anhydride. Then a considerable amount of water is formed from sulfuric acid decomposition and oxidation of organic substances (*4*).

The acid sludge (Table II) of 29.29 per cent free sulfuric acid content showed after heating with xylene 28 per cent water, with almost complete decomposition of sulfuric acid, as is indicated by 0.136 per cent of sulfuric acid left after heating. Otherwise if the same sludge is previously neutralized by mixing 100 grams of dry anhydrous sodium carbonate with 25 grams of acid sludge, only 7.2 per cent of water is obtained after distillation with xylene—i. e., the water included by the acid and arising from acid neutralization.

For lack of a method of water determination in acid sludge, the water content was not taken into consideration in the present determinations, but further work is to be done in this connection.

In working out a method of sludge analysis as complete as possible, the authors neglected also the small amounts of sulfurous anhydride.

A difficulty in the described method involves the removal of the final traces of amyl alcohol owing to the instability of sulfonic acids, which gives higher results for sulfonic acids.

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Determination of Protein Nitrogen

Accelerating the Kjeldahl-Gunning-Arnold Digestion by Addition of Phosphates

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ALTHOUGH the official (*1*) Kjeldahl-Gunning-Arnold method for protein nitrogen gives good results, it requires a long digestion period, especially if the source of heat is not entirely adequate. Various rapid methods of digestion have been reported.

Mears and Hussey (*13*) and Bimmerman and Frank (*2*) used perchloric acid to accelerate the Kjeldahl digestion. Kleeman (*9*) and Heuss (*8*) found that 25 ml. of 30 per cent hydrogen peroxide added to 1-gram samples of plant or animal material before addition of sulfuric acid shortened the digestion period.

Sborowsky and Sborowsky (*22*) and Richards (*19*) reported more rapid digestion of carbonaceous matter by substitution of mercurous iodide for mercuric oxide. Hassig (*7*) found no acceleration by the use of mercurous iodide and reported that its use is disadvantageous because of the sublimation of iodine on the neck of the flask. Parri (*16*) obtained more rapid clearing of the solution when a mixture of vanadium pentoxide and cupric oxide was used than when either of these catalysts was used alone. Lepper (*12*) used 5 grams of copper sulfate, 15 grams of potassium sulfate, and 20 ml. of sulfuric acid. He reported clearing of the solution for 1-gram sample of feeding stuff in 15 minutes and complete digestion in 45 minutes.

Lauro (*11*) substituted selenium oxychloride for mercury and obtained digestion of 1-gram samples of cereals in 12 to 55 minutes. Sandstedt (*21*) and Rich (*18*) also reported rapid digestion and satisfactory results using selenium or its compounds as catalyst. Messman (*14*) obtained digestion in 20 minutes, using mercury and selenium together as catalysts on a 550-watt electric heater. Osborn and Krasnitz (*15*) found no more rapid digestion using selenium as a catalyst than when using mercury but advise a combination of selenium with either mercury or copper; later they advised the combined use of selenium and mercury. They analyzed a wide variety of materials for nitrogen and obtained a 25 per cent saving of time over the use of mercuric oxide alone. Davis and Wise (*3*), after a survey of cereal laboratories, concluded that selenium as a Kjeldahl catalyst does not appear to be as universally adaptable to general laboratory conditions as does mercury, and its use in combination with common catalysts, especially mercury, is to be discouraged. Snider and Coleman (*24*) found that selenium, as a Kjeldahl catalyst, gave low results, caused undue frothing, and produced obnoxious odors. Clearing of the solution took place rapidly, but this was no indication of complete digestion.

Harrel and Lanning (*6*) found that, for a given heat source, the time required for complete digestion can be varied by changing the ratio of sodium sulfate to acid. Low protein results, they believe, can be explained by failure to use sufficient sodium sulfate.

Pickel (*17*) obtained digestion of miscellaneous materials by the Kjeldahl-Gunning-Arnold method in 30 minutes using the full flame of a Bunsen burner. Shedd (*23*) stated that complete digestion by the Kjeldahl-Gunning-Arnold method may be obtained in 20 minutes over a grid burner, provided mercury, not copper, is used as the catalyst.

Robinson and Schellenberger (*20*) added a gram of potassium persulfate to their microdigest to complete the digestion of cereal products in a short time. Folin and Wright (*4*) used a mixture of phosphoric and sulfuric acids with mercury and ferric chloride as catalysts in the digestion of urine. Kuehl and Gottschalk (*10*) used 15 ml. of a mixture of 100 grams of phosphorus pentoxide to 200 grams of sulfuric acid to digest 1 gram of feed in 15 to 17 minutes. Potassium sulfate and mercury were added to hasten the reaction. Guillemet and Schell (*5*) used 4 ml. of sulfuric acid and 10 drops of glacial phosphoric acid for the microdetermination of protein in cereal products. In the following work potassium phosphate or equivalent reagents are substituted in part for sodium sulfate in the Kjeldahl-Gunning-Arnold digestion.

Experimental

Samples of mixed feed, wheat products, pasture grasses, poultry feces, dried blood, fish meal, soy-bean meal, and dried skim milk were digested in duplicate by phosphate modifications of the Kjeldahl-Gunning-Arnold method and at the same time duplicate determinations were made by the official (*1*) Kjeldahl-Gunning-Arnold method. Blank determinations for the two methods were the same. Distillations were made on an electric still equipped with block tin condensers. The standard acid and alkali used were 0.1142 *N*. One milliliter of the standard acid is equivalent to 1 per cent of protein

(factor 6.25) when a 1-gram sample is used. Milliliters of acid multiplied by 0.16 give per cent of nitrogen.

REPLACING SODIUM SULFATE COMPLETELY BY POTASSIUM PHOSPHATE. Two grams of mixed feed were placed in a 500-ml. Kjeldahl flask and 12 grams of dipotassium phosphate trihydrate or 10 grams of the anhydrous salt, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. The salts were well mixed with the feed, 25 ml. of concentrated sulfuric acid were then added, and the flask was well shaken. Heating and charring occurred. The flask was placed over the full flame of a Bunsen burner. Vigorous digestion took place immediately, almost filling the flask with froth, but this seldom reached the neck of the flask. Clearing took place in about 20 minutes and digestion was continued for another 20 minutes.

Analyses are reported in Table I. Clearing time was decreased appreciably by use of the phosphate, but low results were obtained on replacing sodium sulfate completely by 10 grams of potassium phosphate when compared with the official (*1*) method.

TABLE I. PROTEIN DETERMINATIONS ON MIXED FEEDS

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with K_2HPO_4 and H_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.28	0.15	−0.12
483	20.98	0.05	20.83	0.05	−0.15
484	22.76	0.18	22.45	0.10	−0.31
485	21.47	0.10	21.22	0.12	−0.25
486	19.98	0.15	19.84	0.07	−0.14
487	20.87	0.10	20.72	0.04	−0.15
488	14.50	0.20	14.27	0.00	−0.23
489	20.45	0.22	20.41	0.02	−0.03
490	17.44	0.15	17.28	0.15	−0.16
491	21.87	0.10	21.58	0.12	−0.29
492	33.46	0.20	33.40	0.00	−0.06
493	20.00	0.30	19.74	0.07	−0.26
494	22.40	0.05	22.15	0.00	−0.25
495	21.79	0.02	21.26	0.12	−0.53
496	18.19	0.02	18.08	0.05	−0.11
497	19.16	0.12	19.00	0.10	−0.16
498	15.68	0.05	15.49	0.13	−0.09
499	22.08	0.05	21.97	0.00	−0.11
500	19.13	0.05	19.00	0.10	−0.13
501	15.05	0.20	14.62	0.10	−0.43
502	19.38	0.05	19.20	0.30	−0.18
503	17.76	0.02	17.53	0.15	−0.23

[a] HgO and $CuSO_4$ catalysts.

ADDING POTASSIUM PERSULFATE TO CLEARED DIGEST. In another series of analyses, samples of mixed feeds were digested by the mixture just described. Clearing occurred in from 15 to 25 minutes. One gram of potassium persulfate was then added and, after bringing the solutions to boiling, the heating was discontinued. The data are reported in Table II. The results are still slightly lower than those obtained by the official method and also lower than those obtained by rapid methods using potassium phosphate together with 6 grams of sodium sulfate which are later described. While clearing took place rapidly with potassium phosphate, these results seem to substantiate the findings of Snider and Coleman (*24*) with selenium that digestion is not necessarily complete when the solution becomes clear.

TABLE II. PROTEIN DETERMINATION ON MIXED FEEDS

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with K_2HPO_4 and H_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
508	21.75	0.00	21.45	0.10	−0.30
509	19.90	0.00	19.60	0.10	−0.30
510	20.54	0.13	20.38	0.15	−0.16
511	20.03	0.05	19.80	0.00	−0.23
512	18.40	0.00	18.13	0.05	−0.27
513	20.38	0.01	20.15	0.20	−0.23

[a] $CuSO_4$ and HgO used as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

COMBINING POTASSIUM PHOSPHATE AND SODIUM SULFATE. Since 1 gram of potassium persulfate added to the potassium phosphate apparently did not complete the digestion, 6 grams of anhydrous sodium sulfate were added to the above to bring about more complete digestion. Although the gas supply available for this work was barely sufficient to keep the digest boiling, clearing took place on 2-gram samples in 15 to 20 minutes over Bunsen flames. One gram of potassium persulfate was then added and the boiling was continued 5 minutes more. All digestions were terminated in less than 30 minutes. The results on mixed feeds, pasture grass, and poultry feces are given in Tables III, IV, and V. They agree closely with analyses by the official Kjeldahl-Gunning-Arnold method.

A further modification of this method was also used which included the substitution of phosphorus pentoxide plus potassium hydroxide for the potassium phosphate. Phosphorus pentoxide equivalent to 10 grams of anhydrous dipotassium phosphate was added to the sample with the sulfuric acid and potassium hydroxide was then added. Two-gram samples were placed in 500-ml. Kjeldahl flasks and 6 grams of anhydrous sodium sulfate, 0.7 gram of mercuric oxide, and 0.3 gram of copper sulfate were added. Twenty-five milliliters of the sulfuric acid–phosphoric anhydride mixture, containing 16 grams of phosphorus pentoxide per 100 ml. of sulfuric acid, were added and then mixed with the sample. About 4 grams of stick potassium hydroxide were added and the flask was swirled. After the initial vigorous action ceased the flask was placed over the burner. Vigorous digestion began immediately. Using the gas flames available, clearing took place in 15 to 20 minutes and the flask was removed after 25 minutes. These results are presented in the second part of Table III.

TABLE III. PROTEIN DETERMINATIONS ON MIXED FEEDS

Sample No.	Digested with Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
482	19.40	0.05	19.43	0.15	+0.03
483	19.98	0.05	21.03	0.05	+0.05
488	14.50	0.20	14.40	0.10	−0.10
508	21.75	0.00	21.60	0.00	−0.15
509	19.90	0.00	19.80	0.04	−0.10
510	20.54	0.13	20.45	0.06	−0.08
511	20.03	0.05	20.09	0.18	+0.06
512	18.40	0.00	18.39	0.13	−0.01
513	20.38	0.01	20.30	0.20	−0.08
514	19.20	0.10	18.92	0.05	−0.28
515	16.45	0.00	16.40	0.20	−0.05
516	15.75	0.00	15.72	0.05	−0.03
517	22.85	0.10	22.82	0.10	−0.03
518	19.94	0.17	20.00	0.10	+0.06
519	21.50	0.10	21.22	0.00	−0.28
520	22.73	0.25	22.73	0.05	0.00
521	18.70	0.00	18.51	0.08	−0.19
522	15.50	0.00	15.35	0.10	−0.15
523	24.00	0.10	23.90	0.00	−0.10
400	19.11	0.07	18.96	0.06	−0.15
402	16.13	0.10	16.32	0.02	+0.19
408	19.84	0.20	19.98	0.10	+0.14
410	16.38	0.08	16.21	0.11	−0.17
414	18.44	0.14	18.34	0.02	−0.10
424	16.58	0.05	16.53	0.06	−0.05
445	18.43	0.14	18.43	0.04	0.00
381	16.47	0.06	16.45	0.06	−0.02
373	15.19	0.08	15.22	0.03	+0.03
41	16.30	0.13	16.24	0.12	−0.06
23	16.44	0.05	16.39	0.05	−0.05
42	18.36	0.03	18.28	0.15	−0.08
68	17.98	0.15	17.76	0.07	−0.22
58	15.87	0.02	15.72	0.05	−0.15
46	16.31	0.01	16.16	0.01	−0.15
			Digested with H_2SO_4, P_2O_5, Na_2SO_4, HgO, $CuSO_4$, and KOH		
485	21.47	0.10	21.44	0.13	−0.03
486	19.97	0.15	19.90	0.00	−0.07
487	20.87	0.10	20.95	0.10	+0.08
488	14.50	0.20	14.40	0.15	−0.10
489	20.45	0.22	20.54	0.07	+0.09
490	17.43	0.15	17.27	0.00	−0.16
491	21.87	0.10	21.73	0.10	−0.14
494[b]	22.40	0.05	22.19	0.17	−0.21
495[b]	21.79	0.02	21.50	0.05	−0.29
496[b]	18.19	0.02	18.15	0.00	−0.04
497[b]	19.16	0.12	19.09	0.17	−0.07
498[b]	15.68	0.05	15.66	0.12	−0.02
499[b]	22.08	0.05	21.96	0.12	−0.12
500	19.13	0.05	19.13	0.05	0.00
501	15.05	0.20	14.80	0.10	−0.25
502	19.38	0.05	19.06	0.22	−0.32

[a] HgO and $CuSO_4$ as catalysts. 1 gram of $K_2S_2O_8$ added after clearing.
[b] No $K_2S_2O_8$ was added to these digestions.

TABLE IV. NITROGEN DETERMINATION ON POULTRY FECES

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
50	3.92	0.03	3.88	0.02	−0.03
51	3.99	0.02	4.02	0.00	+0.03
52	3.78	0.06	3.79	0.03	+0.01
53	3.81	0.04	3.81	0.05	0.00
54	3.66	0.00	3.69	0.00	+0.03
55	3.77	0.02	3.74	0.02	−0.03
56	3.94	0.00	3.90	0.01	−0.04
57	4.08	0.01	4.05	0.02	−0.03
58	3.87	0.01	3.83	0.01	−0.04
59	4.03	0.01	4.01	0.01	−0.02
60	4.42	0.04	4.36	0.01	−0.06
61	4.06	0.04	4.04	0.02	−0.02

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

TABLE V. PROTEIN DETERMINATIONS ON PASTURE GRASS

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, K_2HPO_4, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
B	27.00	0.00	26.95	0.20	−0.05
C	26.50	0.20	26.43	0.25	−0.07
D	25.18	0.05	25.35	0.20	+0.17
E	22.85	0.10	22.70	0.00	−0.15
F	21.50	0.00	21.53	0.25	+0.03
G	23.18	0.15	23.00	0.20	−0.18
H	20.17	0.03	20.15	0.00	−0.02
M	30.54	0.01	30.38	0.04	−0.16
O	29.03	0.02	28.84	0.08	−0.19
P	29.31	0.07	29.25	0.10	−0.06

[a] HgO and $CuSO_4$ catalysts. 1 gram of $K_2S_2O_8$ added after clearing.

TABLE VI. PROTEIN DETERMINATION ON WHEAT PRODUCTS

Sample No.	Digested by Kjeldahl-Gunning-Arnold Method	Difference between duplicates	Digested with H_2SO_4, P_2O_5, KOH, and Na_2SO_4[a]	Difference between duplicates	Difference between Methods
	%	%	%	%	%
30	15.32	0.00	15.21	0.02	−0.11
31	14.68	0.05	14.49	0.08	−0.19
32	14.88	0.05	14.89	0.02	+0.01
34	14.55	0.04	14.46	0.11	−0.09
35	14.09	0.02	14.00	0.07	−0.09
39	13.65	0.06	13.65	0.00	0.00
41	16.75	0.00	16.86	0.14	+0.11
42	10.15	0.00	10.21	0.08	+0.06
43	11.25	0.00	11.33	0.05	+0.08
44	13.33	0.05	13.15	0.00	−0.18
36	13.30	0.00	13.33[b]	0.00	+0.03
37	11.81	0.09	11.82[b]	0.03	+0.01
38	13.20	0.10	13.23[b]	0.05	+0.03
40	14.78	0.13	14.75[b]	0.10	−0.03
45	18.23	0.05	18.25[b]	0.00	+0.02
46	11.88	0.05	11.88[b]	0.00	0.00
25	13.10	0.10	12.93[c]	0.07	−0.17
26	12.41	0.08	12.31[c]	0.10	−0.06
27	13.45	0.08	13.43[c]	0.20	−0.02
28	15.56	0.01	15.48[c]	0.05	−0.08
29	14.27	0.17	14.12[c]	0.02	−0.15
33	13.60	0.10	13.61[c]	0.11	+0.01

[a] HgO, $CuSO_4$, and $Fe_2(SO_4)_3$ used as catalysts.
[b] K_2HPO_4 used in digestion instead of P_2O_5 and KOH.
[c] Digested in 9 minutes on glimmer heater.

Attempts were made to substitute sodium phosphate, phosphoric acid plus potassium sulfate, or phosphorus pentoxide without potassium hydroxide, in place of dipotassium phosphate. The clearing time for any such substitution was longer than where dipotassium phosphate was used. The addition of larger quantities of the potassium phosphate caused vigorous frothing, while smaller quantities resulted in slower digestion.

Another modification following Folin and Wright's (*4*) suggestion included the addition of iron to the mixture of sodium sulfate, mercuric oxide, copper sulfate, potassium hydroxide, and sulfuric acid–phosphorus pentoxide mixture. The results of the addition of iron in the form of ferric sulfate to this digestion mixture previously described, when used in the analysis of wheat, flour, and bran, are given in Table VI.

A 700-watt hot plate was used to determine the effect of more intense heat. When the flasks were placed on the preheated hot plate, clearing occurred in 4 to 5 minutes and the digestion was completed in about 9 minutes, as indicated in Table VI. The results agree well with those by the official method.

The method is also applicable to high-protein samples.

An acid mixture was made by adding 16 grams of anhydrous phosphorus pentoxide per 100 ml. of sulfuric acid in a Kjeldahl flask, cooling, and adding 16 grams of potassium hydroxide with cooling. Fifteen to twenty milliliters of this mixture were added to the sample in a Kjeldahl flask together with 6 grams of sodium sulfate and 0.7 gram of mercuric oxide. Over grid burners clearing occurred in 5 to 8 minutes and digestion was terminated at 15 minutes. Over Bunsen burners clearing occurred in 25 minutes and digestion was terminated after 45 minutes and 90 minutes to determine the effect of longer boiling. At the same time, samples were digested by the Kjeldahl-Gunning-Arnold method for 120 minutes. Results are given in Table VII.

TABLE VII. PROTEIN DETERMINATION ON HIGH-PROTEIN MATERIALS

Substance Analyzed	Weight of Sample	Digested with Na_2SO_4 and H_2SO_4[a]: 15 minutes Grid burner	45 minutes Bunsen burner	90 minutes Bunsen burner	Kjeldahl-Gunning-Arnold Digestion: 120 Minutes Bunsen Burner
	Grams	%	%	%	%
Meat scrap	1.0	59.93	59.55	59.95	60.00
Herring meal	0.8	68.71	69.18	69.03	69.11
Mixed feed	1.0	48.23	47.75	47.90	48.00
Meat meal	0.8	56.88	56.82	57.12	56.71
Dried blood	0.8	63.20	62.40	61.94	63.19
Meat meal and bone	0.8	58.50	58.37	58.25	58.80
Herring meal	0.7	72.96	72.83	73.00	72.94
Herring meal	0.7	73.13	73.28	73.11	73.28
Soy-bean meal	1.0	47.65	47.50	47.50	47.15
Dried skim milk	1.5	36.23	36.05	36.02	36.08

[a] 6 grams of Na_2SO_4 and 20 ml. of H_2SO_4 containing 3.5 grams of P_2O_5 and 3.5 grams of KOH-HgO catalyst.

The results obtained by the rapid digestion of high-protein materials, wherein potassium phosphate is substituted in part for sodium sulfate, agree well with the longer Kjeldahl-Gunning-Arnold method. Satisfactory results were also obtained when using Bunsen flames, although a somewhat longer digestion period was required.

Discussion

The substitution of dipotassium phosphate for part of the sodium sulfate in the Kjeldahl-Gunning-Arnold protein digestion shortened the required digestion time. Using Bunsen flames total digestion time for low-protein materials was reduced to 25 minutes or less. Trials made with a 700-watt plate indicated that digestion time may be reduced to 10 minutes or less. With high-protein samples digestion was completed in 15 minutes with a grid burner. The results of analysis of mixed feeds, wheat products, pasture grasses, and poultry feces, as well as difficultly digestible high-protein material, agreed well with results obtained by the official method. The mixture served a double purpose by shortening the digestion period and at the same time furnishing a solution, the vapors from which condensed and washed the sides of the flask. The charred material carried to the top of the flask and into the bottom of the neck by rapid heating on the hot plate was washed down rapidly by condensing vapors, thus obviating the necessity of swirling the flask during digestion. The solution cooled much more without solidifying than digests using sodium sulfate.

Similar results were obtained with a sulfuric acid solution to which 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. were added. When 15 to 25 ml. of this solution were added to samples, together with 0.7 gram of mercuric oxide and 6 grams of sodium sulfate, rapid digestion occurred and good results were obtained.

Low results were obtained when the sodium sulfate was completely replaced by 10 grams of potassium phosphate. The addition of iron to the catalysts and the use of potassium persulfate to complete the digestion were not shown to be necessary.

The use of phosphate partially to replace sulfate will, of course, slightly increase the cost of reagents used in the protein determination. The saving in gas or electricity during the shorter digestion period should, however, more than offset the increase in reagent cost. If anhydrous dipotassium phosphate is used, a mixture of 64 per cent dipotassium phosphate and 36 per cent sodium or potassium sulfate may be prepared and added to the sample from a dipper. When the phosphorus pentoxide–potassium hydroxide modified digestion is employed, a sulfuric acid solution containing 16 grams of phosphorus pentoxide and 16 grams of potassium hydroxide per 100 ml. may be prepared. The digestion mixtures in either case should be added to the sample not more than a few minutes before placing the flasks on the heaters.

Summary

Ten grams of anhydrous dipotassium phosphate or 12 grams of dipotassium phosphate trihydrate, or an equivalent quantity of phosphorus pentoxide plus potassium hydroxide, were substituted for ten-sixteenths of the sodium or potassium sulfate used in the digestion of samples for protein nitrogen determinations.

Two-gram samples of feeds and wheat products were digested in 25 minutes or less over the Bunsen flames available and in 9 minutes on a preheated 700-watt electric plate. Samples of dried blood, fish meal, soy-bean meal, and dried skim milk were digested in 15 minutes over grid burners. The results obtained compared well with analysis by the official Kjeldahl-Gunning-Arnold method.

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Determination of Manganese and Magnesium in Soils and Silicate Rocks

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THE methods of rock, mineral, and soil analysis commonly suggested by Hillebrand and Lundell (*4*) and the Association of Official Agricultural Chemists (*1*) require that manganese be determined on a separate portion of the sample, because of incompleteness of separation of manganese by precipitation with bromine, persulfate, and ammonium sulfide. Furthermore, because of this incompleteness of separation, Hillebrand and Lundell recommend that the magnesium, when determined, be corrected for contaminating manganese. Thus, if both manganese and magnesium are to be determined, it requires that two fusions and two determinations of manganese be made.

Since manganese may be quantitatively precipitated as manganese ammonium phosphate, and since it generally exists in soils and silicate rocks in much smaller quantities than magnesium, it appeared possible to develop a method in which the manganese and magnesium are precipitated and weighed or titrated together as the phosphate, after which the manganese is determined colorimetrically or volumetrically and the amount of magnesium obtained by difference.

Precipitation and Titration of Manganese Ammonium Phosphate

The first step in this investigation was to determine whether manganese could be completely precipitated under the same conditions as magnesium and ultimately titrated by the method developed by Handy (*3*).

Measured portions of standardized 0.05 *N* potassium permanganate were mixed with 100 cc. of 0.5 *N* hydrochloric acid and a few drops of a 1 per cent solution of oxalic acid added to bring about complete reduction. The solution was neutralized with ammonia, and 20 cc. of a 10 per cent solution of sodium ammonium hydrogen phosphate were added, followed by 10 cc. more of concentrated ammonia. The solution was then boiled and allowed to cool at room temperature overnight. After filtration, the precipitate and paper were washed with 0.5 *N* ammonium hydroxide. The filter with precipitate were removed and allowed to dry at room temperature until ammonia-free—that is, until ammonia fumes could no longer be detected with bromocresol purple test paper. The filter paper containing the precipitate was then placed in a 250-cc. flask, 50 cc. of carbon dioxide–free distilled water and an excess of standard sulfuric acid were added, the flask was shaken until the paper was pulped, and the solution back-titrated to pH 4.5, using bromocresol green as an indicator. [J. A. Chucka (unpublished data) found that bromocresol green is superior for this purpose to the indicator used by Handy.] The filter paper pulp was then filtered off and the manganese determined volumetrically, using the bismuthate method of Park (*5*). The results of this test are given in Table I.

These data indicate that manganese may be quantitatively precipitated as manganese ammonium phosphate, and this in turn titrated according to the method of Handy (*3*).