

**RESEARCH ON SHORTENING TIME WITHOUT AFFECTING  
THE ACCURACY OF DYER'S MODIFIED METHOD FOR  
THE DETERMINATION IN SOILS, OF PHOSPHORIC  
ACID, LIME AND POTASH SOLUBLE IN CITRIC  
ACID SOLUTION (1 PER CENT)**

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Since the soil survey of Puerto Rico started in 1928 under the joint cooperation of the U. S. Bureau of Chemistry and Soils and the P. R. Insular Experiment Station, the soil samples sent by the field staff have been analyzed for phosphoric acid, lime and potash soluble in 1 per cent citric acid solution. Before this research was undertaken as one of the projects of the new Soils Division officially created in June 1931, the method used was as follows:

**DYER'S MODIFIED METHOD (3)**

“Place 100 grams of the air dried soil sample in a Winchester acid bottle. Add 1 liter of a 1 per cent citric acid solution. Shake in a shaking machine 6 hours. Let stand overnight to clear. Filter off about 700 cc of the clear supernatant liquid through a double filter paper. Evaporate exactly 500 cc nearly to dryness in a 600 cc beaker on the hot plate, then transfer the resulting dark colored solution to a platinum dish (using hot water) and evaporate to dryness on a water bath. Completely dry the sticky residue (2 hours in a hot air oven at a temperature of about 120° C.).

“Ignite the residue in the platinum dish in a muffle at low temperature (dull redness) for about 2 hours to remove organic matter. The char should now be gray in color. Moist with con. HCl, add a little hot water and evaporate to dryness on the water bath. Leave on water bath at least 1 hour to dehydrate any silicic acid still remaining as such. Take up in a little con. HCl; add a little water; heat one-half hour on a water bath; add more hot water and filter. Wash five times with hot water slightly acidified with HCl; make up to at least 300 cc with hot water. To the clear filtrate add 2 or 3 cc of con. HNO<sub>3</sub> and boil 15 to 20 minutes to oxidize all organic matter in solution. Precipitate Fe, Al, Ti and P<sub>2</sub>O<sub>5</sub> with NH<sub>4</sub>OH in

hot solution, filter and wash free from chlorides with hot water. In case of insufficient Fe to color the solution slightly brown, add a few cc of a 10 per cent  $\text{FeCl}_3$  solution before precipitation. (This is to insure complete ppt. of  $\text{P}_2\text{O}_5$ .)

#### Phosphoric Acid, $\text{P}_2\text{O}_5$

“Dissolve the above ppt. in dil.  $\text{HNO}_3$  and boil. Cool slightly, *nearly* neutralize with  $\text{NH}_4\text{OH}$  add 5 grm.  $\text{NH}_4\text{NO}_3$  and ppt.  $\text{P}_2\text{O}_5$  with 25 cc molybdate sol. at  $65^\circ \text{C}$ . Let stand 20 min. at  $65^\circ$  then let cool. Filter through asbestos, thoroughly wash and det.  $\text{P}_2\text{O}_5$  volumetrically.

#### Lime, $\text{CaO}$

“Evaporate down to 150 cc the filtrate from Fe and Al, make very slightly alkaline with  $\text{NH}_4\text{OH}$  and ppt. Ca as oxalate with ammonium oxalate in hot solution. Let stand on the water bath 1 hour then cool over night. Filter, wash with cold water, dissolve in  $\text{H}_2\text{SO}_4$  (1 to 5 by vol.) and titrate with a standard  $\text{KMnO}_4$ .

#### Potash, $\text{K}_2\text{O}$

“Acidify filtrate from Ca slightly with dil.  $\text{H}_2\text{SO}_4$ . Evaporate to dryness in a beaker, transfer to platinum dish and run to dryness. Carefully ignite off excess of  $\text{H}_2\text{SO}_4$  and all ammonium salts over a free flame; take up residue with hot water, filter into porcelain evap. dish and add 2 or 3 drops of dil.  $\text{HCl}$  and sufficient platonic chloride sol. to ppt. all the potassium. Evaporate nearly to dryness, filter, wash and weigh as potassium platonic chloride in the usual gravimetric way.”

#### EXPERIMENTAL

The modified procedures introduced have been as follows:

Place 150 grams of the air dried soil sample in a Winchester acid bottle. Add 1500 cc of a 1 per cent citric acid solution. Shake in a shaking machine, 6 hours. Let stand overnight to clear. Filter.

#### Phosphoric Acid, $\text{P}_2\text{O}_5$

Measure in a beaker, 500 cc of the filtered citric acid extract. Add 10 cc  $\text{HNO}_3$  and 30 cc  $\text{HCl}$ . Evaporate in hot plate, nearly to dryness. Transfer to evaporating dish and dry residue carefully, in sand bath. Ignite the residue at low temperature to destroy the un-

decomposed organic matter and complete the dehydration and destruction of silicates. Dissolve in 5 cc  $\text{HNO}_3$  and 15 cc  $\text{HCl}$ , dilute with water and filter. Follow official molbydate volumetric method. (If a brown color due to manganese persists in the solution after neutralizing with  $\text{NH}_4\text{OH}$  and acidifying with  $\text{HNO}_3$ , heat to coagulate the colloidal suspension and filter.)

#### Lime, $\text{CaO}$

Measure in a beaker, 100 cc of the filtered citric acid extract. Determine lime by Chapman's (4) method as follows:

To the solution containing Ca, Mg, Mn, Fe, Al, Ti, and  $\text{P}_2\text{O}_5$  add about 6 grams of  $\text{NH}_4\text{Cl}$ . One gram of oxalic acid in solution, 10 cc of 1.76 normal acetic acid, and 10 drops of .04 per cent brom cresol green, are added. The solution is made to a volume of about 200 cc and brought nearly to boiling. Dilute ammonia is added slowly until a drop of the solution added to a drop of brom cresol green in a porcelain spot plate changes from yellow thru yellowish green to the first pure green (pH3.9-4.2). The solution is then boiled gently for five minutes, the calcium precipitating in a coarse crystalline state. The precipitate is then allowed to stand on a steam bath until it wholly subsides. Allow the solution to cool before filtration. Wash five times with cold water. Determine  $\text{CaO}$  by the official permanganate volumetric method.

#### Potash, $\text{K}_2\text{O}$

Evaporate 500 cc of the filtered extract nearly to dryness, on the hot plate. Transfer the resulting dark colored solution to a silica dish (using hot water) and carefully evaporate to dryness on a sand bath. Ignite the residue in a muffle to about  $1000^\circ \text{F}$ . (incipient red heat) for about 2 hours to remove organic matter. Add 15 cc  $\text{HCl}$ , add a little hot water and evaporate to dryness on the water bath. Take up in 5 cc of  $\text{HCl}$  and water, heat for 30 minutes on a water bath; add more hot water and filter. Wash three times with hot water and make up to about 200 cc. To the clear filtrate add 2 cc of  $\text{HNO}_3$  and boil 10 minutes to oxidize all organic matter in solution. In hot solution, precipitate Fe, Al, Ti and  $\text{P}_2\text{O}_5$  with  $\text{NH}_4\text{OH}$  adding also 25 cc of saturated ammonium oxalate solution to precipitate Ca and Mg. Filter and wash well with hot water. (In case of insufficient Fe to color the solution slightly brown, add a few cc of a 10 per cent  $\text{FeCl}_3$  solution before precipitation. This is to insure complete precipitation of  $\text{P}_2\text{O}_5$ .)

To filtrate add 2 cc  $H_2SO_4$  (1:1) and evaporate to dryness in sand bath. (It is convenient to add 5 cc of  $HNO_3$  before evaporating to dryness to avoid losses due to the creeping out of the salts.) Ignite to whiteness to expel ammonium salts. Extract with hot water and filter. Determine  $K_2O$  by the official Lindo-Cladding method.

#### ANALYTICAL RESULTS OF PERCENT $CaO$ BY CHAPMAN'S METHOD

Comparative values by Student's method of percent  $CaO$  as determined by Dyer's modified and Chapman's methods are expressed in table I. To eliminate personal error, all analyses by both methods were performed in the same extraction by the same chemist, F. A. Villamil. The letters A or B following a sample number represent duplicate extractions. The values in columns A and B represent percent  $CaO$  obtained respectively, by the Dyer modified method and by the Chapman method. The values of column (A-B) are obtained by subtracting the values of column B from those of A. The factor .9702 was obtained by dividing the total of column A by that of B. The values of column C are obtained by multiplying that factor by the values of column B. The values of column (A-C) are obtained by subtracting the values of column C from those of A. The values D and  $D^1$  represent mean deviations. The standard deviation of the mean of column (A-B) is obtained by the formula:

$$S. D. = \sqrt{\frac{SmD^2}{n(n-1)}}$$

where  $SmD^2$  is the sum of the values  $D^2$  and  $n$ , the number of observations. The standard deviation of the mean of column (A-C) is obtained by that same formula substituting  $Sm(D^1)^2$  for  $SmD^2$ .

The value  $Z$  represents the ratio of the mean of column (A-B) to the square root of the mean of the values  $D^2$ . The value ( $Z^1$ ) represents the ratio of the mean of column (A-C) to the square root of the mean of the values  $(D^1)^2$ . The statistical interpretation of the results was obtained with values  $Z$  and  $n$  in the Student's table modified by Love (9),  $n=91$  in this case.

TABLE I.

COMPARATIVE VALUES BY STUDENT'S METHOD OF PERCENT CaO AS DETERMINED BY DYER'S MODIFIED AND CHAPMAN'S METHODS.

No.	Dyer's A % CaO	Chapman's B % CaO	A-B	D (A-B+.014)	D <sup>2</sup>	C (.9702B)	A-C	D' (A-C-.0004)	(D') <sup>2</sup>
1	.266	.288	-.022	-.008	.000064	.279	-.013	-.0134	.00017956
2	.697	.781	-.084	-.020	.000400	.709	-.012	-.0124	.00015376
3	.241	.260	-.019	-.005	.000025	.252	-.011	-.0114	.00012996
4	.118	.126	-.008	-.006	.000036	.122	-.004	-.0044	.00001936
5	.084	.118	-.034	-.020	.000400	.114	-.030	-.0304	.00092416
6	.051	.064	-.013	-.001	.000001	.062	-.010	-.0114	.00012996
7	.518	.529	-.011	.003	.000009	.513	-.005	-.0046	.00002116
8	.065	.070	-.005	.009	.000081	.068	-.003	-.0034	.00001156
9	.081	.095	-.014	0	0	.092	-.011	-.0114	.00012996
10	.868	.958	-.090	-.076	.005776	.929	-.061	-.0614	.00376996
11	.110	.137	-.027	-.012	.000169	.133	-.023	-.0234	.00054756
12	.087	.098	-.011	.003	.000009	.095	-.008	-.0084	.00007056
13	.378	.403	-.025	-.011	.000121	.391	-.013	-.0134	.00017956
14	.079	.084	-.005	.009	.000081	.081	-.002	-.0024	.00000576
15	.171	.168	-.003	-.017	.000289	.163	-.008	-.0076	.00005776
16	.266	.314	-.048	-.034	.001156	.274	-.039	-.0394	.00155236
17	.952	.960	-.008	.005	.000025	.931	-.021	-.0206	.00042436
18	.554	.596	-.042	-.028	.000784	.578	-.024	-.0244	.00059536
19	.137	.151	-.014	0	0	.147	-.010	-.0104	.00010816
20	.129	.154	-.025	-.011	.000121	.149	-.020	-.0204	.00041616
21	.224	.238	-.014	0	0	.231	-.007	-.0074	.00005476
22	.756	.795	-.039	-.025	.000625	.771	-.015	-.0154	.00023716
23	.286	.305	-.019	-.005	.000025	.296	-.010	-.0104	.00010816
24	.244	.252	-.008	.006	.000036	.244	0	-.0004	.00000016
25	.594	.605	-.011	.003	.000009	.587	.007	.0066	.00004356
26	.532	.546	-.014	0	0	.530	.002	.0016	.00000256
27	.644	.650	-.006	.008	.000064	.631	-.013	-.0126	.00015876
28	.487	.504	-.017	.003	.000009	.489	.002	-.0024	.00000576
29	.616	.622	-.006	.008	.000064	.603	.013	.0126	.00015876
30	.305	.314	-.009	.005	.000025	.305	0	-.0004	.00000016
31A	.64	.067	-.063	.011	.000121	.065	-.001	-.0014	.00000196
31B	.064	.067	-.003	.011	.000121	.065	.001	-.0014	.00000196
32	.599	.602	-.003	.011	.000121	.584	.015	.0146	.00021316
33	.160	.165	-.005	.009	.000081	.160	0	-.0004	.00000016
34	.132	.134	-.002	.012	.000144	.130	.002	-.0016	.00000256
35	.269	.274	-.005	.009	.000081	.266	.003	-.0026	.00000676
36	1.310	1.330	-.020	-.006	.000036	1.290	.020	-.0196	.00038416
37	.089	.087	-.002	.016	.000256	.084	.005	-.0046	.00002116
38A	.692	.700	-.008	.006	.000036	.679	.013	.0126	.00015876
38B	.694	.703	-.009	.005	.000025	.682	.012	.0116	.00013456
39A	.694	.689	-.005	.025	.000625	.668	.031	.0306	.00093636
39B	.689	.686	-.003	.017	.000289	.666	.023	.0226	.00051076
40A	.644	.647	-.003	.011	.000121	.628	.016	.0156	.00024936
40B	.641	.652	-.011	.003	.000009	.633	.008	-.0076	.00005776
41A	.549	.554	-.005	.009	.000081	.537	.012	.0116	.00024356
41B	.548	.548	-.005	.009	.000081	.532	.011	-.0106	.00011236
42A	.196	.246	-.050	-.036	.001296	.239	-.043	-.0434	.00185956
42B	.196	.241	-.045	-.031	.000961	.234	-.038	-.0384	.00147456
43A	.440	.448	-.008	.006	.000036	.435	.005	-.0046	.00002116
43B	.428	.454	-.026	-.012	.000144	.440	-.012	-.0124	.00015376
44A	.336	.353	-.017	-.003	.000009	.342	-.006	-.0064	.00004096
44B	.353	.358	-.005	.009	.000081	.347	.006	.0056	.00003136
45A	2.128	2.134	-.006	.008	.000064	2.070	.058	.0576	.00317776
45B	2.122	2.139	-.017	-.003	.000009	2.075	.047	.0466	.00211556
46A	.428	.437	-.009	.005	.000025	.424	.004	.0036	.00001296
46B	.423	.426	-.003	.011	.000121	.413	.010	.0096	.00091216
47A	.235	.246	-.011	.003	.000009	.239	-.004	-.0044	.00001936
47B	.224	.235	-.011	.003	.000009	.228	-.004	-.0044	.00001936
48A	.333	.336	-.003	.011	.000121	.326	.007	.0066	.00004356
48B	.333	.336	-.003	.011	.000121	.323	.007	.0066	.00004356
49A	.126	.154	-.028	-.014	.000196	.149	-.023	-.0234	.00054756
49B	.157	.149	-.009	-.023	.00529	.144	.013	.0126	.00015876
50	.700	.706	-.006	.003	.000009	.685	.015	.0146	.00021316
51	.655	.700	-.045	-.031	.000961	.679	-.024	-.0244	.00059536
52	.865	.888	-.023	-.009	.000081	.862	.003	.0026	.00000676
53	.784	.792	-.008	.006	.000036	.768	.016	.0156	.00024336
54	1.123	1.212	-.089	-.075	.045625	1.176	-.053	-.0534	.00285156
55	.073	.064	.009	.023	.000529	.062	.011	.0106	.00011236
56	.081	.095	-.014	0	0	.092	-.011	-.0114	.00012996
57A	.591	.599	-.008	.006	.000036	.581	.010	.0096	.00091216
57B	.594	.602	-.008	.006	.000036	.584	.010	.0096	.00091216
58A	.406	.412	-.006	.008	.000064	.400	.006	.0056	.00003136
58B	.420	.428	-.008	.006	.000036	.415	.005	.0046	.00002116

TABLE I.

COMPARATIVE VALUES BY STUDENT'S METHOD OF PERCENT CaO AS DETERMINED BY DYER'S MODIFIED AND CHAPMAN'S METHODS—Continued.

No.	Dyer's A % CaO	Chapman's B % CaO	A - B	D (A-B+.014)	D <sup>2</sup>	C (.9702B)	A - C	D' (A-C-.0004)	(D') <sup>2</sup>
59A	.409	.412	-.003	.011	.000121	.400	.009	.0086	.0007396
59B	.406	.409	-.003	.011	.000121	.397	.009	.0086	.0007396
60A	.185	.193	-.008	.006	.000036	.187	-.002	-.0024	.0000576
60B	.179	.188	-.009	.005	.000025	.182	-.003	-.0034	.00001156
61A	.428	.431	-.003	.011	.000121	.418	.010	.0066	.00009216
61B	.428	.431	-.003	.011	.000121	.418	.010	.0086	.00009216
62A	.140	.140	0	0	0	.136	.004	.0036	.00001296
62B	.140	.137	.003	.017	.000289	.133	.007	.0066	.00004356
63A	2.078	2.168	-.090	-.016	.000256	2.045	.033	.0326	.00106276
63B	2.078	2.168	-.090	-.016	.000256	2.045	.033	.0326	.00106276
64A	.081	.104	-.023	-.009	.000081	.101	-.020	-.0204	.00041616
64B	.092	.109	-.017	-.003	.000009	.106	-.014	-.0144	.00020736
65	.107	.118	-.011	.003	.000009	.114	-.007	-.0074	.00005476
66	.192	.184	.008	.012	.000144	.180	.002	.0016	.00000326
67	.196	.202	-.006	.008	.000064	.196	0	.0004	.0000016
68	.362	.370	-.008	.006	.000036	.359	.003	.0026	.00000676
69	.070	.070	0	0	0	.068	.002	.0016	.00000256
70	.118	.118	0	0	0	.114	.004	.0036	.00001296
Sum.	40.752	42.005	-1.253		.025531	40.748	.004		.00007736
Mean	.448	.462	-.014		.00028		.0004		.00034

$$Z = \frac{.014}{\sqrt{.00028}} = .82$$

Odds over 9999:1

$$Z' = \frac{.0004}{\sqrt{.00034}} = .022$$

Odds below 2:1

When both methods are statistically compared,  $Z = .82$  and the odds from the table (9) are found to be over 9999:1. The odds indicate a real difference in the analytical results between the two methods; since according to the table odds over 21:1 indicate a significant difference in the results.

The evidence suggests that Chapman's method tends to give higher results with a mean deviation of .014 per cent  $\pm$  .0017 per cent in 91 determinations or values that may fluctuate between .0123 per cent and .0157 per cent. For comparison purposes the results obtained by either method may be considered entirely satisfactory. That either is as good as the other is corroborated by the excellent checks obtained by each method in the duplicate of different extractions for samples 31, 38-49 inclusive, and 57-64 inclusive. The statistical interpretation, therefore, does not invalidate at all, Chapman's method.

Chances for personal analytical error are much less in the Chapman method since the work is greatly facilitated by the elimination of the cumbersome procedure required for the precipitation of Al, Ti, and  $P_2O_5$  with  $NH_4OH$  in the Dyer modified method. The former method saves about 66 per cent of the time required by the latter.

Were it necessary to convert results obtained by Chapman's

method to those in terms of the Dyer modified method, it would be proper to multiply by the factor .9702. The value  $Z^2$ , after the application of such a factor to each result obtained by Chapman's method becomes .022, and the odds from the table are found to be below 2:1. The odds indicate that there is no significant difference between the analytical results of both methods. Results indicate that the increase by Chapman's method tends to be constant. The mean deviation becomes now, .0004 per cent  $\pm$  .0017 per cent or a fluctuation between —.0013 per cent and .0021 per cent which is extremely low.

#### COLORIMETRIC METHODS FOR PHOSPHORIC ACID

Studies were made of the molybdate blue method with the modifications of Briggs and Doisy applied by Arrhenius (1) to citric acid extracts. The method is as follows:

"Ten cc of the citric acid extract are placed in a 100 cc volumetric flask and diluted to about 80 cc; 1 cc conc.  $H_2SO_4$ , 5 cc ammonium molybdate (25 gms. ammonium molybdate dissolved in 300 cc. water) and then 200 cc dilute sulphuric acid (75 cc conc.  $H_2SO_4$  filled up to 200 cc with water), 1 cc sodium sulphite (20 g.  $Na_2SO_3$  + 80 cc water), and 1 cc hydroquinone (0.5 g. per 100 cc and one drop conc. sulphuric acid), are added. The flask is filled to the mark and the solution shaken. The color is, after 12 to 24 hours, compared with a standard series of solutions with known  $P_2O_5$  content varying between .05 and .90 mgm.  $P_2O_5$  per 100 cc." The so-called Arrhenius molybdate blue method for  $P_2O_5$  determinations in citric acid extract is based on the one recommended by Bell-Doisy-Briggs (2) for  $P_2O_5$  determinations in urine and blood, with the exception that the addition of trichloroacetic acid for the precipitation of protein material is eliminated.

Although Arrhenius claims that results obtained are accurate below 0.50 mgm.  $P_2O_5$  (.05 per cent  $P_2O_5$  in the 10 cc citric acid aliquot used by us), our results were entirely inconsistent. The citrate ion colored by the presence of iron salts causes difficulty in matching the colors of the unknown and the standard in the colorimeter.

Studies were made of the method that Warren and Pugh (11) worked out at the Rothamsted Experimental Station based on the colorimetric determination of phosphoric acid in citric acid extractions of soils as follows:

"Seventy-five cc of the citric acid extract are pipetted into a 300 cc Kjeldahl flask, 10 cc conc. HCl added and followed by 12 cc of 20 per cent sodium permanganate. The sides of the flask are washed



down with a little water. After standing half an hour the contents are vigorously digested till no manganese precipitate remains (about  $\frac{1}{2}$  hr. more). The contents are transferred with a minimum amount of water to a 100 cc graduated flask; 4 cc of 10 per cent potassium ferrocyanide are added slowly, drop by drop, with frequent shaking. Several minutes later the mixture is titrated with 1:1 ammonia until the blue color just turns purple; 1.5 cc 2N sulphuric acid are then added and made to the mark with water. After the solution has been filtered and the first few cc discarded, the color is developed in an aliquot by one of the following methods:

Fiske—Subbarow (6) "10 to 50 cc are pipetted into a 100 cc graduated flask, diluted to 75 cc approximately, 10 cc of ammonium molybdate added, then 4 cc aminonaphthol sulphonic acid solution and the liquid made to the mark. The flask should be shaken during each addition. The contents are finally poured into a 100 cc conical flask; 15 minutes later the test compared with a standard phosphate solution".

Deniges (5)—"1 to 25 cc are pipetted into a 100 cc graduated flask, diluted to 90 cc, and 1 cc ammonium molybdate and three drops of stannous chloride solution added, the flask being shaken with each addition. After diluting to the mark the contents are poured into a 100 cc conical flask, and compared after 5 minutes with a standard phosphate solution".

Our results with the Warren and Pugh method were extremely low compared with those obtained by the usual Dyer method. This may be due to the adsorption of phosphates by the manganese ferrocyanide precipitate. Ward (10) states that "the ferrocyanide precipitate is difficult to filter, because of its colloidal condition and that the amount of phosphorous present in the sodium permanganate is of the same order of magnitude as that in the sample, and inaccurate results are certain to follow in the case of soils low in  $P_2O_5$ ".

Lonstein (8) applied the method of Deniges, so widely used for water extracts, to citric acid extracts of a number of South African soils and obtained good agreement with the gravimetric method. His method briefly consists in evaporating a small volume of the citric acid extract to dryness after the addition of calcium acetate solution. The residue is ignited to destroy the organic matter and to render the silica insoluble, and then extracted with 10 per cent sulphuric acid. After filtration the excess of the acid is neutralized with ammonia and the color developed with ammonium molybdate and stannous chloride solutions.

Although we were favorably impressed by the Lonstein method we disregarded it because the figures obtained with it by Warren and Pugh (11) "reveal the presence of some disturbing factor in the analyses of the heavier soils used, especially when the Deniges method



of color production was used. The blue color developed slowly and had a green tint. The view was sustained that the sulphuric acid extracts from the clay soils contained appreciable amounts of ferric iron as the interfering constituents”.

One of the latest contributions to the subject on the colorimetric determination of phosphorus in citric acid extracts of soils is the work of Ward (10), chemist of the Experiment Station of the Hawaiian Sugar Planters' Association. Ward's procedure for the preparation of the citric acid extract is as follows: "To 100 ml. of citric acid extract, add 50 ml. of concentrated nitric acid, 15 ml. of concentrated hydrochloric acid, and 10 ml. of 20 per cent sulfuric acid free from phosphorus and arsenic. Evaporate slowly till fumes of  $\text{SO}_3$  are evolved. Take up in hot water and boil". The iron is removed by electro dialysis into a special electrolytic cell. The color is developed by the method of Zinzadze as follows: "Aliquots from the solutions of citric acid extract prepared for analysis are neutralized to the yellow end point of alpha—dinitrophenol indicator with 10 per cent ammonia solution. Dilute the solutions to 90 ml., add 1.4 ml. of molybdenum blue reagent (molybdic acid reduced by molybdenum metal in sulphuric acid solution), heat for 30 minutes on the steam bath, cool, and make up to exactly 100 ml. Employ a sensitive colorimeter for comparison with the standard solution”.

The work of different investigators reveal that the accurate colorimetric determinations of phosphoric acid in soils extracted with 1 per cent citric acid, demands attention on the destruction of the citrate ion, and of the soluble silicates and organic matter; the absence of large amounts of silica; the absence of phosphorous in the chemical reagents used; the elimination of the ferric ion; and a controlled acidity. Ward (10) calls the attention to the presence of titanium and to the use of colorimetric standards which are very close to the unknown in color intensity so as to reduce errors due to deviations from Beer's (12) law.

#### TREATMENTS OF THE CITRIC ACID EXTRACTS FOR THE PHOSPHORIC ACID DETERMINATIONS

In view of the several difficulties that we encountered in obtaining accurate results with the application of colorimetric methods for the determinations of phosphoric acid in soils extracted with 1 per cent citric acid we proceeded to study the simplification of the chemical treatments given to such extracts in the Dyer modified method and then followed the official molybdate volumetric method for phosphoric acid.

Our first attempt was to precipitate directly phosphoric acid as ammonium phosphomolybdate in aliquots of the citric acid extracts. In some cases, good checks were obtained with the results by the Dyer modified method. In other cases, no precipitate was obtained; and in other cases, lower results were obtained. This may be explained on the basis that citric acid, extracts from certain soils, phosphates in organic combinations that are not precipitated by ammonium molybdate, and that the presence of the undecomposed soluble silicates may hold by absorption the phosphate ions in solution.

Our second attempt was to destroy the organic and silicate compounds by evaporation almost to dryness, with aqua regia. The residue was taken with a few cc of aqua regia, diluted with water, and filtered. Phosphoric acid was determined in the filtrate by the official molybdate volumetric method. Although our results checked much better with those obtained by the Dyer modified method we were unable to obtain the ammonium phosphomolybdate precipitate in several of the treated extracts. It seems that the aqua regia treatment was not drastic enough, in some cases, to decompose some of the silicates that would tend to establish a competition for the adsorption of the phosphate ions in solution.

Our next procedure was then to evaporate the citric acid extracts to dryness with aqua regia and ignite the residue at low temperature to destroy the undecomposed organic matter and complete the dehydration and destruction of silicates. This treatment served as a basis for our recommended procedure (see pp. 288-289). Analytical results are expressed in Table II.

#### ANALYTICAL RESULTS OF PERCENT $P_2O_5$ BY OUR SHORT PROCEDURE

All analyses by both methods were performed in the same extraction. The letters A and B following a sample number represent duplicate extractions. All the analyses by Dyer's modified method and by our short procedure in samples 18, 20 and 23-27 inclusive, were made by the same chemist, F. A. Villamil. All other analyses by our short procedure were made by the senior author. The values in columns A and B represent percent  $P_2O_5$  obtained respectively by the Dyer modified method and by our short procedure. The values of column A-B are obtained by subtracting the values of column B from those of A. The values D represent the mean deviations. The number of determinations  $n=45$ . The value Z represents the ratio of the mean of columns (A-B) to the square root of the mean of the values  $D^2$ . The statistical interpretation of the results were obtained with values Z and n in the Student's table modified by Love (9).

TABLE II.

COMPARATIVE VALUES BY STUDENT'S METHOD OF PERCENT P<sub>2</sub>O<sub>5</sub> AS DETERMINED BY THE DYER MODIFIED METHOD AND OUR SHORT PROCEDURE

No.	Dyer's A % P <sub>2</sub> O <sub>5</sub>	Short Procedure B % P <sub>2</sub> O <sub>5</sub>	A-B	D (A-B-.0003)	D <sup>2</sup>
1A	.014	.016	-.002	-.0023	.0000529
1B	.014	.015	-.001	.0013	.0000169
2A	.010	.009	.001	.0007	.0000049
2B	.010	.009	.001	.0007	.0000049
3A	.003	.003	0	-.0003	.0000009
3B	.002	.003	0	-.0003	.0000009
4A	.007	.007	0	-.0003	.0000009
4B	.007	.007	0	-.0003	.0000009
5A	.013	.011	.002	.0017	.0000289
5B	.013	.010	.003	.0027	.0000729
6A	.005	.005	0	-.0003	.0000009
6B	.004	.005	-.002	-.0023	.0000529
7A	.002	.004	-.002	-.0023	.0000529
7B	.002	.005	-.003	-.0033	.0001089
8A	.017	.017	0	-.0003	.0000009
8B	.015	.017	-.002	-.0023	.0000529
9A	.006	.008	-.002	-.0023	.0000529
9B	.007	.006	.001	.0007	.0000049
10	.018	.017	.001	.0007	.0000049
11A	.036	.039	-.003	-.0033	.0001089
11B	.036	.039	-.003	-.0033	.0001089
12A	.146	.148	-.002	-.0023	.0000529
12B	.145	.155	-.010	-.0103	.00010609
13A	.023	.015	.008	.0077	.00005929
13B	.023	.014	.009	.0087	.00017569
14A	.013	.013	0	-.0003	.0000009
14B	.013	.013	0	-.0003	.0000009
15A	.019	.016	.003	.0027	.0000729
15B	.019	.016	.003	.0027	.0000729
16A	.023	.025	-.002	-.0023	.0000529
16B	.023	.025	-.002	-.0023	.0000529
17	.003	.002	.001	.0007	.0000049
18	.023	.020	.003	.0027	.0000729
19A	.052	.054	-.002	-.0023	.0000529
19B	.051	.053	-.002	-.0023	.0000529
20	.033	.038	-.005	-.0053	.0002809
21A	0.9	.013	.006	.0057	.0003249
21B	.018	.013	.005	.0047	.0002209
22A	.005	.004	.001	.0007	.0000049
22B	.006	.004	.002	.0017	.0000289
23	.004	.001	.003	.0027	.0000729
24	.006	.005	.001	.0007	.0000049
25	.007	.005	.002	.0017	.0000289
26	.002	.001	.001	.0007	.0000049
27	.004	.002	.002	.0017	.0000289
Sum	.924	.908	.016		.00047045
Mean	.0205	.0202	.0003		.0000105

$$Z = \frac{.0003}{\sqrt{.0000105}} = .09$$

Odds: Below 3:1

When both methods are statistically compared, Z = .09 and the odds from the table (9) are found to be below 3:1. The odds indicate that there is no significant difference between the analytical results obtained by both methods.

That either method is as good as the other is corroborated by the excellent checks of the duplicates in different extractions.

Chances for personal analytical error are much less in the short

procedure since the work is greatly facilitated by the elimination of the cumbersome procedure required for precipitation of Fe, Al, Ti and  $P_2O_5$  with  $NH_4OH$  in the Dyer modified method. The former method saves about 30 per cent of the time required by the latter.

### POTASH

Several modifications for the Dyer modified method were tried. Our results were unsatisfactory. We recommend the Dyer modified method with the following modification: Precipitate the lime together with the iron and phosphoric acid. (See pp. 289-290).

Through the courtesy of Dr. W. W. G. Moir, agricultural technologist of the American Factors, Limited, Hawaii, and L. E. Davis, associate chemist of the Experiment Station of the Hawaiian Sugar Planters' Association, we obtained a reprint of Gow's (7) work on a rapid colorimetric method for the determination of potash. "This method consists essentially of precipitating potassium chloroplatinate by means of its insolubility in alcohol, dissolving the precipitate in water and developing a color by the addition of stannous chloride. The intensity of the yellow color thus produced is directly proportional to the amount of platinum present in the precipitate and hence to the amount of potash present."

### SUMMARY

Research was undertaken with the purpose of shortening time without affecting accuracy of the Dyer modified method for the determination in soils, of phosphoric acid, lime and potash soluble in 1 per cent citric acid solution.

A short method is recommended for the lime determination based on the Chapman's method (4) for the precipitation of calcium oxalate in acid solutions (pH 3.9-4.2) in the presence of iron, aluminum, titanium, manganese, magnesium and phosphates. A short method is recommended for the phosphoric acid determination. Results are analyzed statistically by Student's method. Several of the colorimetric methods recommended for the phosphoric acid determination are also discussed.

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