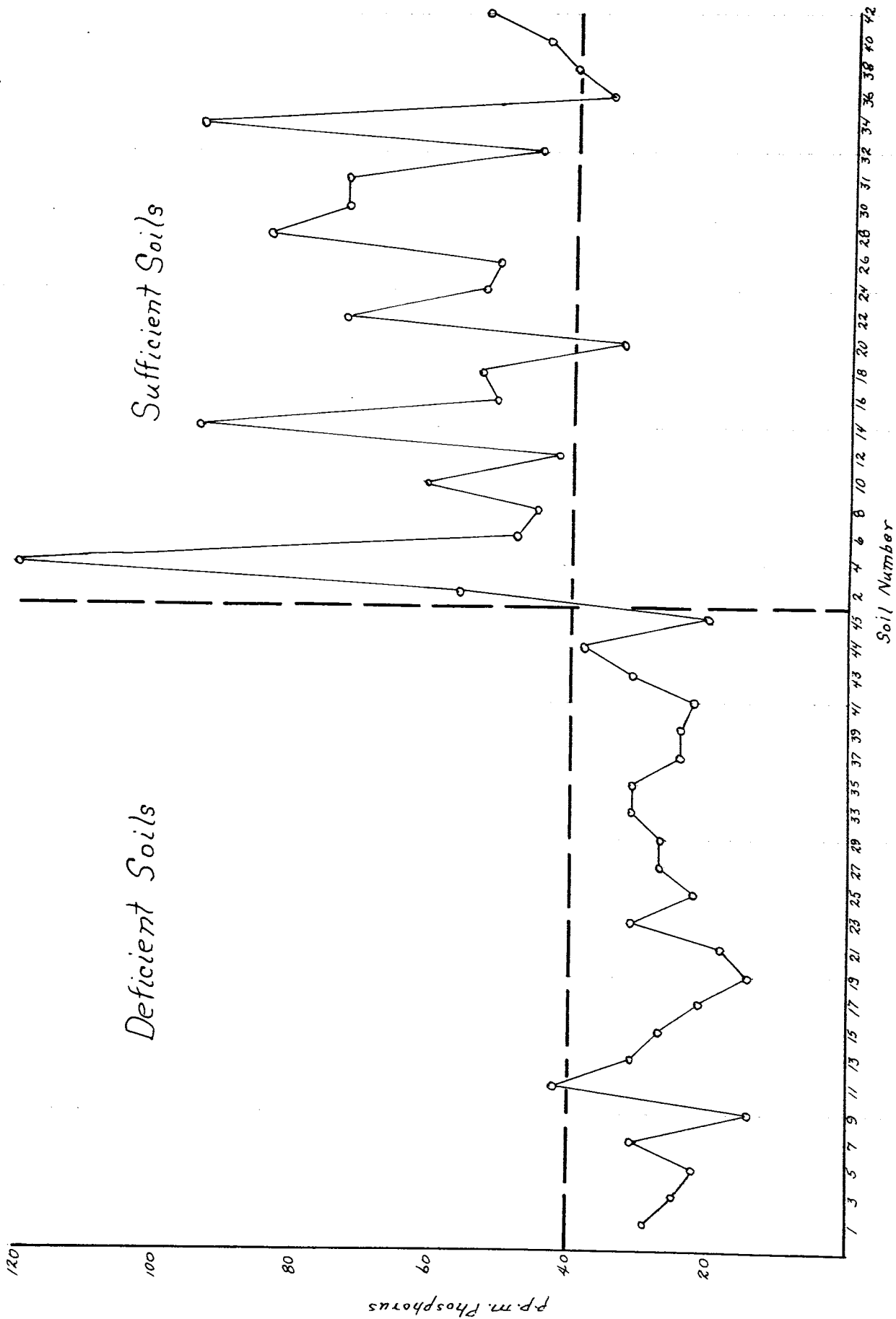


Fig. I H_2CO_3 -Soluble Phosphorus

8.9 percent in the doubtful class

4.4 percent do not agree with field results

86.7 percent agree with field results

This comparison of the three methods for determining plant available phosphorus indicates the water-extractant method to be the best.

The theoretical effect of a change in pH in the soil suspension being electro dialysed has been discussed. The maximum and minimum antimony electrode voltage obtained during the 9 hours of electro dialysis of each soil is given in fig. VI. A comparison of fig. VI with fig. III, indicates that the minimum voltage curve is correlated negatively with the phosphate curve. That is, the lower the pH obtained, the greater the phosphorus electro dialysed. The correlation coefficient between phosphorus electro dialysed per 1,000 coulombs and the minimum antimony electrode voltage during the period of electro dialysis is -0.5762 (Table 6).

In fig. VII, the carbonate contents of the soils are presented graphically. The lime contents of the sufficient soils in general are lower than in the deficient soils. The theoretical correlation between carbonates, pH, and electro dialyzable phosphorus has been suggested. A comparison of figs. III, VI and VII indicates this relationship. There is a correlation coefficient (Table 6) of 0.8522 between the carbonate content of the soils and the minimum

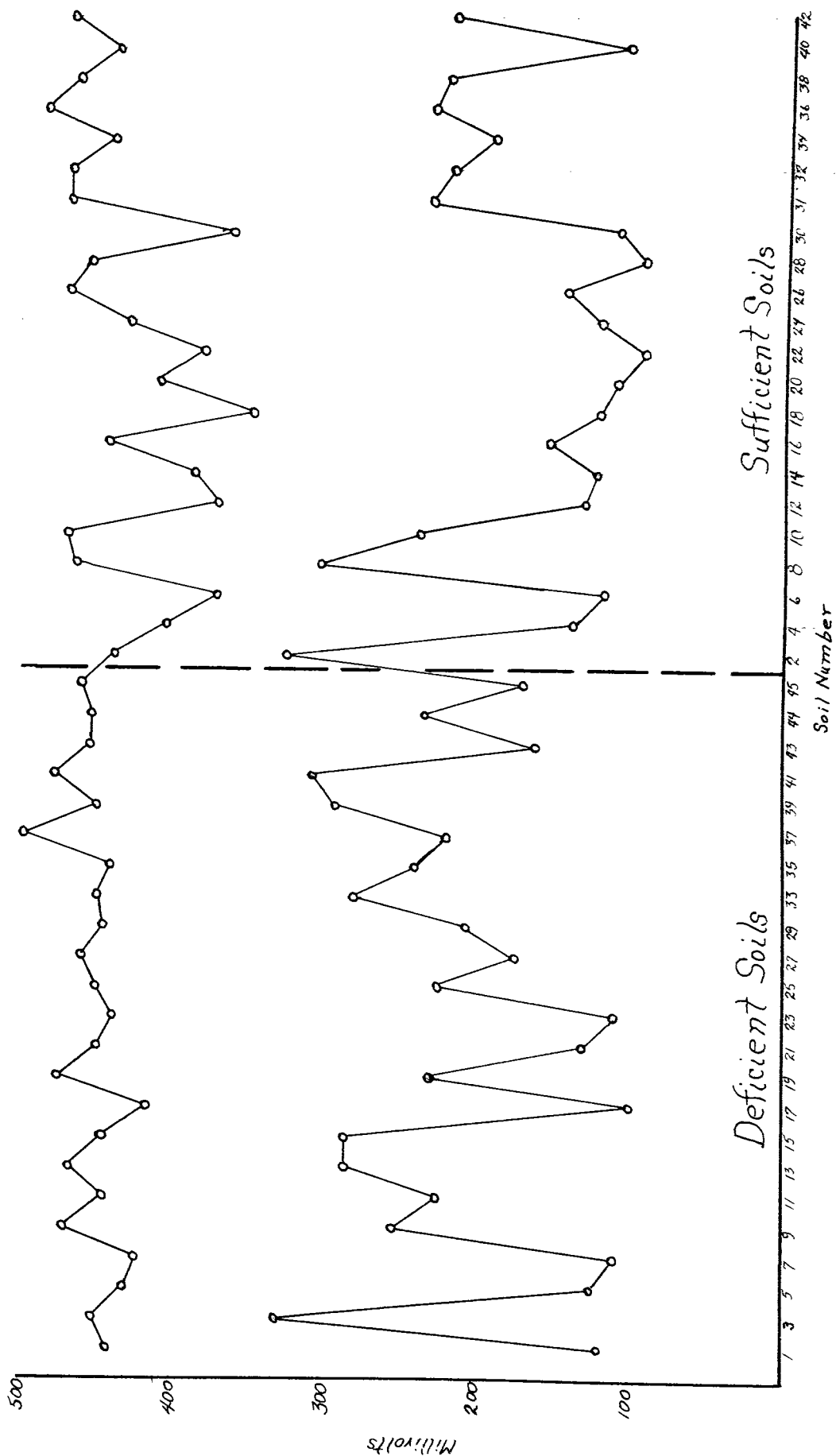


Fig. VII Sb-Electrode Potentials

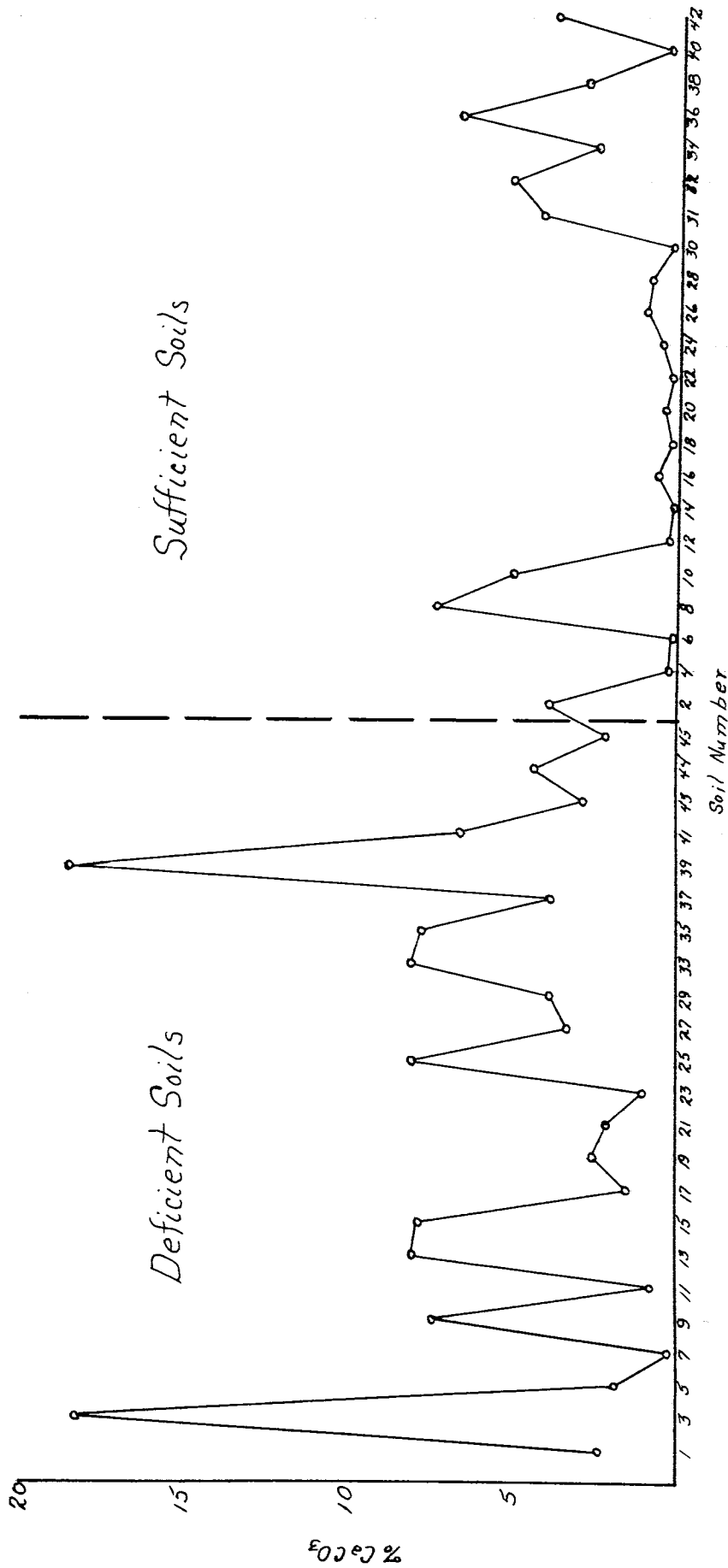


Fig. VIII Lime Content of Electrolyzed Soils

antimony-electrode voltage obtained during the 9-hour period of electro dialysis. The correlation coefficient between carbonate contents of the soils and phosphorus electro dialyzed per 1,000 coulombs is 0.2079. This correlation is not significant, which may be due to the fact that there is a solid phase CaCO_3 in many soils throughout the period of electro dialysis and the effect of lowered pH on transport numbers is taken into consideration when the phosphorus electro dialyzed is based upon coulombs transferred. The correlation coefficient between the carbonate contents of the soils and the phosphorus actually electro dialyzed is 0.5840. These results agree with the data presented in Table 1 on the effect of adding CaCO_3 to the soil suspension. Calcium carbonate may account partly for the poor agreement between the phosphorus actually electro dialyzed and field response to phosphate fertilizers.

The pH, soluble salt content, lime content and coulombs transferred are measurably interrelated, as is brought out in Table 6. The high and very significant correlation of 0.9084 between K_2CO_3 soluble phosphorus and phosphorus electro dialyzed per 1,000 coulombs is very interesting as compared with the low but significant correlation of 0.2981 between the phosphorus actually electro dialyzed and phosphorus electro dialyzed per 1,000 coulombs. As would be expected there is also a high correlation between water soluble phosphorus and K_2CO_3 soluble phosphorus and between water soluble phosphorus and phosphorus electro dialyzed per 1,000 coulombs. The

Table 6. - Correlations Between Factors Affecting
Electrodialyzed Phosphorus

Correlation between	Correlation Coefficient (r)	Obtained "t" value	Expected "t" Value (P = .01)
Carbonates and P actually electro- dialyzed	0.5840	4.708	2.750
Carbonates and Minimum Sb-volts	0.8322	9.842	2.750
Carbonates and P per 1,000 coulombs	0.2079	1.394	2.576
Minimum Sb-volts and P per 1,000 coulombs	0.5762	4.623	2.750
P actually electro- dialyzed and coul- ombs transferred	0.7578	13.394	2.750
Water soluble salts and minimum Sb-volts	0.6219	5.208	2.750
K ₂ CO ₃ soluble P and electrodialyzed P per 1,000 coulombs	0.9084	14.247	2.750
Water soluble P and electrodialyzed P per 1,000 coulombs	0.8598	10.864	2.750
Water soluble P and K ₂ CO ₃ soluble P	0.8188	9.243	2.750
Actual P electro- dialyzed and P per 1,000 coulombs	0.2981	2.048	2.576
Water soluble salts and P electrodialyzed per 1,000 coulombs	0.3911	2.787	2.750
Water soluble salts and coulombs trans- ferred	0.6857	6.144	2.750

measurability of the theoretical factors affecting electro-dialyzable phosphorus is brought out by all of these correlations. The effects of these variables are reduced to a large extent by obtaining the ratio of phosphorus electro-dialyzed to coulombs transferred.

It was observed that the greater the current transferred, the greater the electro-endosmosis. This agrees with the theoretical discussion of Michaelis (48) wherein he shows that the water transferred is directly proportional to the current only.

The antimony-electrode voltages show in all of the soils electro-dialyzed that the cations are removed more rapidly than the anions. In many of the soils which did not respond to phosphate fertilizers, the pH decreased much more rapidly than in most of the soils which did respond to phosphate fertilizers. This may indicate a possible change in phosphate solubility due to a lowered pH as a result of the less-buffered soils. Several of the antimony-electrode voltage curves have been graphed in fig. VIII, which illustrates the pH change of many of the soils electro-dialyzed.

The rate of anion and cation removal, as measured by titration, is highly variable between soils and differs considerably within the three replications for many of the soils. It is doubtful whether the titratable anions or cations, especially when measured over such a short period of time, mean very much in view of such large salt content variations between soils of apparently equal fertility.

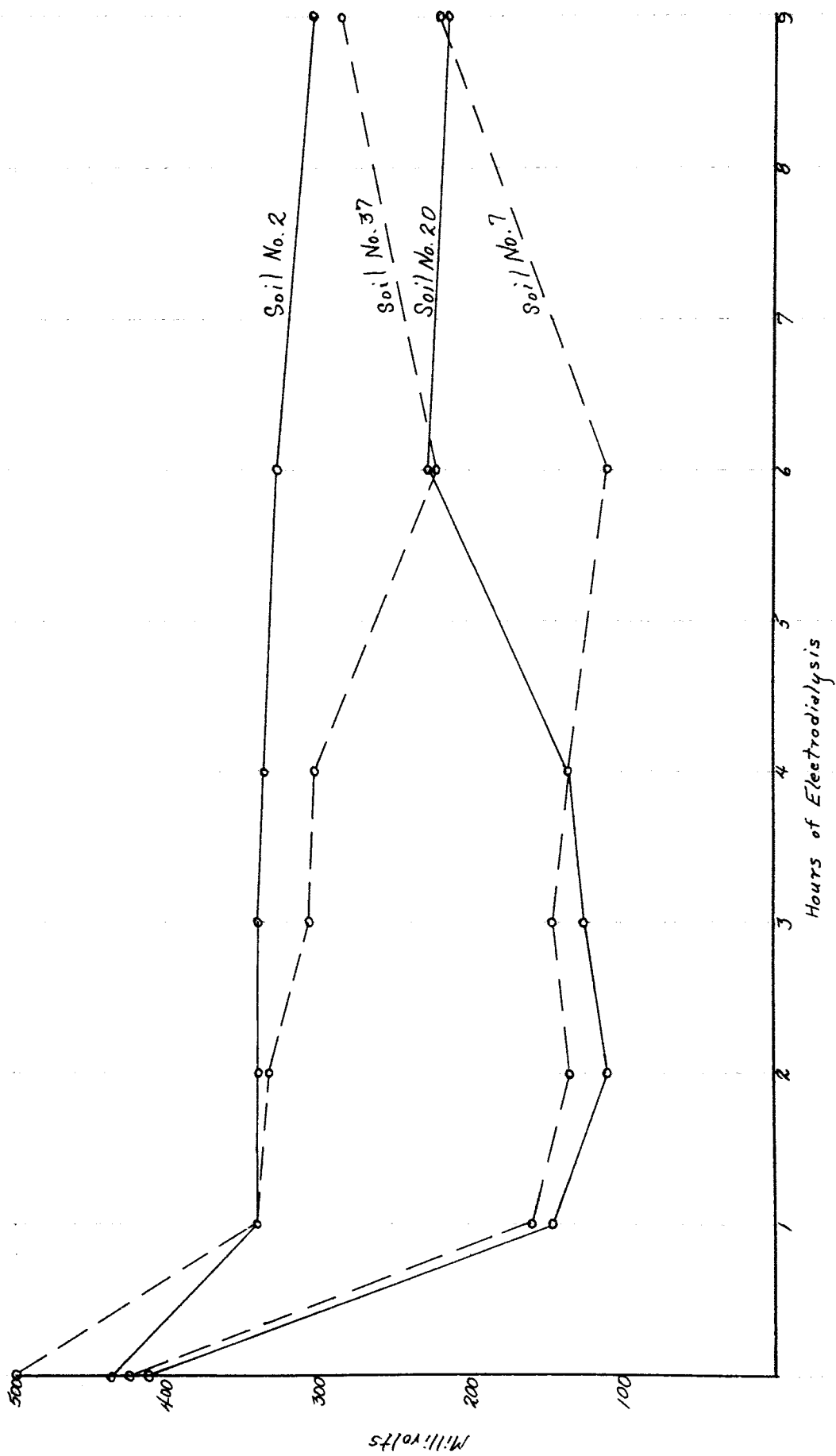


Fig. VIII Antimony Electrode Potentials

SUMMARY

This investigation of electro dialysis as a means of determining plant available phosphorus, is the result of the need for a more reliable method of measuring mineral deficiencies in the soil. Most of the irrigated soils of Colorado are supplied fairly well with total phosphorus. In many cases a marked increase in crop yield is obtained by the application of phosphate fertilizers. This shows that part of the phosphorus already contained in the soil is in an "unavailable" form. Most of these soils are calcareous and as a result the dilute acid extractants usually used for determining available phosphorus are of little value.

It has been shown that the method of electro dialysis as used by other investigators is of little value for measuring the available phosphorus in Colorado's highly variable soils. Total salt content, kind of salts, lime content, rate of pH change in the soil suspension being electro dialyzed, stirring of the soil suspension being electro dialyzed, temperature change during electro dialysis and the amount of current transferred during the period of electro dialysis have been shown to measurably affect the phosphorus extracted by electro dialysis. These factors are variables which cannot be overlooked in a quantitative study of electro dialyzable phosphorus in Colorado soils.

A modification of the center compartment in the Brad-

field three-compartment electrodialysis cell is described. This modification facilitates stirring, temperature measurements and pH determinations of the soil suspension during electrodialysis. A method of electrodialysis has been developed which permits corrections to a large degree for the variables which affect electrodialyzable phosphorus. Forty-five soil samples, from fields upon which crop response to phosphate fertilizers was known, were collected from many parts of the state and electrodialysed in triplicate. The data obtained are analyzed statistically to determine the accuracy of the method and the agreement of electrodialysed phosphorus with actual field response to phosphate fertilizers.

Some chemical analyses of the 45 soil samples are given, showing the variability of those factors which affect electrodialyzable phosphorus. Water soluble phosphorus and K_2CO_3 soluble phosphorus are compared with the phosphorus extracted by electrodialysis. The agreement of the three methods with actual field trials is given.

CONCLUSIONS

1. Water soluble phosphorus and K_2CO_3 soluble phosphorus agree better with actual field response to phosphate fertilizers than does the phosphorus extracted by electrodialysis. These methods are much more rapid and less liable to errors than the method of electrodialysis.

2. Salt and lime content of soils, stirring, temperature and pH change of the soil suspensions during electrodialysis markedly affect the phosphorus extracted by electrodialysis.

3. The variability in electrodialyzable phosphorus due to these factors is reduced when the phosphorus extracted is based upon coulombs transferred.

4. An application of 125 pounds per acre of treble superphosphate increases the phosphorus content of the soil by about 15 parts per million of phosphorus. The difference necessary for significance in electrodialyzable phosphorus is 19.6 parts per million of phosphorus as determined from this investigation. These results indicate that the method of electrodialysis is not sufficiently sensitive to measure the increase in phosphorus due to an ordinary application of a phosphate fertilizer.

5. The process of electrodialysis is the least reliable of the three methods studied for estimating "plant available" phosphorus in Colorado soils under the conditions of this experiment.

ADDENDUM

The results of an investigation on electrodialysis as a means of studying the nature of soil phosphates have been published by Dean⁴ since this manuscript was written. He concludes from his study of acid soils that "The determination of readily soluble phosphorus for practical purposes can be made not only more quickly and economically by acid extraction than electrodialysis, but also with greater dependability."

⁴Dean, L. A. 1934 Electrodialysis as a means of studying soil phosphates Soil Sci. 57 : 255 - 56.

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THESIS ABSTRACT

THE USE OF ELECTRODIALYSIS IN SOIL PHOSPHORUS STUDIES

(By James B. Goodwin)

This investigation of electrodialysis, as a means of determining plant "available" phosphorus, is the result of a need for a more reliable method of measuring mineral deficiencies in soils.

Several investigators, in a study of acid soils, have used electrodialysis for this purpose. They report varying degrees of success with the method. McGeorge has studied the process of electrodialysis as a means of determining the readily soluble, or plant available, phosphorus in some of Arizona's calcareous soils as well as soils from other parts of the United States. He concluded that the method was an excellent means of determining plant available phosphorus with least interference from the CaCO_3 present.

Most of the irrigated soils of Colorado are supplied fairly well with total phosphorus. However, in many cases a marked increase in crop yield is obtained by the application of phosphate fertilizers. This fact indicates that much of the phosphorus already present in the soil is not in a plant available form. These soils usually are calcareous and, as the result, the dilute acid extractants

commonly used for determining available phosphorus are of little value.

The soils of arid and semi-arid regions contain wide range in quantity of soluble salts. The percentage of carbonates present varies from less than 1 percent to 20 or 30 percent expressed as CaCO_3 . These soils vary in pH from almost neutral to above a pH of 8.0 with apparently very little difference in productivity. There is only a slight correlation between any of the above factors and actual field response to phosphate fertilizers.

Faraday's law governs to some extent the results which reasonably may be expected from any procedure wherein a quantitative measure of the ions transporting the current is concerned. Two soils with exactly the same available phosphorus content but with different soluble salt contents would not have the same transport numbers. Hence, the passage of an equal number of coulombs through soils with varying soluble salt contents theoretically is of little value in determining plant available phosphorus. This reasoning is shown to hold experimentally also. The method of electrodialysis used by other investigators is of little value in measuring plant available phosphorus in Colorado's highly variable soils.

The study of a possible method of electrodialysis was undertaken wherein plant available phosphorus would be represented by the phosphorus extracted by electrodialysis.

Theoretically, the following factors affect electro-dialyzable phosphorus.

1. Internal resistance of the electro-dialysis cell.
2. Potential across the cell electrodes.
3. Coulombs transferred.
4. Current carried per unit of time.
5. Total time of electro-dialysis.
6. Time of removing dialysates.
7. Size of soil samples electro-dialyzed.
8. Stirring of soil suspension during electro-dialysis.
9. Rate of pH change in the soil suspension during electro-dialysis.
10. Temperature change in the soil suspension during electro-dialysis.

The effects of these factors are discussed. Each of these factors was studied experimentally and shown to measurably affect electro-dialyzable phosphorus.

A modification of the Bradfield three-compartment cell is described which facilitates temperature control, stirring and measurement of rate of pH change in the center compartment. The application of the quinhydrone electrode, the glass electrode, the hydrogen electrode, and the antimony electrode for measuring the pH

of the soil suspension during electrodialysis is discussed. The antimony electrode was used throughout this investigation for this purpose.

A method of electrodialysis is presented in which the variables already mentioned are reduced. The ratio of phosphorus electrodialed to coulombs transferred gives a more accurate comparison of electrodialed phosphorus than does the actual phosphorus electrodialed.

Forty-five soil samples, from fields upon which crop response to phosphate fertilizer was known, were collected from many parts of the state and electrodialed in triplicate according to the procedure given. The data obtained were statistically analyzed to determine the accuracy of the method and the agreement of electrodialed phosphorus with actual field response to phosphate fertilizer.

As a result of the investigation the following conclusions were made.

1. Water soluble phosphorus and K_2CO_3 soluble phosphorus agree better with actual field response to phosphate fertilizer than does the phosphorus extracted by electrodialysis. These methods are much more rapid and less liable to errors than the method of electrodialysis.

2. Salt and lime content of soils, stirring, temperature and pH change of the soil suspensions during electrodialysis markedly affect the phosphorus extracted by electrodialysis.
3. The variability in electrodialyzable phosphorus due to these factors is reduced when the phosphorus extracted is based upon coulombs transferred.
4. An application of 125 pounds per acre of treble superphosphate increases the phosphorus content of the soil by about 13 parts per million of phosphorus. The difference necessary for significance in electrodialyzable phosphorus is 19.6 parts per million of phosphorus as determined from this investigation. These results indicate that the method of electrodialysis is not sufficiently sensitive to measure the increase in phosphorus due to an ordinary application of a phosphate fertilizer.
5. The process of electrodialysis is the least reliable of the three methods studied for estimating "plant available" phosphorus in Colorado soils under the conditions of this experiment.