Technical Bulletin 12 February, 1935

THE USE OF ELECTRODIALYSIS FOR ESTIMATING PHOSPHATE AVAILABILITY IN CALCAREOUS SOILS

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THE USE OF ELECTRODIALYSIS FOR ESTIMATING PHOSPHATE AVAILABILITY IN CALCAREOUS SOILS[1]

By JAMES B. GOODWIN

Accurate, practical laboratory methods for measuring available plant nutrients in the soil would be a valuable aid to agriculture. All of the methods, both chemical and biological, so far advanced for this purpose have limitations. Recently electrodialysis has been proposed by several investigators as a possible method for studying soil fertility. The purpose of the investigation reported in this paper was to determine the value of electrodialysis as a means of estimating phosphate availability in the highly variable soils of Colorado.

Most of the irrigated soils of the state are supplied fairly well with total phosphorus. However, in many cases a marked increase in crop yield is obtained by the application of treble super-phosphate. This indicates that much of the phosphorus already present in the soil is only slightly available to plants. These soils usually are calcareous, and as a result the acid extractants commonly used for determining available phosphorus are of little value (18)[2].

REVIEW OF LITERATURE

Cameron and Bell (9), in 1905, used an electric current for removing the bases and hydrolyzed products of minerals. König, Hasenbäumer, and Hassler (22), 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 soil.

Yegorov (34), in 1905, observed that after an electric current had been passed through a soil, the citric acid soluble phosphorus was increased almost 100 percent while the nitrate nitrogen was decreased.

Rost (30) attached little value to electrodialysis as a method for determining plant available phosphorus. Taranov (33), Köttgen and Diehl (23), Di Gleria (12), Harper (16), and Brewer and Rankin (6) have compared electrodialysis with other methods, especially the Neubauer, for measuring the availability of mineral nutrients. They report varying degrees of agreement between the methods. Harper (16) found a very close agreement between electrodialyzable phosphorus, dilute acid soluble phosphorus, and plant response to phosphate fertilizers. Neither the pH values nor the lime contents of the soils which he used is given, but it is probable that they were non-

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[1] Part of a thesis submitted to the faculty of the Colorado State College, in partial fulfillment of the requirements for the degree of master of science.

[2] Reference by number (in parentheses) is to "Literature Cited."

calcareous, judging from the close agreement obtained between field response to phosphate fertilizers and dilute acid soluble phosphorus.

McGeorge (25), after studying some of the calcareous soils of Arizona, as well as soils from other parts of the United States, concludes that electrodialysis as a means of determining plant-available phosphorus presents much that is promising.

The chemical analysis of the soils used by these investigators is not reported, and this omission limits the ability of the reader to draw specific conclusions from the electrodialysis data given. In many cases it is probable that the soils used were acid which would minimize certain variables affecting electrodialyzable phosphorus, such as total soluble salts and lime content. An available phosphorus deficiency in such soils might indicate a low total phosphorus content which is not usually the case in western calcareous soils.

Several investigators have shown that more rapid methods agreed with actual field trials almost as well as electrodialysis. Their data are not sufficient to determine whether the differences between the various methods used are statistically significant or due merely to chance.

Dean (11) has published the results of a study on electrodialysis as a means of determining the nature of soil phosphates since the completion of this investigation. The results reported herein are in close agreement with Dean's findings. 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."

THEORETICAL DISCUSSION

The soils of arid and semi-arid regions contain a wide range in quantity of soluble salts, varying from a few hundred to several thousand parts per million. The carbonates present vary from less than 1 to as much as 15 or 20 percent expressed as $CaCO_3$. These soils have a pH range from almost neutral to above 8.0 with apparently very little difference in productivity. There is a very small correlation, if any, between soluble salt content, lime content, pH value, or total phosphorus content and actual field response to phosphate fertilizers.

A more accurate interpretation of the phosphorus removed from arid and semi-arid soils could be made if it were possible to control the temperature and pH change of the soil suspension during electrodialysis, the kind and amount of each of the more readily soluble salts present, and the hydration of ions. Since, of course, this is impossible, a knowledge of the manner in which these variables affect the removal of the phosphate ions during the process of electrodialysis is essential.

A study of Faraday's law indicates the results which reasonably can be expected from any electro-chemical experiment wherein the quantitative movement of ions by means of an electric current is concerned. 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 inter-action of each variable factor affecting electrodialyzable phosphorus cannot be over-emphasized.

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 release equal amounts of phosphorus to the anode chamber for one faraday of current transferred. It is evident from Ohm's law that the RI drop across the electrodialysis cell is a function of the resistance offered by the soil suspension. Therefore, if the above-mentioned soils were electrodialyzed under equal and constant potential for the same period of time, all other factors remaining constant, 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 regardless of the salt content.

EFFECT OF MEMBRANES.—Bradfield (4), Bradfield and Bradfield (5), Komagata (21), and Löddesöl (24) have studied the effects of positively and negatively charged membranes on the rate of ion removal from pure solutions and soil suspensions. Their results show that a measurable difference exists between these two general types of membranes. The work of Michaelis (26), (27) on membrane permeability to electrolytes and electroendosmosis elucidates the effect of ion hydration. 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. Jenny (19) has shown that there is a large difference in the hydrodynamic radii of ions. Michaelis (27) further states that a change in pH may increase the friction due to the bound charge on the capillary walls and thus retards or increases the velocity of the passing ion.

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

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 two membranes (cathode and anode) are not equally permeable to their respective ions, there will be a rapid pH change until most of the readily soluble salts have been removed. As a result, the solubilities of all compounds present are altered, conductivity changes, and temperature fluctuates. Consequently, the transport numbers are changed 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 (15), 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 (7) states that there is very little difference between the mobility of $H_2PO_4^-$ and HPO_4^{--}. The effect of pH change on membrane permeability has been mentioned previously.

The equation which Heymann (17) derives, for the amount of current carried by a pure solution of an electrolyte, expresses the relation between these variables. The equation is as follows:

$$J = q \cdot e \cdot 10^{-3} \cdot \alpha \, (u + v) \cdot c$$

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.

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" (14) 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 electrodialysis 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 (14). 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 the $\sqrt{2}$.

The estimation of covariance was made by means of the correlation coefficient, Fisher's "t" test (14) 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 differ so greatly in soluble salt and lime contents that the variability due to these factors should be near a maximum.

The apparatus used in this investigation is the Bradfield three-compartment type. However, the center compartment was modified in order to permit determination of temperatures and pH values as well as the stirring of the soil suspensions during electrodialysis. A 250 cc. pyrex beaker from which the top and bottom had been removed and a cluster of four holes drilled 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 5- to 300-volt potential. A voltmeter and a wide-range ammeter remained in the circuit at all times.

The procedure outlined by McGeorge (25) was followed as closely as possible using the above described equipment. The constant amperage was reduced to 0.1 ampere because of heating. However, it was found impossible to maintain accurately a constant current throughout a period of 9 hours or more. To overcome this difficulty, two electrodialysis cells were connected in series. This, of course, necessitated the same current passing through both units. Therefore, the phosphorus electrodialyzed from the two cells for any one run is comparable providing there are no differences within the cells. To determine any difference between the two cells, the same soil was placed in each cell 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. A platinum anode and a nickel cathode, as supplied with the cells, were used throughout the 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. Also 180 cc. of distilled water were added to the center compartment and 100 cc. of distilled water were added to the anode and to the cathode chambers.

The dialysates were analyzed for phosphorus by the Denigès colorimetric method as modified by Hockensmith, et al (18). The other ions were far below the concentrations which Chapman (10) shows interfere with the blue-colored formation. The dialysates were removed from both cells at the same time within each run, but the total time of electrodialysis and the intervals between the dialysate removals vary for the different runs. This was done for the purpose of determining the most suitable procedure.

Table 1.—Results with Cells in Series*

Run No.	Soil No.	Field response to P	Total soluble salts	Carbonates expressed as $CaCO_3$	pH	Textural grade	K_2CO_3 Soluble P	Time electrodialyzed	$CaCO_3$ added	NaOH 0.1 N	HCl 0.1 N	P Electrodialyzed	Average temperature
			p.p.m.	pct.			p.p.m.	hrs.	gm.	cc.	cc.	mgm.	°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
2	129A	None	595	1.70	8.45	C. Loam	69	28	None	2.85	13.55	0.653	23.7
	129A	None	595	1.70	8.45	C. Loam	69	28	None	3.20	15.65	0.650	23.7
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	0.3	2.10	8.20	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	1.80	9.65	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	1050	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

*A potential of approximately 180 volts.

It can be seen that the results of the two cells are comparable from runs 1 and 2 (Table 1). Hence, the data obtained from the two cells in 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 gram of $CaCO_3$ has reduced the phosphorus electrodialyzed from 0.696 milligram to 0.120 milligram. 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 soluble phosphorus[3] 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 $CaCO_3$ 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 percentage 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 again may 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 are in accordance with the laws of physical chemistry. 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 (25), investigators have used soils which probably were acid. Acid soils usually are formed under conditions of exces-

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[3] The 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 (18.)

sive leaching which means the soluble salt content is probably 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 phosphorus electrodialyzed.

The next part of the investigation was to find, if possible, some procedure whereby electrodialyzable phosphorus would represent "plant available" phosphorus. It was thought advisable 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 MEMBRANES.—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 KH_2PO_4 solution containing approximately 18 parts per million of phosphorus 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. 1. 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 makes the cellophane membrane less desirable than the collodion hemoglobin membrane for the electrodialysis of Colorado soils which usually are 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 electrodialyzable 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. 1 is the average of triplicate electrodialysis analyses and each point on the cellophane curve is the average of duplicate analyses. The experiment was performed with the collodion membrane so that it was pos-

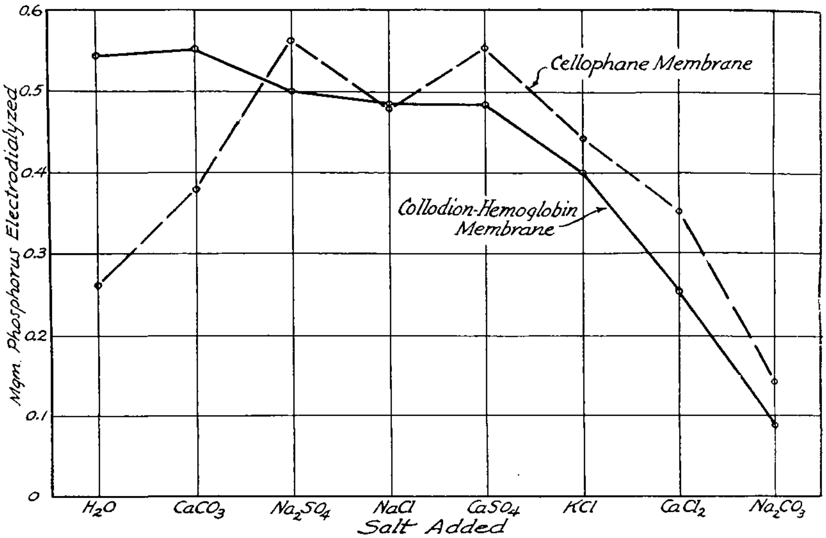


Fig. 1.—Effect of salts and kind of anode membrane of electrodialyzable phosphorus.

sible 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 electrodialyzed significantly when compared with no salt added.

VOLTAGE.—The external voltage to be used in electrodialyzing 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:

Table 2.—Effect of Salts on Electrodialyzable Phosphorus

Salt	P (average of 3 replications)	Deviation from no treatment
	mgm.	percent
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= -0.3359 for replications, 5 percent pt. = 0.6594, 1 percent pt. = 0.9370
Z= 2.9428 for treatments, 5 percent pt. = 0.5099, 1 percent pt. = 0.7287
S. E. of mean = 0.008
Difference for significance = 0.023
S. E. in percentage of mean = 2.07

1.—Conductivity of soil suspension—the more current carried the greater the heating. (The theoretical effects of increased temperature on electrodialyzable phosphorus have been discussed.)

2.—Amount of electrodialyzable phosphorus contained in the soil.

3.—Large enough soil sample to be representative.

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 been shown already, electrodialysis 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 electrodialyzed and such wide differences in conductivity between soils. A study of the magnitude and a possible correction of this error was undertaken. Soil 15 was chosen for this purpose because of the large amount of electrodialyzable 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 electrodialysis. All experiments were continued for a 9-hour period in which the dialysates were removed each hour for 4 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 and 100 cc. of distilled water were placed in the anode and cathode compartments. Collodion hemoglobin-coated anode membranes and parchment paper cathode membranes were used.

The results are given in Table 3. The soil was electrodialyzed twice in cell 1 and once in cell 2 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 1 degree. The total amount of phosphorus actually electrodialyzed varies to the extent of 0.3 milligram of phosphorus, but the actual coulombs of current transferred vary in the same order which suggested the possibility of a constant ratio between coulombs transferred and phosphorus electrodialyzed. These data are given under the column headed "P per 1,000 coulombs." The variability between different runs and the two cells has been reduced from 0.3 milligram to 0.087 milligram of phosphorus. This is what would be expected if temperature variation did not change markedly the ratio of transport numbers between the phosphate ions and the other ions present.

Table 3.—Effect of Temperature and Stirring on Electrodialyzable Phosphorus

Run number	Soil number	Average temperature	NaOH 0.1 N	HCl 0.1 N	Total P electrodialyzed	Current transferred	P per 1,000 coulombs	Cell number	Remarks
		°C	cc.	cc.	mgm.	coul.	mgm.		
1	15	25.4	8.7	42.9	1.590	1301	1.222	1	Check
2	15	24.4	8.2	37.9	1.290	986	1.309	1	Check
3	15	25.2	8.4	40.8	1.410	1107	1.273	2	Check
4	15	23.2	5.9	11.5	0.260	364	0.714	1	Center compartment not stirred
5	15	23.3	5.5	11.0	0.243	346	0.703	2	Center compartment not stirred
6	15	42.2	8.6	53.8	2.020	1479	1.366	1	Temperature increased
7	15	41.1	7.7	41.8	1.460	1140	1.281	2	Temperature increased
8	15	25.6	7.6	27.2	0.886	692	1.280	1	Electrodes moved 1 cm. from membranes

To study further 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. Without stirring 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 electrode to be used for determining the pH of the center compartment must meet certain requirements. Few ions should be liberated from the electrode 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 (8) 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.

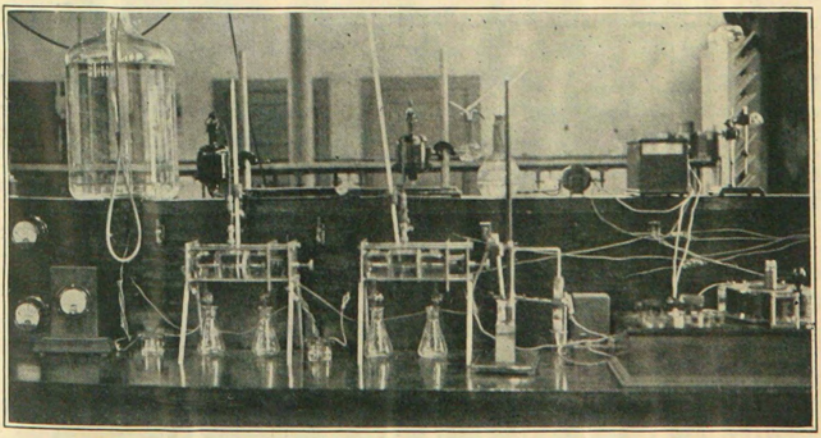
Since the electrode was to be left in the soil suspension only long enough to make the reading, the antimony electrode seemed best suited for the purpose because of its mechanical strength, rapid equilibrium potential and because it does not require the addition of any foreign material. Kolthoff and Hartong (20) and Roberts and Fenwick (29) 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 (1), (2), (3), (13), (28), (31), (32). Antimony amalgam electrodes were prepared according to Shukoff and Awsejewitsch (31). Considerable "drifting" was observed with this type of electrode. The electrodeposited antimony gradually diffused off which necessitated the construction of new electrodes at frequent intervals. Stick antimony electrodes prepared according to Parks and Beard (28) were found to give the best results. When checked against the quinhydrone electrode and buffer solutions, the equation of Shukoff and Awsejewitsch (31) closely approached the correct pH value.

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

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: Five 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 130 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 electrodialysis. 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 one-tenth-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 these measurements. Collodion hemoglobin anode membranes, prepared according to Bradfield and Bradfield (5), 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.



Electrodialysis apparatus used in the 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 ampere 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 electrodialysis run, each anolyte was analyzed for phosphorus by the Denigès colorimetric method as modified by Hockensmith, et al (18). A simple calculation[4] places this quantity of phosphorus on a basis which permits comparison with the data of other electrodialysis runs.

EXPERIMENTAL RESULTS

Triplicate electrodialysis 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 electrodialyzed in three series. In the first series the soils were electrodialyzed 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 electrodialyzed 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 electrodialysis in the third series. Randomization is necessary for the application of the analysis of variance.

A rather complete chemical analysis also was made on most of the soils studied to aid in interpreting the electrodialysis results. These data, together with the average milligrams of phosphorus electrodialyzed per 1,000 coulombs transferred in the three 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 electrodialyzable phosphorus and field response to phosphate fertilizers when a constant current is applied to each soil for a definite period of time. The carbonates, expressed as $CaCO_3$, varied from 0.1 percent to 18.5 percent.

The water soluble phosphorus was determined by the "molybdenum blue" method of Zinzadze (35), (36) 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 (18).

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[4] $\frac{\Sigma P}{C} \times 1000 = P$ per 1,000 coulombs transferred

Where ΣP = summation of the phosphorus from each dialysate of a run

C = coulombs transferred during entire time of electrodialysis

Table 4.—Chemical Analyses of Soils Electrodialyzed

Soil number	Field response to P	P per 1,000 coulombs	K_2CO_3 soluble P	Water soluble P	Total P_2O_5	Soluble salts*	Carbonates expressed as $CaCO_3$	Organic matter
		mgm.	p.p.m.	p.p.m.	pct.	p.p.m.	pct.	pct.
1	Yes	0.258	29	0.01	0.158	5720	2.4	2.3
2	No	0.450	56	0.07	0.183	1980	3.9	2.8
3	Yes	0.152	25	0.01	0.152	1910	18.3	4.1
4	No	4.906	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	48	0.03	0.145	2340	0.1	2.2
7	Yes	1.856	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	0.460	14	0.01	0.163	1730	7.5	0.9
10	No	0.483	61	0.09	0.196	3530	5.0	2.3
11	Yes	0.865	42	0.03	0.185	6550	0.9	2.0
12	No	1.422	42	0.07	0.129	1650	0.3	1.5
13	Yes	0.548	31	0.01	0.188	3810	8.1	2.7
14	No	2.818	95	0.16	0.171	900	0.1	1.6
15	Yes	1.268	27	0.02	0.228	6190	7.8	2.0
16	No	1.869	51	0.11	0.154	2320	0.6	1.6
17	Yes	0.379	21	0.01	0.129	20720	1.5	1.6
18	No	1.828	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	18	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	0.178	2660	1.0	2.2
24	No	2.777	58	0.11	0.174	1220	0.5	1.3
25	Yes	0.490	22	0.01	0.187	1940	8.1	1.5
26	No	1.511	51	0.07	0.150	1480	1.1	1.6
27	Yes	0.584	27	0.02	0.158	1910	3.4	2.0
28	No	2.004	84	0.23	0.167	1550	0.8	2.4
29	Yes	0.562	27	0.01	0.161	1580	3.9	1.9
30	No	2.451	73	0.08	0.150	830	0.2	2.1
31	No	0.872	73	0.17	0.214	1730	4.2	2.0
32	No	1.184	45	0.03	0.212	1300	5.1	1.6
33	Yes	0.750	31	0.01	0.207	9200	8.1	2.3
34	No	2.720	95	0.11	0.353	6410	2.5	1.7
35	Yes	0.353	31	0.01	0.191	2160	7.8	0.7
36	No	0.537	35	0.04	0.192	1620	6.7	1.9
37	Yes	0.308	24	0.01	0.098	3110	3.8	1.2
38	No	0.895	40	0.06	0.195	1390	2.7	1.7
39	Yes	0.401	24	0.01	.. ..	1380	18.5	2.7
40	No	1.533	42	0.11	.. ..	1550	0.3	2.5
41	Yes	0.270	22	0.01	.. ..	2230	6.6	1.5
42	No	0.458	53	0.11	.. ..	3060	3.8	3.0
43	Yes	0.560	31	0.01	.. ..	3780	2.8	2.0
44	Yes	0.474	38	0.02	.. ..	1220	4.4	3.0
45	Yes	0.186	20	0.01	0.207	5360	2.2	2.5

*The salts were determined electrometrically in a 1 to 36 soil water suspension, so these values are much higher than would be obtained by the usual method of determining soluble salts in soils.

The complete electrodialysis 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 ob-

Table 5.—Electrodialysis Analyses of Soils, Average of Three Analyses.

Soil number	Field response to P	Total P electro-dialyzed	Current trans-ferred	P per 1,000 coulombs	Average temper-ature	Anions NaOH 0.1 N	Cations HCl 0.1 N	Anions per 1,000 coulombs	Cations per 1,000 coulombs
		mgm.	coulombs	mgm.	°C.	cc.	cc.	cc.	cc.
1	Yes	0.131	510	0.258	25.2	5.6	21.2	10.9	41.5
2	No.	0.320	715	0.450	25.6	3.8	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	0.460	24.0	3.9	29.2	4.3	31.8
10	No	0.413	851	0.483	24.2	3.7	31.0	4.4	36.6
11	Yes	0.690	796	0.865	24.1	4.4	29.2	5.5	36.8
12	No	0.492	342	1.422	24.6	2.2	10.0	6.5	31.1
13	Yes	0.579	1073	0.548	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	23.8	1.9	9.4	11.9	57.6
17	Yes	0.360	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	0.648	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	0.338	222	1.511	23.2	1.8	9.6	8.0	43.8
27	Yes	0.310	530	0.584	24.0	2.9	21.5	5.5	40.5

Table 5.—(Continued)

Soil number	Field response to P	Total P electro-dialyzed	Current trans-ferred	P per 1,000 coulombs	Average temper-ature	Anions NaOH 0.1 N	Cations HCl 0.1 N	Anions per 1.000 coulombs	Cations per 1,000 coulombs
		mgm.	coulombs	mgm.	°C.	cc.	cc.	cc.	cc.
28	No	0.498	249	2.004	23.6	1.9	11.2	7.3	45.3
29	Yes	0.274	489	0.562	25.0	2.7	18.8	5.4	38.3
30	No	0.535	221	2.451	24.0	1.5	7.5	6.9	35.7
31	No	0.710	806	0.872	23.8	3.8	27.4	4.8	35.1
32	No	0.825	699	1.184	24.1	3.3	26.3	4.7	37.7
33	Yes	0.982	1312	0.750	24.8	10.4	45.2	8.0	34.5
34	No	2.100	772	2.720	23.9	7.3	29.7	9.5	38.5
35	Yes	0.487	1360	0.353	24.4	4.9	45.6	3.6	33.4
36	No	0.715	1319	0.537	24.8	4.0	43.4	3.1	33.1
37	Yes	0.243	783	0.308	24.7	3.4	29.7	4.3	36.7
38	No	0.522	585	0.895	22.9	3.2	23.0	5.4	39.3
39	Yes	0.579	1422	0.401	25.9	4.9	47.4	3.4	33.3
40	No	0.391	258	1.533	23.8	2.0	10.4	7.5	41.0
41	Yes	0.308	1138	0.270	24.3	4.4	40.3	3.8	35.4
42	No	0.384	840	0.458	24.0	3.7	29.8	5.6	35.5
43	Yes	0.357	639	0.560	23.7	4.4	23.7	6.9	37.0
44	Yes	0.366	775	0.474	23.4	2.9	25.8	3.7	33.0
45	Yes	0.108	590	0.186	23.1	4.4	23.5	7.5	39.8
Z for replicates		= 1.2844		0.3005		1.3925	1.3932	0.4804	1.6625
5 percent point		= 0.5736		0.5486		0.5736	0.5736	0.5486	0.5736
1 percent point		= 0.8025		0.7637		0.8025	0.8025	0.7636	0.8025
Z for samples		= 1.6183		3.3655		2.3870	1.8175	1.2406	1.5965
5 percent point		= 0.2654		0.2654		0.2654	0.2654	0.2654	0.2654
1 percent point		= 0.3746		0.3746		0.3746	0.3746	0.3746	0.3746
S.E. of mean		= 0.068		0.035		0.25	2.0	0.9	1.2
S.E. in percentage mean		=13.6		3.1		6.3	8.7	12.4	3.2
Diff. for significance		= 0.193		0.098		0.70	5.7	2.5	3.5

tained "Z" value for replicates in the case of actual phosphorus electrodialyzed shows that the differences are highly significant, but when the phosphorus electrodialyzed 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 percentage of the general mean. *From these facts, it may be concluded that the ratio of phosphorus electrodialyzed to coulombs transferred gives a more accurate comparison than does the actual phosphorus electrodialyzed.*

The statistical anlayses of the titratable anions and cations, both the amounts actually electrodialyzed and based upon 1,000 coulombs transferred, are very interesting. When based upon 1,000 coulombs transferred, the standard error in percentage 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 percentage 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 basisity 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:

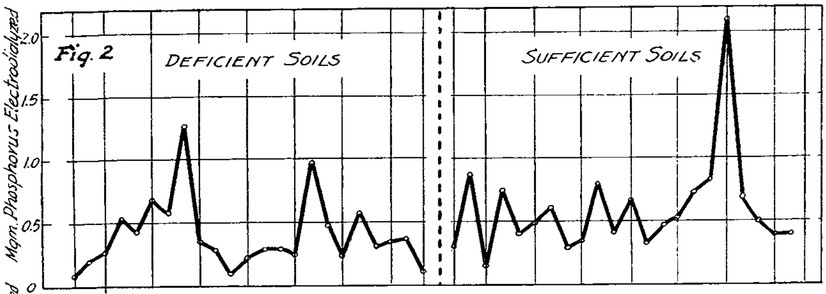
$$Na^{+} + \ominus \rightarrow Na$$

$$Na + HOH \rightarrow NaOH + \tfrac{1}{2}H_2$$

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 electrodialyzed 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 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. 2 presents the actual phosphorus electrodialyzed. 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



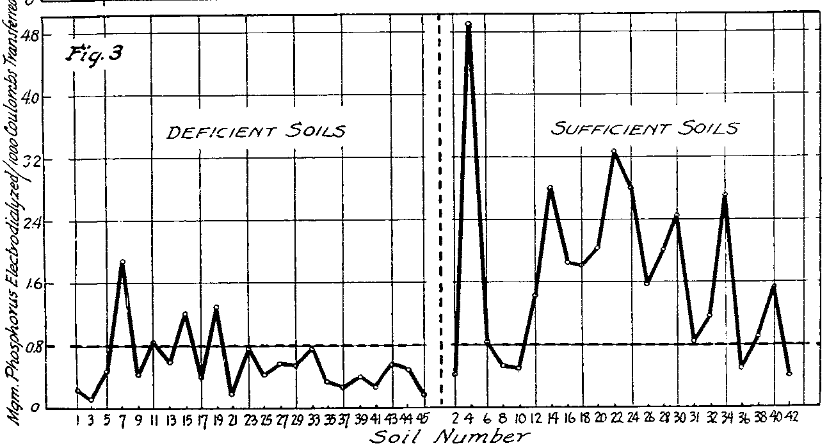
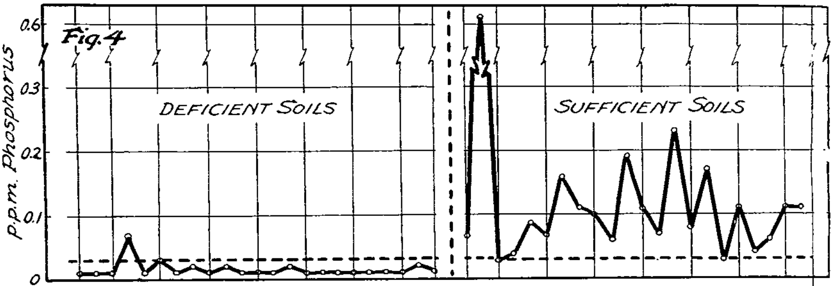


Fig. 2.—Phosphorus actually electrodialyzed from each soil in nine hours.
Fig. 3.—Ratio of phosphorus electrodialyzed to coulombs transferred in each soil.

available phosphorus. There are no marked differences between the amounts of phosphorus electrodialyzed from the deficient soils and the sufficient soils; that is, it would be impossible to pick out those soils which responded to phosphate fertilizers from these electrodialysis data.

The milligrams of phosphorus electrodialyzed based upon 1,000 coulombs transferred, are given in Fig. 3. 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. 2. From the "difference for significance" (Table 5) taking 0.800 milligram of phosphorus as the dividing line between sufficiency and deficiency, soils 11, 23, 33, 6, 31 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 percentage, the results are as follows:

13.3 percent in the doubtful class
17.8 percent do not agree with field results
68.9 percent agree with field results



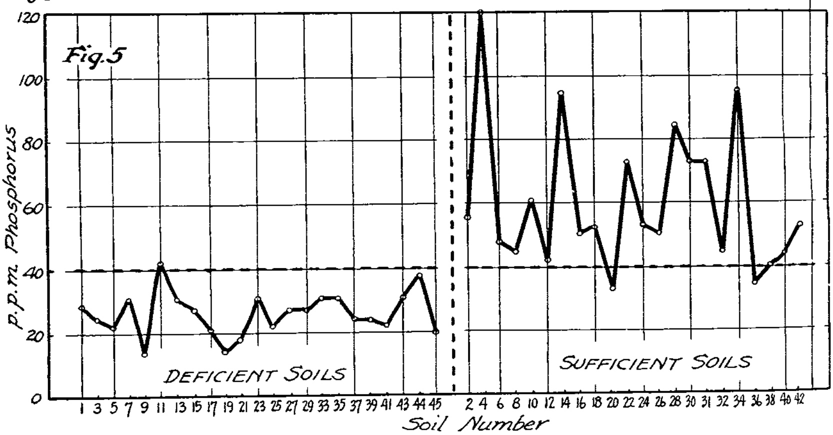


Fig. 4.—Water soluble phosphorus in soils electrodialyzed.
Fig. 5.—Potassium carbonate soluble phosphorus in soils electrodialyzed.

In Fig. 4, 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 32 fall in the doubtful class. Soil 7 does not check with field results. These data, on a percentage basis, are as follows:

6.7 percent in the doubtful class
2.2 percent do not agree with field results
91.1 percent agree with field results

Potassium carbonate soluble phosphorus is given in Fig. 5. Sufficient data for a statistical analysis are lacking here also. Soils 20 and 36 do not check with field results and assuming (18) soils 11, 44, 12 and 38 to be in the doubtful class, the agreement is as follows:

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 electrodialyzed has been discussed. The maximum and minimum antimony electrode voltages obtained during the 9 hours of electrodialysis of each soil are given in Fig. 6. A comparison of Fig. 6 with Fig. 3, indicates that the minimum voltage curve is correlated negatively with the phosphate curve; that is, the lower the pH obtained, the more phosphorus electrodialyzed. The correlation coefficient be-

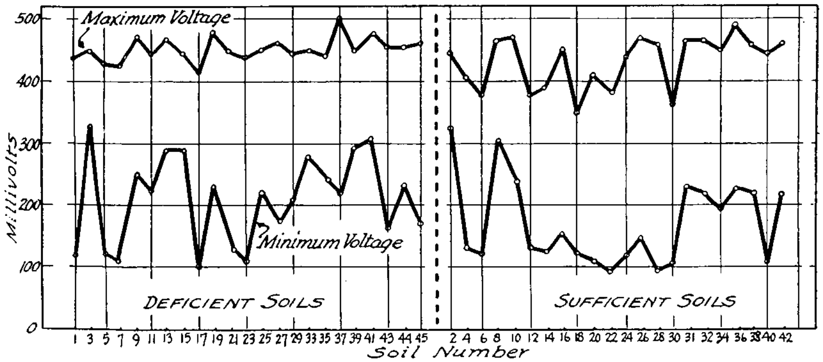


Fig. 6.—Maximum and minimum antimony electrode potentials obtained in each soil during electrodialysis.

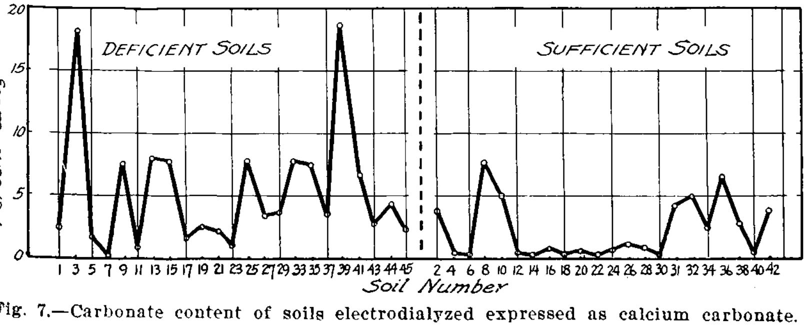


Fig. 7.—Carbonate content of soils electrodialyzed expressed as calcium carbonate.

tween phosphorus electrodialyzed per 1,000 coulombs and the minimum antimony electrode voltage during the period of electrodialysis is -0.4958 (Table 6).

In Fig. 7, 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 electrodialyzable phosphorus has been suggested. A comparison of Figs. 3, 6, and 7 indicates this relationship. There is a correlation coefficient (Table 6) of 0.7845 between the carbonate contents of the soils and the minimum antimony-electrode voltage obtained during the 9-hour period of electrodialysis. The correlation coefficient between carbonate contents of the soils and phosphorus electrodialyzed per 1,000 coulombs is -0.4876, and between the carbonate contents of the soils and the phosphorus actually electrodialyzed is 0.0622. The later correlation indicates that when soils are electrodialzed under a constant potential, the carbonate content does not affect the phosphorus electrodialyzed. On the other hand, when these same data are based upon 1,000 coulombs transferred, there is a significant correlation (-0.4876) between carbonate contents and phosphorus. Since there is much better agreement between field response to phosphate fertilizers and phosphorus electrodialyzed per 1,000 coulombs than between field response to phosphate fertilizers and the phosphorus actually electrodialyzed, it may be concluded that carbonates do affect electrodialyzable phosphorus, and that high carbonates decrease available phosphorus to some extent. 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 electrodialyzed 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 measurability of the theoretical factors affecting electrodialyzable 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 electrodialyzed to coulombs transferred.

It was observed that the greater the current transferred, the greater the electroendosmosis. This agrees with the theoretical discussion of Michaelis (27) wherein he shows that the water transferred is directly proportional to the current only.

The antimony-electrode voltages show in all of the soils electrodialyzed 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

Table 6.—Correlations Between Factors Affecting Electrodialyzable Phosphorus

Correlation between	Correlation coefficient (r)	Obtained "t" value	Expected "t" value (P=0.01)
Carbonates and P actually electrodialyzed	+0.0622	0.409	>2.576
Carbonates and P per 1,000 coulombs transferred	-0.4876	3.662	<2.750
Carbonates and minimum sb-volts	+0.7845	8.295	<2.750
Minimum sb-volts and P per 1,000 coulombs	-0.4958	4.311	<2.750
Water soluble salts and minimum sb-volts	-0.0721	0.474	>2.576
Water soluble salts and P actually electrodialyzed	+0.1100	0.726	>2.576
Water soluble salts and P per 1,000 coulombs transferred	-0.2545	1.726	>2.576
Water soluble salts and coulombs transferred	+0.2621	1.781	>2.576
P actually electrodialyzed and coulombs transferred	+0.2572	3.069	<2.750
P actually electrodialyzed and P electrodialyzed per 1,000 coulombs transferred	+0.4335	3.154	<2.750

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. 8, which illustrates the pH change of many of the soils electrodialyzed. Most of the antimony electrode voltages have been omitted to conserve space.

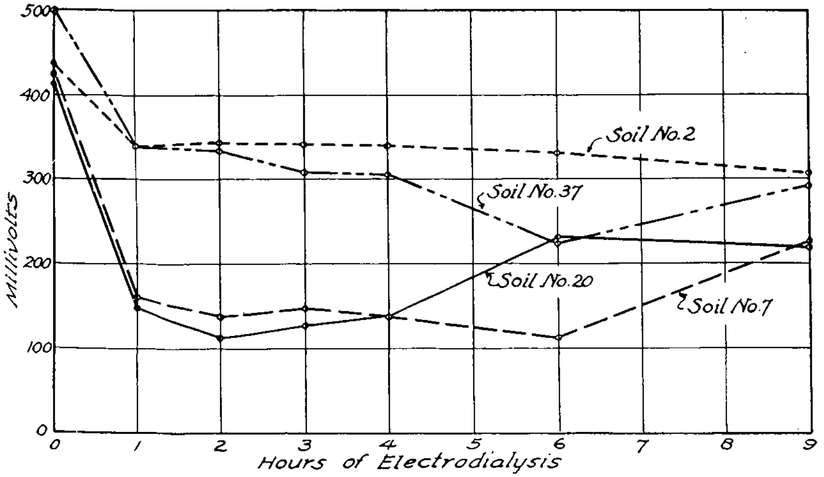


Fig. 8.—Change in antimony electrode potentials during electrodialysis of four of the soils studied.

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.

SUMMARY

This investigation of electrodialysis 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 electrodialysis 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, and rate of pH change, stirring, temperature change, and the amount of current transferred during the period of electrodialysis have been shown to measurably affect the phosphorus extracted by electrodialysis. These factors are variables which cannot be overlooked in a quantitative study of electrodialyzable phosphorus in Colorado soils.

A modification of the center compartment in the Bradfield 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 electrodialyzed in triplicate. *The data obtained are analyzed statistically to determine the accuracy of the method and the agreement of electrodialyzed 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. The phosphorus extracted by electrodialysis is affected markedly by the stirring, temperature and pH change of the soil suspensions, and salt and lime contents of the soils.

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 by electrodialysis 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.

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