

the volatile matter as given off when the coal is fired under a steam boiler or especially when coked in a coke oven, as under these conditions the volatile matter is driven off gradually and during a considerable interval of time, and it appears that the slower driving off of the volatile matter from the sample in the laboratory gives results more in accordance with these conditions than does the official method. This latter fact is, however, a matter of minor importance, for so long as all volatile determinations are done in the same way it makes very little difference what that way is.

In the case of lignites where the application of the official method causes mechanical losses it appears desirable and necessary that the committee so modify the official method for volatile matter in lignites as to prevent this loss, and the results of these foregoing determinations and experiments are published at this time with a view of bringing this matter before the committee and the public.

U. S. GEOLOGICAL SURVEY,
FUEL TESTING LABORATORY.

THE RELATION OF SODIUM TO POTASSIUM IN SOIL AND SOLUTION CULTURES.¹

BY J. F. BREAZEALE.

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THE determination of the exact amount of salt absorbed from solution by plants during the process of growth has been the subject of many experiments in former years. The ordinary gravimetric or volumetric methods which have usually been employed in such investigations have been on the whole inadequate for such work. The soil solution or the nutrient solution best suited to the requirements of most plants is usually of such a low total salt content that slight changes in its concentration cannot be detected by ordinary analytical means without the expenditure of an amount of time which is almost prohibitive. In the same way the amount of salt a seedling will absorb from solution in the course of a short period of its growth is usually too small to be detected by such methods.

For several years past the Bureau of Soils has been devising and adapting analytical methods which are well suited to such

¹ Published by permission of the Secretary of Agriculture.

investigations.¹ These methods have opened up a comparatively new field for experimental work with the soil and soil solutions and offer a ready means of attacking some of the hitherto difficult problems of plant nutrition.

During the spring and summer of 1905 while engaged in the study of certain soil problems in coöperation with the Rhode Island Experiment Station an opportunity was offered of carrying on, with water and soil cultures, the experiments which are here reported.

The direct object of these experiments was to bring to bear upon the plot work, on the replacement of potassium by sodium, which is being conducted at the Rhode Island Station, the delicate analytical methods as well as the pot and water culture methods used by the Bureau of Soils.²

The nature of the plants which had best responded to the application of sodium salts in the field—beets, radishes, turnips, etc.—made it almost impossible to use them in such work; so wheat was selected, as it offered few difficulties in the way of sprouting and handling. The seeds were sprouted on a piece of mosquito netting stretched over a shallow basin of distilled water and kept moist by contact with its surface. When the plumules had reached a length of about 5 cm. the seedlings were transferred to bottles containing the nutrient solutions. The seeds were removed from the seedlings before beginning the experiment, and all further supply of nutrient materials from this source was thus eliminated. With the exception of the first experiment the bottles containing the nutrient solutions were of dark brown glass and held 600 cc. each. "Chemically pure" salts were used to make up these solutions. They were accurately standardized in strengths of $1/5$ normal and then diluted to the desired concentrations. The water used in these experiments was shaken up with carbon black and filtered through a Pasteur-Chamberland filter before using.³ The work was carried on in

¹ "Colorimetric, Turbidity and Titration Methods used in Soil Investigations," Bull. 31, Bureau of Soils, U. S. Dept. of Agric., 1906.

² See Annual Reports and Bulletins 104 and 106 of the Rhode Island Experiment Station.

³ On the beneficial effects of this treatment upon distilled water see Breazeale, J. F.: "Effect of Certain Solids upon the Growth of Wheat in Water Cultures," *Bott. Gazz.* 41, 54 (1906).

a greenhouse and the solutions containing the cultures were changed every four days.

After much preliminary work, a series of six nutrient solutions was prepared, having the following salt content in parts per million:

TABLE I.
Parts per million.

1.	2.	3.
CaCl ₂ 44	NaCl..... 44	CaCl ₂ 44
MgSO ₄ 24	MgSO ₄ 24	MgSO ₄ 24
Na ₂ HPO ₄ 38	Na ₂ HPO ₄ 38	(NH ₄) ₂ HPO ₄ ... 38
KNO ₃ 80	KNO ₃ 80	Ca(NO ₃) ₂ 80
FeCl ₃ 12	FeCl ₃ 12	FeCl ₃ 12
Total198	198	198
4.	5.	6.
CaCl ₂ 44	CaCl ₂ 44	CaCl ₂ 44
MgSO ₄ 24	MgSO ₄ 24	MgSO ₄ 24
(Na) ₂ HPO ₄ 38	K ₂ SO ₄ 38	K ₂ SO ₄ 38
NaNO ₃ 80	NaNO ₃ 80	(Na) ₂ HPO ₄ 80
FeCl ₃ 12	FeCl ₃ 12	FeCl ₃ 12
Total198	198	198

It has already been shown that the concentration of the nutrient solution has an important effect upon water cultures,¹ so care was taken to have each of these solutions of the same total salt content and of a concentration well suited to the growth of wheat. Solution No. 1 was a full nutrient solution, *i. e.*, a solution containing all of the bases and acids usually classified as plant foods. No. 2 contained all of these nutrients except calcium, this element being replaced by sodium. In No. 3 both sodium and potassium were left out and ammonium and calcium substituted. In No. 4 potassium alone was omitted and sodium substituted. In No. 5 PO₄ was replaced by SO₄, and in No. 6 NO₃ was replaced by SO₄. It will be noticed that in making these substitutions acids or bases were used which are known to have but little effect upon the plant. They were added for the sole purpose of bringing up the total salt content.

Sixteen wheat seedlings were placed in 240 cc. of each of these solutions in the manner described in Bulletin No. 23 of the Bureau of Soils and allowed to grow for fifteen days. The solutions were

¹ Breazeale, J. F.: Science, N. S. 22, 146 (1905), "Effect of the Concentration of the Nutrient Solutions upon Wheat Cultures."

frequently changed so that an abundance of plant food was always present. At the end of this period the plants were taken from the solutions in which they had been growing and each set placed in 240 cc. of a full nutrient solution having the following concentration of nutrients by analysis:

	Parts per million.
Ca (calcium).....	27.2
K (potassium) ..	42.0
PO ₄ (phosphates).....	51.7
NO ₃ (nitrates).....	68.8

The salts used in this nutrient solution were the same as those in No. 1 but the amounts were increased slightly in order to have enough left for an analysis after the plants had grown in the solution for the period during which they were under observation. The bottles containing the cultures were then weighed and allowed to stand for two days. At the end of that time they were again weighed, the difference in weight representing the amount of water lost by transpiration. The solutions were then made up to their original volume with distilled water and analyzed for calcium, potassium, phosphates and nitrates.

Table II represents the transpiration of the plants in grams and the amounts, in parts per million, of the nutrients removed from the above-mentioned solution.

TABLE II.

Solution in which seedlings grew during first period.	Transpiration of seedlings and the parts per million of nutrients removed from the full nutrient solution during the second period.				
	Trans.	NO ₃ .	Ca.	K.	PO ₄ .
1. Full nutrient.....	65	40.4	4.0	9.0	9.4
2. Nutrient with Ca left out.....	47	42.1	6.4	9.0	4.7
3. Nutrient with both K and Na left out.....	20	10.7	4.0	15.0	0.7
4. Nutrient with K left out	64 ¹	53.8	4.8	36.0	6.6
5. Nutrient with PO ₄ left out.....	26	25.8	4.8	6.0	6.6
6. Nutrient with NO ₃ left out ...	29	60.2	3.2	12.0	0.7

The general development of the plants in this experiment was in the same relative order as their transpirations.² As indicated by the transpiration figures, the plants in No. 1 were

¹ Owing to an oversight the seeds were not removed from the seedlings of No. 4 until one day after the experiment was begun. This accounts for the relatively high transpiration.

² For evidence in regard to the use of transpiration as a criterion here, see Livingston, B. E.: "Relation of Transpiration to the Growth of Wheat," Bot. Gaz. 40, 178 (1905).

more than three times as large as those in No. 3; the proper basis of comparison therefore should be the relative size of the plants. In the absence of the absolute weight of the plants, the data for such a comparison may be obtained by dividing the total amount of the different nutrient constituents taken out of solution by the amount of water transpired by the plants. The following table represents in parts per million the amount of calcium, potassium, phosphates and nitrates removed from the original solution for every 10 grams of water transpired by the plants. Since 240 cc. of water were used, one part per million in the table is equivalent to 24 mg.

TABLE III.

Solution in which seedlings grew during <i>first</i> period.	Parts per million of nutrients removed from the nutrient solution during <i>second</i> period for every 10 grams of water transpired by seedlings.			
	NO ₃ .	Ca.	K.	PO ₄ .
1. Full nutrient.....	6.21	0.61	1.38	1.45
2. Nutrient with Ca left out....	8.95	1.36	1.92	1.00
3. Nutrient with K and Na left out.....	5.35	2.00	7.50	0.35
4. Nutrient with K left out.....	8.40	0.75	5.62	1.03
5. Nutrient with PO ₄ left out...	9.92	1.85	2.30	2.54
6. Nutrient with NO ₃ left out...	20.76	1.10	4.14	0.24

Using as a basis of comparison the full nutrient solution No. 1, it will be noticed both from Table II and from Table III that in the case of the plants which had been grown for the first fifteen days of their life in a solution from which had been omitted either nitrates, phosphates or potash, these plants, when placed in a full nutrient solution, took up relatively a much larger amount of that particular nutrient which had been left out of the first solution. This is probably also true in the case of calcium, as is indicated in Table II, but is not apparent when calculated on the basis of equivalent plant development as is shown in Table III. For example, No. 6 in Table III, which had been previously grown without nitrates, the seedlings when placed in a solution containing that nutrient took up more than twice as much nitrates as did any of the others. From these results it is apparent that in the manner just described a demand for either of the three most important constituents of mineral plant food, nitrates, phosphates, or potash can be created within the plant and that this demand can be measured by analytical methods.

As indicated in both the preliminary work and in the experi-

ment just described, plants which for the first period grew in a solution containing sodium but no potassium drew less heavily upon the potassium of the full nutrient solution than the plants which for the first period grew in a solution containing neither sodium nor potassium. There was a greater absorption of potassium where sodium had been absent than where it had been present. This seemed to indicate that sodium was in some way affecting the absorption of potassium, and to investigate this question the following experiments were carried out.

Four nutrient solutions were prepared having the following salt content in parts per million:

1.	2.	3.	4.
CaCl ₂ 44	CaCl ₂ 44	CaCl ₂ 44	CaCl ₂ 44
MgSO ₄ 24	MgSO ₄ 24	MgSO ₄ 24	MgSO ₄ 24
Na ₂ HPO ₄ ... 38	(NH ₄) ₂ HPO ₄ 38	(NH ₄) ₂ HPO ₄ 38	(NH ₄) ₂ HPO ₄ 38
KNO ₃ 80	KNO ₃ 80	NaNO ₃ 80	Ca(NO ₃) ₂ 80
FeCl ₃ 12	FeCl ₃ 12	FeCl ₃ 12	FeCl ₃ 12
Total198	198	198	198

No. 1 was a full nutrient solution, No. 2 a solution with sodium omitted, No. 3 with potassium omitted, and No. 4 with both sodium and potassium omitted. Eight wheat seedlings were placed in 600 cc. of each of these solutions and allowed to grow for nineteen days with frequent changes of solution. The plants showed marked differences from the first as is shown by the following transpirations.

No.	Solution.	Transpiration. Grams.
1.	Full nutrient.....	130
2.	Nutrient without sodium.....	112
3.	Nutrient without potassium.....	89
4.	Nutrient without both sodium and potassium ...	86

After nineteen days the cultures were taken from these solutions and each placed in 600 cc. of a full nutrient solution containing 18.3 parts per million of potassium and allowed to grow for one day. The losses by transpiration were determined, the solutions made up to their original volumes and analyzed for potassium.

Table VI represents the transpiration of the plants, parts per million of potassium removed from solution, and parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VI.

Solution in which seedlings grew during first period.	Trans- piration. Grams.	Results for the second period.			
		Potassium removed from the nutrient solution.			
		P.p.m.	On the basis of 10 grams of water transpired.		
		P.p.m.	Mgs.		
1. Full nutrient solution.....	39.5	8.16	2.06	1.24	
2. Nutrient without sodium.....	36.	15.71	4.36	2.61	
3. Nutrient without potassium...	26.	12.65	4.86	2.92	
4. Nutrient without both sodium and potassium.....	21.1	16.12	7.63	4.58	

The plants were then mounted and photographed and are shown in Fig. 1.

It will be seen from the figure and by a comparison of the transpiration results of Nos. 1 and 2 that the presence of sodium has increased the transpiration and size of the plants, and this even where there was an abundance of potassium and all the other necessary mineral plant food constituents in solution. Apparently, a direct need for sodium was manifested by the plants in this experiment. This difference in transpiration and size appeared throughout all subsequent work but is seldom noticed when the seeds are not removed from the seedlings before beginning the experiment. It thus seems that the amount of sodium required by the plants during this period of their growth is small.

The difference in transpiration of Nos. 3 and 4 is much larger than appeared in subsequent work, and indeed somewhat larger than the general appearance of the plants would indicate. As a general rule the effect of sodium in increasing the size of the plant is not marked where there is no potassium present as is clearly shown in the experiments to follow.

It will also be noticed from the table that the phenomenon indicated in the first experiment is brought out more strikingly here. There was a greater demand for potassium in the plants growing in solution No. 2 where sodium was left out during the first period than in those of solution No. 1, which had always had an abundant supply of sodium.

In the following experiment the same number of seedlings were grown for fifteen days in solutions prepared in exactly the same way as those of the preceding experiment. At the end of that time the plants were removed from these solutions and all placed

in a full nutrient solution containing 36.4 parts per million of potassium and allowed to grow for two days. The loss by transpiration was then determined, the solutions made up to their original volumes and analyzed for potassium. Table VII represents the transpiration for two days, the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VII.

Solution in which seedlings grew during first period.	Transpiration. Grams.	Results for the second period.		
		Potassium removed from the nutrient solution.		
		P.p.m.	On the basis of 10 grams of water transpired.	
P.p.m.	Mgs.			
1. Full nutrient solution.....	15.8	1.04	0.65	0.39
2. Nutrient without sodium.....	11.0	6.24	5.67	3.40
3. Nutrient without potassium.....	6.1	5.20	8.52	5.11
4. Nutrient without sodium and potassium	7.8	6.24	8.00	4.80

Here also the comparison of the transpiration figures for Nos. 1 and 2 shows the beneficial effects of sodium upon the plants in the presence of an abundance of potassium. In the case of Nos. 3 and 4, however, this effect is not shown.

As in the previous experiment, the measured demand for potassium is much greater in No. 2 than in No. 1, but not so great as in No. 3, as shown in the third column of the table. This indicates that in water cultures the wheat plant does not absorb as much potassium, even when an abundance of that element alone is present, as it does when an adequate supply of sodium is also present.

Whether the ammonium salt which was substituted in Nos. 2, 3 and 4 played any part in the absorption of potassium was a point that was next considered. Four nutrient solutions were prepared in the manner indicated in Table VIII.

TABLE VIII.

	Parts per million.						
	CaCl ₂ .	MgSO ₄ .	(NH ₄) ₂ HPO ₄ .	FeCl ₃ .	KNO ₃ .	NaNO ₃ .	NH ₄ NO ₃ .
1	44	24	38	12	40	40	0
2	44	24	38	12	80	0	0
3	44	24	38	12	0	80	0
4	44	24	38	12	0	0	80

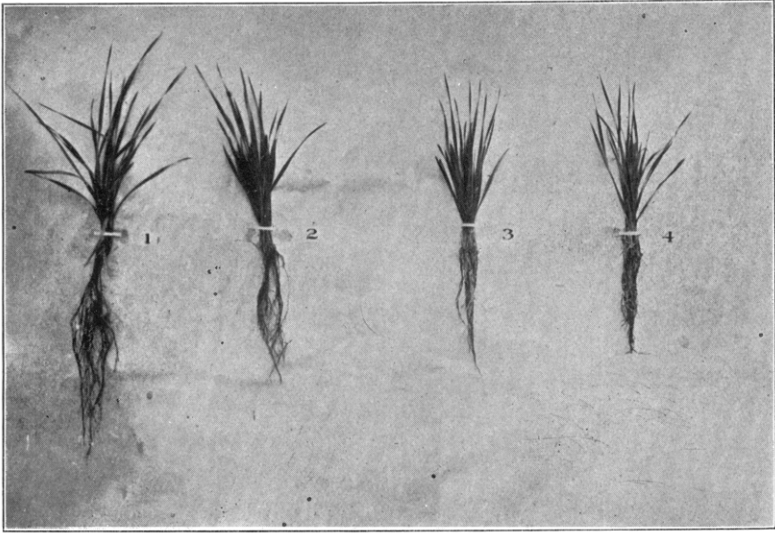


Fig. 1.

No. 1—Full nutrient solution. No. 2—Nutrient without sodium. No. 3—Nutrient without potassium. No. 4—Nutrient without both sodium and potassium.

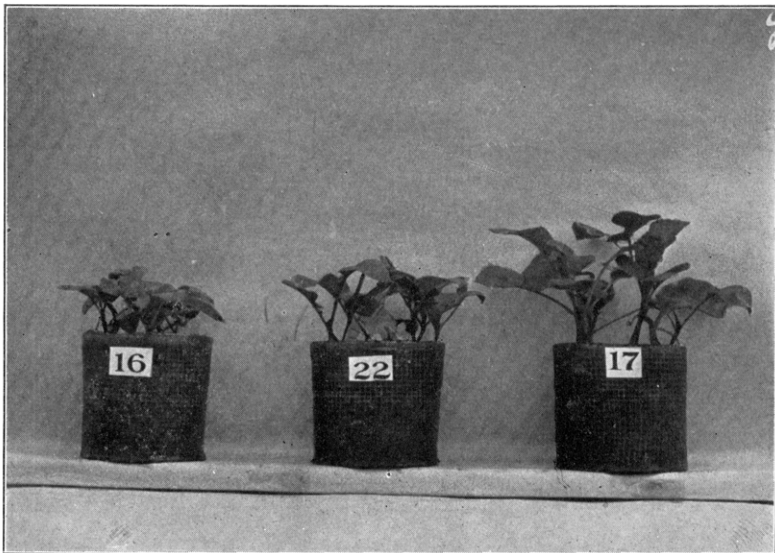


Fig. 2.

Treatment. Plot No. 16—200 lbs. per acre of sodium chloride; no potassium chloride. Plot No. 22—No sodium chloride; 362 lbs. per acre of potassium chloride. Plot No. 17—200 lbs. per acre of sodium chloride; 362 lbs. per acre of potassium chloride.

Twelve seedlings were placed in 600 cc. of each of these solutions and allowed to grow for seven days. The transpirations for the last day were as follows:

No.	Transpiration. Grams.
1.....	8.0
2.....	6.5
3.....	4.0
4.....	3.5

The plants were then removed from these solutions and placed in a full nutrient solution containing 73.9 parts per million of potassium, and allowed to grow for four days. The transpirations were then taken, the solutions made up to their original volumes and the amounts of potassium remaining in solution determined. In Table IX will be seen the transpiration of the plants in grams, the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE IX.

Solution in which seedlings grew during first period.	Trans- piration. Grams.	Results for the second period.		
		Potassium removed from the nutrient solution.		
		P. p. m.	On the basis of 10 grams of water transpired.	
P. p. m.	Mgs.			
1. Full nutrient solution.....	53.6	12.3	2.3	1.38
2. Nutrient without sodium.....	46.7	18.5	4.0	2.40
3. Nutrient without potassium...	33.5	16.2	4.8	2.88
4. Nutrient without sodium and potassium.....	34.7	23.0	6.6	3.96

These results are in harmony with those obtained in the earlier experiments.

The results obtained by keeping the plants in solutions in the first period were of such interest that it seemed desirable to ascertain what results would follow if the plants were kept during the first period in the soil itself. To this end about 500 grams of soil were taken from each of three plots of the Rhode Island Experiment Station. These plots are in what is known as the "soda-potash experiment," and have been under observation for the past ten years.¹ Their numbers are given below. They have all received equal yearly applications of nitrogen and phosphates in some combination, with varying amounts of either

¹ See Annual Reports of the Rhode Island Experiment Station.

potassium chloride or of sodium chloride, or both of these salts, excepting in the years 1902-1904, inclusive. The samples taken were given applications of ammonium nitrate and ammonium phosphate at the rate of 350 and 150 pounds per acre respectively, this being about the rate of application for nitrates and phosphates used in the field on these plots in 1905. Potassium chloride and sodium chloride were then added in the amounts indicated in Table X. This soil had been limed twice and was in good physical condition. The soil was then placed in small paraffined wire pots of the form described in Bulletin 23 of the Bureau of Soils, and eight radish seeds planted in each. The soil was kept at the optimum moisture content and the plants allowed to grow for thirty-two days.

The difference in size of the plants can be seen from Fig. 2, the numbers in the photograph corresponding to the plot numbers.

The plants were then carefully taken from the soil, their roots washed clean, and transferred to bottles of a full nutrient solution containing 61.6 parts per million of potassium and allowed to grow for three days longer. They were then taken from the solution and weighed. The solutions were made up to their original volume and analyzed for potassium. Table X represents the plot numbers, applications of potassium chloride and sodium chloride to the soil, green weight of crop, and parts per million of potassium subsequently removed from the nutrient solution for every gram of crop.

TABLE X.

Plot No.	Amount of potassium chloride and sodium chloride added to soil.	Green weight. Grams.	P. p. m. of potassium removed for every gram of green weight.
16.	No potassium chloride, 200 lbs. per acre of sodium chloride...	4.4	5.9
22.	362 lbs. per acre of potassium chloride. No sodium chloride	6.0	4.1
17.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	11.65	2.5

Plot 16 had not received any potassium for a period of ten years, and this is distinctly shown by the relatively low weight of the crop. The increase in weight of No. 17 over No. 22 is the result of the application of sodium.

Here again as in the solution cultures there was a greater demand for potassium in the plants which had been growing in a soil which had received no potassium than in the plants which had always had a sufficient quantity of that element. There was also a greater absorption of potassium in No. 22 than in No. 17, although in the soil each had the same supply of that element. This indicates, as in the solution cultures, that sodium plays some part in the absorption of potassium. This experiment was repeated as Experiment VI.

The following experiment was similar to the preceding one excepting that soil from plots 4, 10 and 5 was used in this case. These plots corresponded in treatment to plots 16, 22 and 17, respectively, with the exception that plots 4, 10 and 5 had been limed only once. Sixteen radish plants were grown in pots of these soils for twenty-four days. The difference in growth is fairly represented by the following transpirations for one day at the end of that period.

Plot No.	Transpiration in grams.
4	72.
10	105.5
5	120.0

Four plants were selected from each of these plots, placed in a full nutrient solution containing 56.4 parts per million of potassium and allowed to grow for six days. Table XI represents the treatment of the soil, green weight of the plants used, and the parts per million of potassium removed from solution for every gram of green weight.

TABLE XI.

Plot No.	Amounts of potassium chloride or sodium chloride added.	Green weight. Grams.	P. p. m. of potassium removed for every gram of green weight.
4.	No potassium chloride. 200 lbs. per acre of sodium chloride.....	3.50	7.54
10.	362 lbs. per acre of potassium chloride. No sodium chloride...	2.35	5.10
5.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	4.44	2.97

As the total weight of the crop is not of interest in this connection, plants were selected which were best suited for solution culture. This accounts for the high weight of the four plants selected in No. 4, the average plant in No. 4 being smaller than in

either of the other two. Here again the need of potassium in the plants of No. 4 is strikingly shown by the relatively large amount of that element which they removed from the nutrient solution. The effect of sodium upon the absorption of potassium is also brought out here.

The experiments just described were performed in the spring and summer of 1905. The plots in the "soda-potash" experiment of the Rhode Island Experiment Station were then in turnips and radishes. These were harvested about the middle of August and the plots planted in beets as a second crop. The plots received at the beginning of the season the full application of fertilizers for the year, *viz.*, 1,000 pounds of dried bone, 20 pounds of magnesium sulphate, and 1,500 pounds of dissolved bone. The quantities of potassium and sodium salts when applied to the plots under consideration here were 362 pounds of potassium chloride, and 200 pounds of sodium chloride per acre. No fertilizers were applied when the beets were planted. When the beets were about two weeks old, four plants were taken from each of the plots before mentioned, their roots washed clean, and placed in 100 cc. of a full nutrient solution containing 43.1 parts per million of potassium and allowed to grow for three days. They were then withdrawn and weighed, the solutions made up to their original volumes and analyzed for potassium.

Table XII represents the applications of potassium chloride and sodium chloride, green weight of plants, and parts per million of potassium removed from solution for every 1 gram of green weight.

TABLE XII.

Plot No.	Applications of potassium chloride and sodium chloride.	Green weight. Grams.	P. p. m. of potassium removed from solution for every gram of green weight.
4.	0 pounds per acre KCl		
	200 " " " NaCl	4.20	1.83
10.	362 " " " KCl		
	0 " " " NaCl	8.55	1.08
5.	362 " " " KCl		
	200 " " " NaCl	9.05	0.85
16.	0 " " " KCl		
	200 " " " NaCl	5.50	4.48
22.	362 " " " KCl		
	0 " " " NaCl	8.00	1.15
17.	362 " " " KCl		
	200 " " " NaCl	9.46	0.0

In this experiment it was apparent, as in preceding ones, that the absorption of potassium from the solution of the second period was strikingly decreased when sodium was present in the solution of the first period.

The procedure employed in this paper, using the plant itself as an indicator, and transferring it from soil to solution or from one solution to another, together with the delicate analytical methods which made it possible to measure slight changes in the concentration of the solution, would seem to be applicable to the study of certain phases of the most important agricultural problems.

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REACTIONS OF ACETYLENE WITH ACIDIFIED SOLUTIONS OF MERCURY AND SILVER SALTS.

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FROM work already published on the behavior of acetylene towards neutral and acid solutions of mercury and other metals, it is fair to conclude that there is a possibility of forming compounds other than those already mentioned. Up to the present time the only acetylene derivatives of mercury that have been investigated are the nitrates (mercurous and mercuric), the chloride, bromide and the fluoride. It was expected that with acid solutions such as mercury fluosilicate, fluoborate, cyanide, nitrite, chlorate and perchlorate, compounds analogous to those discussed in the previous work,¹ would be formed under proper conditions.

While the work to be described was in progress there came to our notice an article of Hoffman² in which, among other compounds, he described the formation of acetylene derivatives of mercuric nitrite, chlorate and perchlorate. His method of preparing these substances is almost identical with the method by which we made them. Besides the substances mentioned by Hoffman, we have been working on a number of others about to be described. The general method of procedure was to make

¹ Thesis: "Some Reactions of Acetylene," Notre Dame University Press, 1904.

² Ber. 38, 1899.