

COMPARISON OF METHODS FOR ESTIMATING  
AVAILABLE PHOSPHORUS IN ALKALINE  
CALCAREOUS SOILS

BY R. D. HOCKENSMITH, ROBERT GARDNER, AND JAMES GOODWIN



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# COMPARISON OF METHODS FOR ESTIMATING AVAILABLE PHOSPHORUS IN ALKALINE CALCAREOUS SOILS

BY R. D. HOCKENSMITH, ROBERT GARDNER, AND JAMES GOODWIN

Numerous methods have been suggested for estimating the available phosphorus in soils. The methods may be divided into two groups—chemical and biological. The chemical methods, which have been used most widely, are: the Dyer 1 percent citric acid method (8); the 0.2 normal nitric acid method by Fraps (9); the Illinois "Hi-Lo-Phos" test by Bray (1); the Michigan water-soluble method by Spurway (23); the Wisconsin method by Truog (26) using 0.002 normal  $H_2SO_4$ ; the method of von Wrangell and collaborators (29); the calcium bicarbonate method by Dirks and Scheffer (7); the 1 percent potassium carbonate method by Das (5); the Hibbard method (12) using acetic acid with a pH value of 4.0 in the final extract; the Dahlberg-and-Brown method (4) using sodium acetate; and a modification of the Truog method by Mitchell (14). The chief differences in the above methods are in the procedures for obtaining the soil extract and in the nature of the extracting agent.

Most of the chemical methods involve the use of the Deniges rapid colorimetric method for the determination of phosphorus. A thoro discussion of this method is given by Truog and Meyer (27), Parker and Fudge (18), Chapman (2), (3), and the Imperial Bureau of Soil Science (21).

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Among the biological methods may be mentioned the Neubauer method (16) using rye seedlings; the Mitscherlich plant-culture method (15); the Winogradsky method\* (4), (10), (11), (13), (19), (22), (24), (28), (30), using azotobacter; the Niklas method (17) using *Aspergillus niger*; the Thornton plant test (25) in which portions of the growing plants are used instead of the soil; and the field-plot method.

Very few of the above methods have been used in arid and semi-arid regions where calcareous soils are prevalent. Most of the chemical methods apparently have been devised with the idea of attempting to imitate the power which plants have for securing available phosphorus. The weak-acid-digestion methods have become the most popular. In humid regions where acid soils are prevalent, these methods appear to agree in a high percentage of the cases with field results (1), (6), (20), (26). When these methods, however, have been used with calcareous soils, the results obtained in our laboratory have frequently been disappointing when they are compared with field data. The acid extraction methods usually bring into solution a large amount of soluble phosphorus if the lime content of the soil is small. If the soil contains a large amount of lime, the amount of phosphorus dissolved is usually small. This is especially true when the Bray method (1) is used.

#### METHODS USED

In a preliminary investigation the following methods were used to determine the available phosphorus in soils: The Winogradsky method using azotobacter; the Truog method using 0.002 normal  $H_2SO_4$  buffered with  $(NH_4)_2SO_4$  to a pH value of 3.0 and using a 1-to-200 ratio of soil to extractant; the Mitchell method which is similar to the Truog method, except that the extractant is  $KHSO_4$  buffered with  $K_2SO_4$  to a pH value of 3.0; the Hibbard method in which acetic acid is used in varying concentrations in order to obtain a pH of 4.0 in the final 1:5 soil:solution extract; the 1 percent  $K_2CO_3$  method used by Das in India with calcareous soils (modified by using a soil:solution ratio of 1:75, instead of the 1:10 ratio as used by Das); the Dahlberg-and-Brown method, using 0.25 normal sodium acetate with a pH of 5.0 and a soil:solution ratio of 1:5 (The original procedure as published was followed in this investigation. Since this investigation was started, however, the method has been modified and apparently improved. The modified procedure is yet unpublished); a 1 percent ammonium oxalate solution with a 1:5 soil:solution ratio; and a 1 percent oxalic acid solution with a 1:5 soil:solution ratio.

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\*This method is called, by some investigators, the soil-plaque method, by others the azotobacter method, and by still others, the kneaded-plate method.

## SELECTION OF FIELDS

As a preliminary part of the investigation, soil samples were collected from fields of known response to superphosphate on the Western Slope, in the Arkansas Valley, South Platte Valley and Poudre Valley. Many farmers in the irrigated valleys in Colorado have applied superphosphate to narrow strips of land in their fields. Some have doubled the yield of certain crops such as sugar beets and alfalfa. Others have obtained no increase in yield of crops by applying superphosphate. In collecting the soil samples from fields which gave no response to superphosphate, only the high-producing fields were sampled.

The selection of fields which did not respond to superphosphate was a difficult task. There are to be found many fields that do not respond to superphosphate, but the lack of response in many cases may be due to some other unfavorable condition for plant growth. In some fields, along with a deficiency in available phosphorus, is found an excessive amount of soluble salts, high alkalinity, a lack of nitrate nitrogen or some other nutrient element, an impermeable soil, a clayey or hardpan layer, high water-table, a lack of sufficient irrigation water, or improper use of irrigation water.

Some of the above-mentioned conditions may interfere with the absorption of phosphorus by plants as well as being limiting factors themselves. It is evident that if one or more of these unfavorable conditions are present, the application of superphosphate may not increase crop yields, even tho the soil is deficient in available phosphorus. Many farms were examined where the farmers maintained that phosphate had not increased the yield of their crops. In many cases, however, even after applying superphosphate, the yields of the crops were low. These low-producing fields which did not respond were not considered in this investigation because the lack of response might have been the result of other adverse factors. In selecting fields which did not respond to superphosphate, great care was used to be sure that other conditions for plant growth were favorable. The fields selected for the sufficient group were, therefore, fertile fields which were producing excellent yields of crops. The samples were taken at three depths, namely: 0" to 6", 6" to 12" and 12" to 18". Each sample was a composite of at least 10 borings in small fields and the number of borings was increased according to the size of the field. In every case the samples were taken from the untreated portion of the field.

## DISCUSSION OF PRELIMINARY RESULTS

The data in Table 1 show that the response to superphosphate is not correlated with the amount of organic matter, lime content, pH value of the soil, nor total phosphorus. The soils which responded

averaged  $.1502 \pm .0071$  percent total  $P_2O_5$ , and the soils which did not respond averaged  $.1584 \pm .0033$  percent  $P_2O_5$ , the difference being  $.0082 \pm .0078$ , which is evidently not significant. Definite conclusions, however, cannot be drawn from so few data.

Of the several methods which have been proposed for determining the available phosphorus in soils in an effort to advise farmers as to whether or not they should expect a profitable response to superphosphate, the Winogradsky method has been most extensively used in Colorado. The data in Table 1 show that all the soils used in this part of the investigation were deficient by the Winogradsky method and should have responded to an application of superphosphate. It is noted, however, that eight of these samples were from four fields where superphosphate gave no increase in yield.

The results obtained by using the Truog method and the Mitchell method are similar. The striking point of interest in these data is that the pH values of the final extract vary considerably for different soils. Samples 10A and 10B with a low buffer capacity have low pH values, and consequently an unusually large amount of phosphorus is brought into solution. These data indicate that it would be advisable to use a different amount of acid on different soils such that the pH of the final extract would be the same for all soils. It seems evident that comparable results cannot be obtained with calcareous soils by using the same concentration of acid on all soils. Hibbard (12) has proposed a method in which three different concentrations of acetic acid are used. One of the three concentrations is such that the final pH of the extract will be about 4. The other concentrations are such that one will have a pH slightly below 4 and one above 4. The results are plotted and from the graph, the phosphate in solution at pH 4 is obtained. Hibbard found the method fairly reliable with some California soils, but with Colorado soils, the results obtained did not correlate very well with field results as shown in Table 1. A more detailed study is being made of the Hibbard method and in a subsequent paper the agreement between this method and field results will be reported for a large number of soils. The Dirks and Scheffer calcium bicarbonate method is also being studied and will be reported in the same paper.

The use of 1 percent ammonium oxalate and 1 percent oxalic acid proved rather unsatisfactory.

The Dahlberg-and-Brown sodium acetate method agreed with field results in two-thirds of the cases when the upper limit of available phosphorus of deficient soils was set at 2 p.p.m.

The 1 percent  $K_2CO_3$  method agreed with field results in one-half of the cases when the soil:extract ratio of 1:10 was used. When the ratio was widened to 1:75, the results agreed in every case, except one.

Table 1.—Analyses of Soil Samples from Fields of Known Response to Superphosphate and a Preliminary Comparison of Methods for Estimating Available Phosphorus.

Soil No.	Organic Matter Pct.	Lime Pct.	pH	Total P <sub>2</sub> O <sub>5</sub> Pct.	Field Response	Wino-gradsky Method	Available Phosphorus in p.p.m. of Soil									
							Truog Method		Mitchell Method		Hibbard Method		Ammonium Oxalate 1 Pct.	Oxalic Acid 1 Pct.	NaAc .25 N	K <sub>2</sub> CO <sub>3</sub> Method 1 Pct.
							P	pH	P	pH	P at pH 4	P at pH 4				
1A*	2.3	5.0	8.4	.1205	Great	Deficient	52	6.8***	86	6.7***	65	7.5	37	2.3	45	
1B**	2.1	6.7	8.4	.1443	Great	Deficient	30	7.0	52	6.9	58	1.5	31	4.5	45	
2A	0.8	4.7	7.7	.0796	Great	Deficient	19	7.0	44	7.1	30	3.8	11	2.5	33	
2B	0.7	11.2	8.1	.0822	Great	Deficient	26	7.3	10	7.3	37	3.8	8	1.5	15	
3A	3.0	3.7	8.4	.1783	Great	Deficient	26	6.9	36	7.6	10	3.3	53	4.5	45	
3B	2.2	3.5	8.2	.1716	Great	Deficient	32	6.7	36	7.7	9	2.5	53	1.5	33	
4A	2.4	6.1	8.0	.1866	Great	Deficient	26	7.2	36	7.3	10	3.3	46	2.5	45	
4B	2.1	4.9	8.0	.1842	Great	Deficient	26	6.9	36	7.4	11	2.3	50	1.5	25	
5A	2.4	2.5	7.6	.1727	Great	Deficient	68	6.2	86	5.9	30	6.5	22	5.5	45	
5B	1.5	3.5	7.7	.1488	Great	Deficient	30	6.7	26	6.8	21	2.3	31	2.5	45	
6A	3.7	4.0	8.1	.1482	Great	Deficient	26	7.0	20	6.9	6	5.0	54	0.2	25	
6B	1.7	7.0	8.4	.1280	Great	Deficient	13	7.3	12	7.1	8	3.0	22	0.2	45	
7A	3.2	7.4	8.2	.1429	Great	Deficient	26	7.3	20	7.0	7	4.3	54	0.3	33	
7B	3.3	9.9	8.4	.1280	Great	Deficient	13	7.5	10	7.1	5	2.2	45	0.2	45	
8A	1.9	9.2	8.3	.1914	Great	Deficient	26	7.3	26	7.2	18	6.0	28	0.7	75	
8B	0.9	11.6	8.3	.1765	Great	Deficient	26	7.4	12	7.3	13	4.3	22	0.3	15	
9A	1.6	2.5	8.2	.1211	None	Deficient	48	7.1	86	7.0	40	5.5	22	3.5	108	
9B	1.3	11.1	8.2	.1132	None	Deficient	19	7.5	26	7.0	43	4.5	11	2.5	100	
10A	2.1	2.4	8.1	.1348	None	Deficient	160	4.8	182	4.1	43	6.3	26	2.5	75	
10B	0.9	1.5	8.0	.1826	None	Deficient	80	4.9	130	3.9	13	5.5	16	2.5	55	
11A	2.4	4.3	8.1	.1906	None	Deficient	20	6.8	26	6.9	13	3.3	27	3.3	100	
11B	1.1	9.7	8.4	.1818	None	Deficient	12	7.3	10	7.1	17	4.0	20	2.5	83	
12A	2.5	4.3	8.2	.1803	None	Deficient	26	7.0	36	6.9	13	7.5	75	3.0	83	
12B	1.4	7.8	8.4	.1729	None	Deficient	11	7.2	20	7.2	12	5.0	22	0.7	55	

\*A represents surface 6-inch samples.

\*\*B represents 6 to 12-inch samples.

\*\*\*The pH of the final extract

THE PROPERTIES OF THE SOILS USED IN THE  
MAIN INVESTIGATION

The data in Table 2 give the pH value, the lime content, the soluble salt content, organic matter and textural grade for each of the soil samples used in comparing the Winogradsky,  $K_2CO_3$ , Truog and Dahlberg-and-Brown methods with field results. The data show that all of the soils are alkaline and most of them are calcareous. Since the soil samples were taken from well-drained soils, the soluble salt contents are not excessive. The mean pH value for the surface 6-inch samples from the 93 fields was  $8.23 \pm 0.018$ . The mean pH value for the 6 to 12-inch samples was  $8.25 \pm 0.019$  while for the 12 to 18-inch samples, the mean pH value was  $8.28 \pm 0.020$ . The mean percentage of lime in the surface 6-inch samples was  $4.98 \pm 0.33$  while for the samples taken at the depths 6 to 12 inches and 12 to 18 inches, the lime contents were  $6.60 \pm 0.45$  percent and  $8.79 \pm 0.53$  percent, respectively. The mean soluble salt content was  $931 \pm 36.5$  p.p.m. for the samples representing the surface 6 inches.

There appears to be no correlation between phosphate response and the pH value, lime content, organic matter content, or soluble salt content within the limits of these data. The pH values were determined electrometrically with the quinhydrone electrode. A 1:2 soil: water suspension was used. The soluble salts were determined by the conductivity soil bridge. Organic matter was estimated by multiplying the organic carbon by the factor 1.724. The total carbon was determined by means of the Fleming combustion train in which the carbon was collected in ascarite bulbs and weighed as  $CO_2$ . The inorganic carbon was determined on another sample and then subtracted from the total carbon. The difference was assumed to be organic carbon. The lime contents are calculated as  $CaCO_3$ . Undoubtedly, a part of the carbonate exists as  $MgCO_3$  but for the purpose of this investigation all the  $CO_3$  was calculated as  $CaCO_3$ .

COMPARISON OF THE WINOGRADSKY METHOD AND THE  
 $K_2CO_3$  METHOD WITH FIELD TRIALS

The results obtained in the preliminary investigation indicated that the  $K_2CO_3$  method gave promise of indicating with a fair degree of accuracy the available phosphorus in alkaline calcareous soils. The agreement with field results was 95.8 percent. The detailed procedure adopted is described later in this bulletin. The procedure used in this investigation for testing the soil samples for phosphate deficiencies by the Winogradsky method was the same as described by Sackett and Stewart (22). The results are expressed in Table 3 herein and are designated in the following manner.



Table 2.—The pH Values, Lime Contents, Soluble Salt Contents, Organic Matter Contents, and Textural Grades of Soils Used in Determining the Reliability of the Winogradsky, K<sub>2</sub>CO<sub>3</sub>, Truog and Dahlberg-and-Brown Methods.

Soil No.	Field Response	pH Value			Percentage Lime			Soluble Salts	Organic Matter	Textural Grades
		0 to 6"	6 to 12"	12 to 18"	0 to 6"	6 to 12"	12 to 18"	p.p.m. 0 to 6"	Percentage 0 to 6"	
30	Great	7.80	7.10	8.10	5.85	9.82	12.30	580	3.84	Loam
31	Great	8.10	8.30	8.25	7.03	7.00	14.50	660	3.87	Clay loam
32	Great	8.25	8.25	8.25	7.97	9.90	10.27	1200	2.31	Clay loam
32A	Great	8.35	8.35	8.50	5.10	6.55	9.56	1300	2.54	Clay
33	None	8.20	8.20	8.40	5.57	12.37	13.65	840	1.49	Loam
33A	Great	7.79	8.10	8.50	5.50	11.82	25.40	880	0.85	Clay loam
34	Great	8.40	8.15	8.40	5.50	8.35	8.42	*	*	Clay loam
34A	Great	8.00	8.00	7.70	7.26	6.10	6.01	500	2.36	Clay loam
35	None	8.10	8.00	8.60	2.37	4.49	7.62	580	2.31	Loam
37	None	7.90	8.10	8.30	3.77	7.12	14.45	*	2.75	Heavy loam
37A	None	8.40	8.30	8.50	4.34	7.67	12.47	500	2.83	Clay loam
38	Great	7.60	7.70	8.20	2.58	6.70	6.50	*	2.72	Loam
54	Great	8.10	8.05	8.15	1.57	3.68	6.90	650	1.71	Fine sandy loam
55	None	8.20	8.05	8.00	7.38	11.12	11.07	2000	1.31	Loam
56	None	8.25	8.20	8.10	7.57	9.70	13.92	900	1.38	Clay loam
57	None	8.30	8.25	8.15	7.00	10.97	20.35	960	1.87	Clay loam
58	None	8.05	8.10	8.20	1.20	0.62	5.15	630	3.34	Clay loam
59	None	8.50	8.50	8.50	11.10	23.00	24.40	440	1.12	Loam
60	None	8.40	8.40	8.30	5.72	9.43	21.72	970	1.17	Clay loam
61	None	7.70	7.65	7.50	0.40	0.45	0.47	1100	2.02	Clay loam
62	None	7.70	7.70	8.00	0.36	0.40	4.80	865	2.11	Loam
63	None	8.20	8.30	8.50	10.75	14.60	31.60	830	1.38	Loam
65	Great	7.85	7.90	7.35	6.00	6.07	7.35	4800	2.44	Clay
66	Great	8.25	8.25	8.20	4.75	5.72	7.02	475	2.10	Loam
70	None	8.30	8.30	8.40	11.65	14.90	14.87	455	1.13	Loam
72	Great	8.30	8.05	8.20	13.75	29.25	32.50	455	4.99	Loam
74	Great	8.30	8.10	8.20	17.20	27.40	27.37	410	4.49	Clay loam
76	Great	8.20	8.05	8.10	25.28	32.12	40.52	385	2.92	Clay loam
77	None	8.10	8.30	8.20	4.20	9.10	12.52	585	1.25	Clay loam
78	Great	8.10	8.10	8.30	0.97	6.62	10.90	*	1.92	Loam

\*Insufficient sample.

Table 2.—(Continued)

Soil No.	Field Response	pH Value			Percentage Lime			Soluble Salts	Organic Matter	Textural Grades
		0 to 6"	6 to 12"	12 to 18"	0 to 6"	6 to 12"	12 to 18"	p.p.m. 0 to 6"	Percentage 0 to 6"	
82	None	8.30	8.40	8.50	2.07	9.41	13.05	550	2.13	Loam
83	None	8.30	8.00	8.00	0.50	0.35	0.52	535	2.25	Loam
85	None	7.85	8.10	8.10	2.90	1.62	2.72	500	1.41	Clay loam
86	None	8.30	8.30	8.40	4.60	14.17	13.80	500	2.40	Clay loam
87	None	8.20	8.20	8.30	*	2.57	11.02	865	*	Clay loam
90	None	8.30	8.30	8.30	0.86	1.05	0.97	*	2.59	Clay loam
94	None	8.25	8.20	8.20	0.75	7.02	12.61	830	2.61	Loam
95	None	8.30	8.30	8.10	6.07	10.85	13.85	875	2.92	Loam
97	None	8.60	8.60	8.80	0.45	2.50	4.06	550	0.82	Sandy
99	None	8.40	8.20	8.30	0.30	0.70	3.10	345	1.49	Sandy
101	None	8.70	8.70	8.70	0.30	3.75	8.80	335	2.04	Sandy loam
102	None	8.30	8.30	8.30	0.90	3.92	8.96	3300	1.25	Sandy loam
103	None	8.25	8.35	8.15	0.20	0.92	0.60	430	1.92	Sandy loam
107	None	8.15	8.40	8.40	0.37	0.45	1.20	1650	1.46	Loam
108	None	8.30	8.30	8.30	1.80	2.12	3.62	1650	1.43	Fine sandy loam
110	None	8.20	8.25	8.25	0.55	2.22	3.10	660	1.65	Loam
111	Great	8.30	8.40	8.40	2.80	1.95	2.67	700	1.24	Fine sandy loam
117	None	8.10	8.50	8.50	0.40	0.60	0.97	1750	1.49	Loam
118	None	8.00	7.90	8.10	4.50	4.80	5.50	965	1.53	Clay loam
119	Great	8.30	8.20	8.00	1.75	1.25	3.62	1500	1.11	Fine sandy loam
120	None	8.35	8.50	8.40	2.37	3.05	5.85	505	1.61	Fine sandy loam
121	None	8.30	8.60	8.50	8.25	8.75	11.12	1400	2.27	Loam
122	None	8.60	8.60	8.45	5.50	6.07	6.12	1700	1.76	Loam
123	None	8.40	8.60	8.45	0.80	3.50	6.92	1000	2.06	Sandy loam
125	None	8.30	8.40	8.40	0.57	0.62	2.40	400	1.18	Sandy loam
126	None	8.40	8.30	8.10	3.25	0.65	0.87	700	1.26	Loam
127	None	8.15	8.45	8.45	7.30	11.42	12.92	1950	2.91	Clay loam
128	None	8.25	8.35	8.20	3.65	4.42	9.00	1235	1.53	Clay loam
129	None	8.45	8.80	8.80	1.70	4.30	9.27	595	1.60	Clay loam
130	None	8.45	8.55	8.55	5.60	4.62	6.55	700	2.15	Clay loam
131	None	8.60	8.60	8.60	7.75	8.92	8.88	825	1.47	Loam
132	None	8.40	8.40	8.30	3.52	4.37	3.20	1160	1.86	Clay

\*Insufficient sample.

Table 2.—(Continued)

Soil No.	Field Response	pH Value			Percentage Lime			Soluble Salts	Organic Matter	Textural Grades
		0 to 6"	6 to 12"	12 to 18"	0 to 6"	6 to 12"	12 to 18"	p.p.m. 0 to 6"	Percentage 0 to 6"	
133	Slight	8.30	8.30	8.50	4.10	2.35	2.37	1165	2.56	Clay
134	None	8.50	8.50	8.40	3.88	4.47	0.75	810	1.79	Sandy loam
135	None	8.40	8.40	8.30	5.20	4.20	7.40	800	2.59	Loam
136	Slight	8.40	8.45	8.50	8.90	6.10	7.82	1650	2.92	Clay loam
137	None	8.40	8.45	8.60	5.70	10.62	6.87	925	1.22	Clay
138	None	8.50	8.65	8.65	21.95	23.60	24.75	1400	2.00	Clay loam
139	Slight	8.60	8.70	8.70	7.10	6.50	8.72	1070	1.75	Loam
141	Slight	8.45	8.50	8.50	2.45	2.52	7.45	725	1.32	Sandy
142	None	8.60	8.60	8.55	5.70	7.95	6.50	750	1.33	Sandy loam
143	None	8.50	8.45	8.50	2.50	6.85	12.37	875	1.74	Loam
144	None	8.40	8.60	8.50	9.10	5.90	6.22	825	2.51	Clay loam
145	None	8.70	8.60	8.65	11.90	7.32	7.47	1110	2.16	Clay loam
147	None	8.45	8.55	8.55	12.07	4.90	6.12	1400	2.68	Clay loam
149	None	8.40	8.40	8.50	12.07	7.37	7.45	1300	2.28	Clay loam
151	None	8.50	8.50	8.55	11.70	7.32	7.42	1300	2.44	Loam
154	None	8.35	8.35	8.45	12.10	8.62	8.70	1450	2.81	Clay loam
R51	Slight	7.40	7.20	7.10	0.30	0.11	0.20	410	2.73	Loam
R53	None	7.60	7.70	8.20	1.00	0.80	4.30	700	2.52	Loam
R54	None	7.85	7.85	7.85	0.60	0.22	0.25	435	3.42	Loam
R56	None	8.30	8.20	7.20	1.70	1.05	3.55	300	1.25	Fine sandy
R58	None	8.50	8.50	8.50	3.87	4.50	6.12	530	1.84	Loam
R59	None	8.50	8.50	8.60	7.75	6.82	6.77	600	2.34	Clay loam
R60	None	7.60	7.80	7.80	0.15	0.05	0.87	535	1.30	Sandy loam
R62	None	8.15	8.15	8.40	1.70	0.90	7.35	580	3.41	Loam
R63	Great	8.30	8.00	7.80	7.37	9.60	9.52	600	3.95	Clay loam
R65	None	8.35	8.35	8.55	2.31	1.90	3.52	340	1.39	Fine sandy loam
R66	Great	8.35	8.35	8.50	4.50	3.65	3.67	530	1.68	Fine sandy loam
R67	None	7.70	7.80	7.70	0.01	0.05	0.22	675	2.80	Loam
R68	Great	7.70	7.90	7.90	1.50	1.10	2.02	1050	1.45	Fine sandy loam
R69	None	7.90	8.10	7.80	0.57	0.11	0.67	790	1.82	Loam
R70	Great	8.10	8.20	8.20	7.00	20.50	7.48	795	3.04	Loam
Mean		8.23±.018	8.25±.019	8.28±.020	4.98±.33	6.00±.45	8.70±.53	931±36.5	2.10±.065	

- “V. D.”—Very Deficient  
 “M. D.”—Moderately Deficient  
 “S. D.”—Slightly Deficient  
 “S.” —Sufficient or not deficient  
 “N. G.”—No Growth of Azotobacter colonies

Table 3.—Comparison of Winogradsky Method and K<sub>2</sub>CO<sub>3</sub> Method With Field Results.

Soil Number	Crop	Response to Super-phosphate	Winogradsky			p.p.m. Phosphorus in 1 Percent K <sub>2</sub> CO <sub>3</sub>		
			0-6"	6-12"	12-18"	0-6"	6-12"	12-18"
			30	Alfalfa	Great	M.D.	M.D.	M.D.
31	Alfalfa	Great	M.D.	M.D.	M.D.	42	38	35
32	Alfalfa	Great	V.D.	V.D.	V.D.	38	35	35
32A	Beets	Great	V.D.	V.D.	M.D.	51	45	38
33	Alfalfa	None	V.D.	M.D.	V.D.	65	45	42
33A	Alfalfa	Great	V.D.	V.D.	M.D.	38	35	42
34	Alfalfa	Great	V.D.	V.D.	V.D.	45	38	38
34A	Wheat	Great	V.D.	V.D.	V.D.	42	38	35
35	Alfalfa	None	V.D.	V.D.	V.D.	69	38	35
37	Alfalfa	None	V.D.	V.D.	M.D.	73	51	42
37A	Alfalfa	None	V.D.	V.D.	M.D.	69	61	45
38	Beets	Great	M.D.	V.D.	M.D.	51	35	27
54	Peppers	Great	M.D.	V.D.	N.G.	42	35	32
55	Alfalfa	None	V.D.	V.D.	V.D.	79	61	45
56	Alfalfa	None	S.D.	S.D.	S.D.	51	35	32
57	Alfalfa	None	S.D.	S.D.	S.D.	69	42	35
58	Alfalfa	None	N.G.	N.G.	N.G.	61	42	38
59	Alfalfa	None	M.D.	V.D.	V.D.	73	45	42
60	Alfalfa	None	S.D.	S.D.	S.D.	69	45	42
61	Beets	None	S.D.	M.D.	M.D.	79	45	61
62	Beets	None	S.D.	V.D.	V.D.	107	68	68
63	Alfalfa	None	V.D.	V.D.	S.D.	79	65	51
65	Alfalfa	Great	V.D.	V.D.	V.D.	45	35	35
66	Beets	Great	V.D.	V.D.	V.D.	38	32	27
70	Beets	None	V.D.	S.D.	S.D.	45	42	39
72	Alfalfa	Great	N.G.	M.D.	N.G.	35	27	23
74	Alfalfa	Great	N.G.	M.D.	M.D.	32	27	27
76	Alfalfa	Great	S.D.	V.D.	S.D.	42	27	35
77	Alfalfa	None	M.D.	V.D.	M.D.	69	42	42
78	Beets	Great	S.D.	S.D.	S.D.	35	35	35
82	Corn	None	V.D.	M.D.	V.D.	101	45	38
83	Beets	None	S.	S.	S.	180	144	61
85	Barley	None	V.D.	V.D.	M.D.	61	35	35
86	Beets	None	V.D.	V.D.	V.D.	45	35	35
87	Beets	None	S.	V.D.	V.D.	137	61	35
90	Beets	None	M.D.	M.D.	V.D.	113	98	86
94	Alfalfa	None	M.D.	V.D.	V.D.	98	61	38
95	Beets	None	V.D.	V.D.	V.D.	61	49	45
97	Potatoes	None	V.D.	V.D.	V.D.	61	61	61
99	Potatoes	None	S.D.	S.D.	M.D.	133	69	69
101	Barley	None	M.D.	M.D.	M.D.	137	101	90
102	Barley	None	S.D.	M.D.	M.D.	133	69	56
103	Potatoes	None	S.D.	S.	M.D.	90	73	69
107	Beets	None	M.D.	V.D.	S.D.	84	65	56
108	Beets	None	M.D.	V.D.	S.	96	56	45
110	Beets	None	S.D.	M.D.	S.D.	96	73	56

\*Insufficient sample.

Table 3.—(Continued)

Soil Number	Crop	Response to Super-phosphate	Winogradsky			p.p.m. Phosphorus in 1 Percent K <sub>2</sub> CO <sub>3</sub>		
			0-6"	6-12"	12-18"	0-6"	6-12"	12-18"
111	Beets	Great	M.D.	M.D.	*	42	35	35
117	Beets	None	M.D.	M.D.	M.D.	69	65	51
118	Beets	None	M.D.	M.D.	*	65	56	42
119	Tomatoes	Great	V.D.	V.D.	V.D.	65	51	35
120	Cabbage	None	M.D.	*	*	79	61	45
121	Beets	None	S.D.	N.G.	M.D.	107	61	56
122	Onions	None	M.D.	M.D.	M.D.	90	61	51
123	Tomatoes	None	M.D.	*	*	61	51	42
125	Tomatoes	None	N.G.	M.D.	V.D.	119	79	65
126	Peppers	None	S.	S.	S.	203	146	69
127	Corn	None	S.D.	S.D.	V.D.	84	51	42
128	Cucumbers	None	S.D.	N.G.	V.D.	84	73	56
129	Beets	None	S.D.	V.D.	V.D.	69	42	38
130	Beets	None	M.D.	M.D.	M.D.	69	51	45
131	Tomatoes	None	S.D.	S.D.	S.D.	101	69	45
132	Beets	None	V.D.	S.D.	S.D.	69	45	42
133	Beets	Slight	V.D.	M.D.	M.D.	56	42	35
134	Tomatoes	None	V.D.	*	*	69	45	38
135	Cantaloupe	None	M.D.	M.D.	V.D.	84	61	45
136	Beets	Slight	V.D.	M.D.	M.D.	61	50	42
137	Tomatoes	None	S.D.	S.D.	S.D.	90	56	42
138	Beets	None	S.D.	S.D.	M.D.	79	65	42
139	Beets	Slight	S.D.	S.	M.D.	56	45	42
141	Tomatoes	Slight	S.D.	V.D.	V.D.	65	45	45
142	Beets	None	S.D.	M.D.	M.D.	61	61	38
143	Tomatoes	None	S.D.	M.D.	M.D.	90	73	45
144	Beets	None	S.D.	M.D.	M.D.	56	73	65
145	Beets	None	V.D.	V.D.	V.D.	100	65	79
147	Beets	None	S.D.	M.D.	M.D.	59	99	90
149	Beets	None	M.D.	M.D.	V.D.	56	79	61
151	Beets	None	M.D.	*	V.D.	90	79	61
154	Beets	None	V.D.	V.D.	V.D.	99	79	47
R51	Alfalfa	Slight	V.D.	*	*	61	56	42
R53	Alfalfa	None	V.D.	V.D.	V.D.	42	32	27
R54	Alfalfa	None	S.	V.D.	M.D.	56	32	27
R56	Alfalfa	None	S.D.	S.D.	S.D.	61	50	35
R58	Alfalfa	None	M.D.	V.D.	M.D.	61	42	50
R59	Alfalfa	None	M.D.	V.D.	M.D.	42	35	35
R60	Beets	None	S.D.	V.D.	N.G.	45	32	32
R62	Alfalfa	None	S.D.	M.D.	M.D.	69	45	45
R63	Alfalfa	Great	M.D.	V.D.	M.D.	42	35	32
R65	Alfalfa	None	S.D.	S.D.	M.D.	35	37	35
R66	Beets	Great	S.D.	S.D.	M.D.	42	32	27
R67	Beets	None	S.	S.D.	M.D.	98	69	65
R68	Barley	Great	V.D.	V.D.	V.D.	42	35	35
R69	Beets	None	M.D.	V.D.	V.D.	98	69	42
R70	Beets	Great	M.D.	*	*	56	32	27

\*Insufficient sample.

The data presented in Table 3 are summarized in Table 4. The fields which gave a slight response as well as those which gave a great response are included in the deficient group in Table 4. In calculating the reliability of the Winogradsky method, three methods of interpretation were used. In the first method of interpretation the

Table 4.—Summary of Data Showing Reliability of Winogradsky and  $K_2CO_3$  Methods.

	Group of Soils Sufficient in Available Phosphor- us by Field Trial			Group of Soils Deficient in Available Phosphor- us by Field Trial		
	0-6"	6-12"	12-18"	0-6"	6-12"	12-18"
Percentage of agreement between field trial and the Winogradsky method according to the first method of interpretation in which the soils which tested S. were considered sufficient and the soils which tested V.D., M.D., and S.D. were considered deficient.....	7.7	5.0	5.0	100.0	95.7	100.0
Percentage of agreement between field trial and the Winogradsky method according to the second method of interpretation in which the soils which tested S. and S.D. were considered sufficient and the soils which tested V.D. and M.D. were considered deficient	44.6	25.0	22.5	79.1	87.5	90.5
Percentage of agreement between field trial and the Winogradsky method according to the third method of interpretation in which the soils which tested S., S.D., and M.D. were considered sufficient and the soils which tested V.D. were considered deficient....	72.7	58.0	62.3	50.0	58.3	38.1
Percentage of agreement between field trial and the $K_2CO_3$ Method.....	90.0	86.6	71.6	73.1	73.1	80.8

soils which fell in the S. class were considered to contain sufficient available phosphorus, while the soils which tested S. D., M. D. and V. D. were considered to be lacking in available phosphorus and should respond to an application of superphosphate in the field. It is noted, however, that only 7.7 percent of the soils which were sufficient by field trial were sufficient by the Winogradsky method. It is apparent that this method of interpretation indicates many soils to be deficient in available phosphorus which do not respond to applications of superphosphate in the field.

Since most of the soils were shown to be deficient in available phosphorus by this method of interpretation, it is obvious that there should be a close agreement between field trial and the Winogradsky method for soils which are actually deficient in available phosphorus. The data in Tables 3 and 4 show this to be true.

With the hope of securing a better agreement between the Winogradsky method and field trial, the data were recalculated. When the samples which tested S. D. are placed in the S. class the agreement with field results was 44.6 percent for the sufficient group but the agreement in the deficient group dropped from 100 percent to 79.1

percent. Even when this second method of interpretation was used, there still remained a very low agreement with field trial for soils which do not respond to superphosphate in the field. To further improve the agreement in this group, the data were again recalculated by placing the soils which tested M. D. in the same class with S. D. and S. This method of calculation increased the agreement for this group from 44.6 percent to 72.7 percent but lowered the agreement in the deficient group from 79.1 percent to 50.0 percent.

Of the 67 surface 6-inch samples which were secured from high-producing fields which gave no response to superphosphate, and were therefore sufficient by field trial, the Winogradsky method indicated:

- 25.6 percent to be very deficient
- 28.3 percent to be moderately deficient
- 35.8 percent to be slightly deficient
- 7.5 percent to be sufficient, and
- 3.0 percent gave no development of azotobacter

colonies, even after inoculation. In calculating the data in Table 4, the samples of soil which gave no growth of azotobacter colonies were not considered in expressing the percentage of agreement. If this had been done, the percentage of agreement with field results would have been lower.

Of the 21 soils which were from fields which gave a great response to superphosphate in the field and were therefore deficient in available phosphorus, the Winogradsky method indicated:

- 42.9 percent to be very deficient
- 33.3 percent to be moderately deficient
- 14.3 percent to be slightly deficient
- 0.0 percent to be sufficient, and
- 9.5 percent gave no growth of azotobacter colonies.

In expressing the reliability of the  $K_2CO_3$  method in Table 4, the soils which showed more than 55 p.p.m. of phosphorus in the 1 percent  $K_2CO_3$  solution were considered to contain sufficient available phosphorus for the 0 to 6-inch samples. The dividing line between sufficient and deficient soils for the 6 to 12-inch and 12 to 18-inch depths was set at 40 p.p.m. The agreement between the  $K_2CO_3$  method and field trial was 90 percent for soils in the sufficient group while for soils in the deficient group, it was only 73.1 percent reliable. It should be noted, however, that there are some fields which gave only a slight response in the field. If the samples from these fields were excluded, the agreement would be 90.5 percent.

The comparison of the Winogradsky and  $K_2CO_3$  methods shows that the  $K_2CO_3$  method gave a more accurate indication of the phosphate needs of the soil than the Winogradsky test. It must be em-

phasized, however, that the  $K_2CO_3$  method is not a completely reliable test and must therefore be supplemented with field trials. This is especially true for the samples which show approximately 55 p.p.m. of phosphorus in the surface 6-inch samples. One should not expect a soil with 54 p.p.m. of phosphorus to be deficient and a soil with 56 p.p.m. to be sufficient. Thus, there are samples in this doubtful range in which the  $K_2CO_3$  method should not be wholly relied upon in making phosphate fertilizer recommendations.

Table 5.—Comparison of the Truog Method and the Dahlberg-and-Brown Sodium Acetate Method with Field Trials.

Soil No.	Response	pH	Lime Percentage	Soluble Salts p.p.m.	Dahlberg & Brown Method p.p.m. P	Truog Method	
						p.p.m. P	pH
30	Great	7.80	5.85	580	1.20	40.0	7.20**
31	Great	8.10	7.03	660	1.20	40.0	6.70
32	Great	8.25	7.97	1200	1.85	48.0	7.30
32A	Great	8.35	5.10	1300	2.70	80.0	7.85
33	None	8.20	5.57	840	2.00	108.0	6.90
33A	Great	7.79	5.50	880	*	*	*
34	Great	8.40	5.50	*	*	*	*
34A	Great	8.00	7.26	500	1.20	74.0	6.80
35	None	8.10	2.37	580	2.90	180.0	5.20
37	None	7.90	3.77	*	1.85	80.0	6.80
37A	None	8.40	4.34	500	2.50	68.0	6.90
38	Great	7.60	2.58	*	3.75	90.0	6.30
54	Great	8.10	1.57	650	3.75	122.0	7.50
55	None	8.20	7.38	2000	2.50	80.0	7.20
56	None	8.25	7.57	900	3.05	122.0	7.40
57	None	8.30	7.00	960	2.70	80.0	7.40
58	None	8.05	1.20	630	1.70	122.0	4.20
59	None	8.50	11.10	440	2.00	80.0	7.30
60	None	8.40	5.72	970	1.70	116.0	7.75
61	None	7.70	0.40	1100	1.70	130.0	3.50
62	None	7.70	0.36	865	2.50	100.0	3.40
63	None	8.20	10.75	830	3.75	74.0	7.20
65	Great	7.85	6.00	4800	1.40	68.0	7.00
66	Great	8.25	4.75	475	1.00	74.0	6.70
70	None	8.30	11.65	455	2.50	40.0	7.40
72	Great	8.30	13.75	455	1.20	74.0	7.40
74	Great	8.30	17.20	410	0.65	40.0	7.50
76	Great	8.20	25.28	385	1.20	26.0	7.40
77	None	8.10	4.20	585	3.25	48.0	7.10
78	Great	8.10	0.97	*	1.40	56.0	5.90
82	None	8.30	2.07	550	3.25	80.0	5.40
83	None	8.30	0.50	535	7.50	150.0	3.70
85	None	7.85	2.90	500	2.00	116.0	3.40
86	None	8.30	4.60	500	2.50	130.0	6.65
87	None	8.20	*	865	*	*	*
90	None	8.30	0.86	*	7.50	320.0	4.20
94	None	8.25	0.75	830	3.25	80.0	4.10
95	None	8.30	6.07	875	*	*	*
97	None	8.60	0.45	550	5.80	324.0	3.40

\*Insufficient sample.

\*\*The pH of the final extract



Table 5.—(Continued)

Soil No.	Response	pH	Lime Per-centage	Soluble Salts p.p.m.	Dahlberg & Brown Method p.p.m. P	Truog Method	
						p.p.m. P	pH
99	None	8.40	0.30	345	8.50	108.0	3.50
101	None	8.70	0.30	335	10.00	225.0	3.50
102	None	8.30	0.90	3300	8.00	232.0	3.40
103	None	8.25	0.20	430	8.50	232.0	3.25
107	None	8.15	0.37	1650	3.40	130.0	3.25
108	None	8.30	1.80	1650	5.00	160.0	4.60
110	None	8.20	0.55	660	4.00	272.0	3.70
111	Great	8.30	2.80	700	2.50	170.0	4.20
117	None	8.10	0.40	1750	3.70	160.0	3.50
118	None	8.00	4.50	965	3.70	160.0	4.70
119	Great	8.30	1.75	1500	2.80	116.0	4.15
120	None	8.35	2.37	505	2.40	108.0	4.70
121	None	8.30	8.25	1400	3.50	80.0	7.20
122	None	8.60	5.50	1700	3.25	160.0	7.30
123	None	8.40	0.80	1000	1.70	170.0	6.75
125	None	8.30	0.57	400	5.40	232.0	3.70
126	None	8.40	3.25	700	6.50	244.0	3.70
127	None	8.15	7.30	1950	7.40	108.0	7.10
128	None	8.25	3.65	1235	2.00	160.0	6.70
129	None	8.45	1.70	595	4.00	130.0	4.50
130	None	8.45	5.60	700	1.30	170.0	6.90
131	None	8.60	7.75	825	5.40	150.0	7.35
132	None	8.40	3.52	1160	4.00	244.0	6.40
133	Slight	8.30	4.10	1165	1.40	150.0	6.40
134	None	8.50	3.88	810	3.75	122.0	6.70
135	None	8.40	5.20	800	2.90	160.0	6.90
136	Slight	8.40	8.90	1650	1.40	116.0	7.20
137	None	8.40	5.70	925	2.50	108.0	6.90
138	None	8.50	21.95	1400	2.00	68.0	7.45
139	Slight	8.60	7.10	1070	2.50	100.0	7.15
141	Slight	8.45	2.46	725	1.85	74.0	6.55
142	None	8.60	5.70	750	3.40	130.0	7.10
143	None	8.50	2.50	875	1.40	130.0	6.65
144	None	8.40	9.10	825	2.80	100.0	7.20
145	None	8.70	11.90	1110	2.00	80.0	7.45
147	None	8.45	12.07	1400	2.90	100.0	7.45
149	None	8.40	12.07	1300	3.50	90.0	7.45
151	None	8.50	11.70	1300	2.50	80.0	7.30
154	None	8.35	12.10	1450	2.20	130.0	7.50
R51	Slight	7.40	0.30	410	*	130.0	3.70
R53	None	7.60	1.00	700	4.65	130.0	3.50
R54	None	7.85	0.60	435	3.25	130.0	3.50
R56	None	8.30	1.70	300	3.75	130.0	3.80
R58	None	8.50	3.87	530	1.75	150.0	5.90
R59	None	8.50	7.75	600	1.40	68.0	7.10
R60	None	7.60	0.15	535	2.00	100.0	3.70
R62	None	8.15	1.70	580	6.10	100.0	3.90
R63	Great	8.30	7.37	600	1.00	90.0	6.95
R65	None	8.35	2.31	340	1.85	108.0	5.40
R66	Great	8.35	4.50	530	3.25	74.0	6.70
R67	None	7.70	0.01	675	4.00	160.0	3.60
R68	Great	7.70	1.50	1950	4.00	100.0	3.80
R69	None	7.90	0.57	790	2.80	80.0	3.35
R70	Great	8.10	7.00	795	1.60	80.0	6.65
Mean		8.23±.018	4.98±.33	931±36.5			

\*Insufficient sample.

COMPARISON OF THE TRUOG METHOD AND THE  
DAHLBERG-AND-BROWN SODIUM ACETATE  
METHOD WITH FIELD TRIALS

The data in Table 5 show the agreement of the Truog method and Dahlberg-and-Brown method with field trials. In expressing the reliability of the Dahlberg-and-Brown method, if the soils which contain less than 2 p.p.m. of phosphorus are considered deficient, the agreement with field results is 65.2 percent for the deficient group and 84.6 percent for the sufficient group. With the Truog method, if the dividing line between deficient and sufficient soils is placed at 95 p.p.m. of phosphorus the agreement with field trials is 66.6 percent for the deficient group and 73.9 percent for the sufficient group. The soils which gave a slight response in the field as well as those which gave a great response were considered deficient in the above calculations. If the fields which gave a slight response are excluded from the deficient group, the agreement for the Dahlberg-and-Brown method is 63.2 percent instead of 65.2 percent and 78.9 percent instead of 66.6 percent for the Truog method.

The last column in Table 5 gives the pH of the 1:200 soil:solution extract by the Truog method. While the pH of the original 0.002 normal  $H_2SO_4$  solution is 3.0, it is noted that the final extracts vary considerably. Undoubtedly, this varying degree of acidity affects the amount of phosphorus which is brought into solution. The pH value of the final extract appears to be influenced by the  $CaCO_3$  and soluble salt content of the soil. When the soil contains a large amount of lime the pH value of the final soil extract is usually alkaline and thus the amount of phosphorus brought into solution is less than it would have been if the final extract had been acid.

TENTATIVE PROCEDURE FOR THE POTASSIUM  
CARBONATE METHOD

A representative soil sample is passed thru a 1 mm. sieve. Two grams of this sample are weighed and placed in a 250 cc. Erlenmeyer flask. To the flask 150 cc. of solution A are added. It is then placed on the hot plate in which the temperature is so regulated that approximately 45 minutes are required to bring the temperature of the solution to a simmer, and it is allowed to simmer for 15 minutes. It is advisable to cover the flasks during digestion to prevent appreciable reduction in volume by evaporation. At the end of the hour the flask is removed from the hot plate and allowed to cool. It may then stand 12 to 24 hours in order to settle or if the determination is desired immediately, 50 cc. may be placed in a centrifuge tube and centrifuged. In either case after the extract has been obtained, 10 cc. are drawn off into a 25 cc. graduated test tube. One cc. of a sat-

urated solution of bromine water is added and allowed to stand approximately 1 hour. A longer time may be necessary for dark-colored extracts. At the end of this time, 0.4 cc. of 5 N HCl and 1 cc. of a 10 percent  $\text{Na}_2\text{SO}_3$  solution are added. After the test tube has been shaken vigorously, 2 drops of phenolphthalein are added and sufficient 0.5 N NaOH is added to produce a red color. This is titrated with 0.5 N HCl or  $\text{H}_2\text{SO}_4$  until the color barely disappears. The solution is then made up to 15 cc. with distilled water and shaken. The phosphorus is now determined by modifications of the Deniges and Dirks-Sheffer methods.

#### COLORIMETRIC PHOSPHORUS DETERMINATIONS

After the acidity has been adjusted and the extract made up to 15 cc. the following method of colorimetrically determining the P present is used.

The Hellige Comparator (Standard Model) is used. Each number on the movable disc or dial is calibrated, by means of standard solutions, expressed in p.p.m. of P. Square 10 cc. graduated test tubes are furnished with the instrument. These test tubes should be marked so that they are placed in the comparator on the same side and facing the same way every time in order to avoid inaccurate results due to variation in the test tubes. The test tubes should be cleaned frequently with cleaning solution.

Ten cc. of the solution with acidity adjusted are placed in the square test tube and the other 5 cc. in the check tube on the left side of the comparator. Three drops of solution D are added to the 10 cc. and 1 drop to the 5 cc. Both are well shaken and the one with 5 cc. placed on the lefthand side of the colorimeter. To the other is added one drop of solution E. The tube is well shaken and read at the end of 30 seconds. This time is very important since the color changes rapidly. See Note 7.

#### SOLUTIONS NECESSARY

Solution A—1 percent by weight  $\text{K}_2\text{CO}_3$ —The resulting solution made to contain the  $\text{=O=}$  of 0.27 p.p.m. P. There is usually approximately this amount in C. P.  $\text{K}_2\text{CO}_3$  so before any P is added to the solution 10 cc. should be drawn off and the acidity adjusted with the same precautions as described in the procedure above and the phosphorus determined in the colorimeter.

Solution B—0.5 N  $\text{H}_2\text{SO}_4$  solution.

Solution C—0.5 N NaOH solution.

Solution D—Ammonium molybdate sulfuric acid solution. Dissolve 25 grams ammonium molybdate in 200 cc. water by heating to

60° C and filter. Dilute 280 cc. of arsenic and phosphorus-free concentrated sulfuric acid (approximately 36N) to 800 cc. When cool add the ammonium molybdate to the sulfuric acid with shaking and make up to 1000 cc.

Solution E—Stannous chloride solution. Dissolve 25 grams  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 cc. of concentrated HCl and make up to 1000 cc. with distilled water.

Solution F—Saturated bromine water.

Solution G—10 percent by weight  $\text{Na}_2\text{SO}_3$ .

Solution H—5 N HCl.

#### NOTES

1.—A wide variation of color was observed in the extracts of different soils after heating, but no correlation was found between this color and soluble phosphorus.

2.—It has been found in this laboratory that 24 samples may be run conveniently at one time, but a definite length of time must be used for the oxidation with bromine water and this same length of time should be used for all samples if comparable results are to be obtained.

3.—In order that some limit (p.p.m. P) may be set, above which all soils are sufficient and below which all soils are deficient, it is suggested that several soil samples be collected from fields in which the field response is known and a phosphorus determination made by the above method. A value in p.p.m. of phosphorus may then be chosen as a dividing line. It will be found that each investigator will obtain slightly different results but if a dividing line between good and poor soils is set in this way comparable results may be obtained.

4.—In standardizing each number on the dial of the colorimeter it may be found that each investigator will read them slightly different. The same square test tube should be used in the colorimeter in all determinations.

5.—From time to time the stannous chloride solution used in producing the blue color should be checked on a standard P solution.

6.—Too much emphasis cannot be given to the importance of adjusting the acidity of the solution on which the phosphorus is to be determined. If the solution is only very slightly alkaline, the results will run high while if acid they run low.

7.—If the solution upon which phosphorus is to be determined is slightly colored, due to a lack of complete oxidation of organic matter, the tube with which it is compared should be filled with the same solution (there will be 5 cc. left in the test tube). One drop of solution D should be added to insure no color in the standard tube due to phenolphthalein. Many times a milky-white ppt. will develop in the solution upon addition of the 1 drop of stannous chloride due to free tin being formed. In such cases one drop of  $\text{SnCl}_2$  should be added

to the check tube instead of the ammonium molybdate (solution D). The colors in the colorimeter should always be the same between the phosphorus-containing tube and the check, if comparable results are to be obtained between various soils. This may be done as suggested above, by adding one drop of  $\text{SnCl}_2$  solution or one drop ammonium molybdate, and in many cases the resulting color will be too dark and should be diluted with water until the same hue as the blue in the solution upon which phosphorus is being determined is obtained.

8.—It will be noted that solution A ( $\text{K}_2\text{CO}_3$ ), after adjusting its pH to phenolphthalein, gives a color equivalent to 0.27 p.p.m. phosphorus. Most C.P.  $\text{K}_2\text{CO}_3$  contains approximately this amount. However, this is a distinct advantage because many deficient soils will absorb some of this P and thus widen the difference between sufficient and deficient soils.

9.—The disc must be recalibrated frequently as has been shown by Chapman (2), (3), at the California Experiment Station.

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#### SUMMARY

Soil samples were obtained from 93 fields of known response to superphosphate in several of the irrigated valleys in Colorado. Twenty-one of these fields showed a marked response to the application of treble superphosphate. Five showed only a slight response and 67 showed no response.

A preliminary comparison was made of several of the proposed methods for determining available phosphorus in soils and a more detailed comparison was made of the Winogradsky, Dahlberg-and-Brown, Truog and  $\text{K}_2\text{CO}_3$  methods.

Of the 67 soils from fields which gave no response to superphosphate and were, therefore, considered to be sufficient in available

phosphorus, the Winogradsky method indicated:

- 25.4 percent to be very deficient,
- 28.3 percent to be moderately deficient,
- 35.8 percent to be slightly deficient,
- 7.5 percent to be sufficient, and
- 3.0 percent gave no visible growth of azotobacter colonies.

Of the 21 soils from fields which gave a great response in the field and were therefore deficient in available phosphorus, the Winogradsky method indicated:

- 42.9 percent to be very deficient,
- 33.3 percent to be moderately deficient,
- 14.3 percent to be slightly deficient,
- 0.0 percent to be sufficient, and
- 9.5 percent gave no visible growth of azotobacter colonies.

With the Truog method, the agreement with field trials for the "sufficient" soils was 73.9 percent while for the soils which gave a great response in the field, the agreement was 78.9 percent.

The Dahlberg-and-Brown method gave an agreement with the "sufficient" soils of 84.6 percent while for the soils which gave a great response, the agreement was 63.2 percent.

The  $K_2CO_3$  method gave an agreement with the "sufficient" soils of 90.0 percent while for the soils which gave a great response in the field, the agreement was 90.5 percent. If, however, the data are calculated in a different way and the soils which gave a slight response are included with those which gave a great response, the agreement for the deficient soils drops from 90.5 percent to 73.1 percent.

Data are presented showing the content of organic matter, calcium carbonate, soluble salts, the pH values and the textural grades for the soils used in this investigation.

Of the methods studied, the  $K_2CO_3$  method appears to give the highest agreement with field results.

It seems probable that no chemical method for estimating the availability of soil phosphorus can imitate exactly the power which plants have for securing available phosphorus. The data show, however, that there is a fairly close relationship between the amount of phosphorus soluble in certain solvents and the amount which is available to plants. An alkaline solvent appears to be more satisfactory for alkaline calcareous soils than an acid extractant.

The results of this investigation indicate that even tho a laboratory test shows the soil to be deficient in available phosphorus, a field trial should be strongly recommended before a large quantity of fertilizer is purchased.—A tentative procedure for the  $K_2CO_3$  method is given.

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