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A FLAME PHOTOMETRIC METHOD FOR POTASH IN FERTILIZERS

ION EXCHANGE SEPARATION OF INTERFERING ANIONS

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INTRODUCTION

The use of the flame photometer offers a rapid and inexpensive method for the determination of the potassium content of fertilizers. For this reason several studies have been made on the applicability of flame photometric methods. Schall and Hagelberg (9) adapted to the flame determination the official gravimetric procedure for the preparation of the potash solution of the Association of Official Agricultural Chemists (A.O.A.C.), and also reported on the interference of magnesium, sodium, and other ions. In a later paper Schall (8) reported on the potassium analysis of twelve years' Magruder Check samples by flame photometry. It was found that phosphate and oxalate ions increased the apparent potassium content. Interference from these anions was compensated for by the addition of each to the standard solutions. Nitrate, chloride, and hydroxide ions had no detectable effect in the presence of oxalate. Blackwell *et al.*, (1) prepared the potassium solution, and lowered the concentration of interfering ions, by the addition of barium hydroxide and boiling to precipitate the sulfate; at the same time dicalcium and dibarium phosphates were precipitated. Crooks (2) studied the flame photometric determination of potassium and made studies on instrument calibration, optimum oxygen and fuel pressures, and concentrations of solutions. West *et al.*, (11) investigated the application of flame spectrophotometry to water analysis. They found that calcium and sodium enhanced the intensity of the potassium line.

Since fertilizers are mixtures of a number of different substances which may affect the emission intensity of the potassium line, it was considered that the simplest approach to obviate interference effects would be to clean up the sample solution. The purpose of this paper is to describe a procedure which has been used successfully in the Missouri Agricultural Experiment Station Laboratories. Basic ammonium carbonate is used to remove the cations (calcium, magnesium, and others) and an anion exchange resin is used to remove interfering sulfate and phosphate anions.

REAGENTS AND APPARATUS

Ammonium carbonate, analytical reagent, 1.5 molar solution.

Methyl red indicator, 0.2 gram of the indicator per 100 ml. of 95% alcohol.

Standard solutions of potassium chloride, reagent grade, from 10 to 100 p.p.m. of potassium in steps of 5 p.p.m. The standard solutions were prepared by weighing the calculated amount of the dried salt, dissolving it in double distilled water and making to volume. The standards of low concentration were prepared by volumetric dilution of a stock solution containing 100 p.p.m. of potassium.

Amberlite IR-4B-C1, an anion exchange resin with a high capacity for phosphate was used. (The Rohm and Haas Company, Philadelphia, Pennsylvania.) The resin was regenerated by the batch process to the chloride form by first exhausting it with three separate portions of 5% sodium carbonate or sodium hydroxide and washing until all excess base was removed. The resin was then treated with 3 separate portions of 5% hydrochloric acid with stirring. Finally the resin was washed with distilled water until there was no further color throw.

A Beckman Model-B flame spectrophotometer with a red sensitive phototube was used. The slit width was held at 0.15 mm., the sensitivity set at 4, and the wave length used was 768 m μ . An oxygen-acetylene flame was used with an oxygen pressure of 15 lbs./in.² and an acetylene pressure of 2 lbs./in.² To obtain increased sensitivity the 500 Megohm resistor was replaced with a 10,000 Megohm resistor. Meter fluctuations were nearly eliminated simply by placing a 40 mfd. capacitor across the terminals of the meter.

ANALYTICAL PROCEDURE

Preparation of the Sample

Weigh a 1.5 gram sample of the fertilizer into a 250 ml. pyrex volumetric flask. Add approximately 100 ml. of water and 15 ml. of 1.5 molar ammonium carbonate. Bring the solution to a boil, and boil for 5 minutes. Remove from heat, add 10 ml. of 1:1 ammonium hydroxide and allow to cool. Dilute to the mark, mix and filter. If there is less than 30% potash in the fertilizer place a 25 ml. aliquot, and if greater than 30%, a 20 ml. aliquot in a 300 ml. Erlenmeyer flask. Add 2 drops of methyl red indicator and adjust to a pH of approximately 5 with hydrochloric acid, shaking to allow the excess carbon dioxide to escape. Add sufficient Amberlite IR-4B-C1 to ensure adequate contact with the solution; 7 to 10 ml. of the wet resin is sufficient. Shake continuously for 5 minutes or intermittently for 15 minutes and filter directly into a volumetric flask. Use Whatman No. 1 or 4 or any other high speed strong filter paper. Wash the resin thoroughly at least three times with distilled water and add the washings to the original solution in the volumetric flask. Use a 250 ml. volumetric for fertilizers of potash content up to 13%, a 500 ml. flask to 40%, and a 1000 ml. flask for potash content above 40%. Dilute to the mark and mix thoroughly.

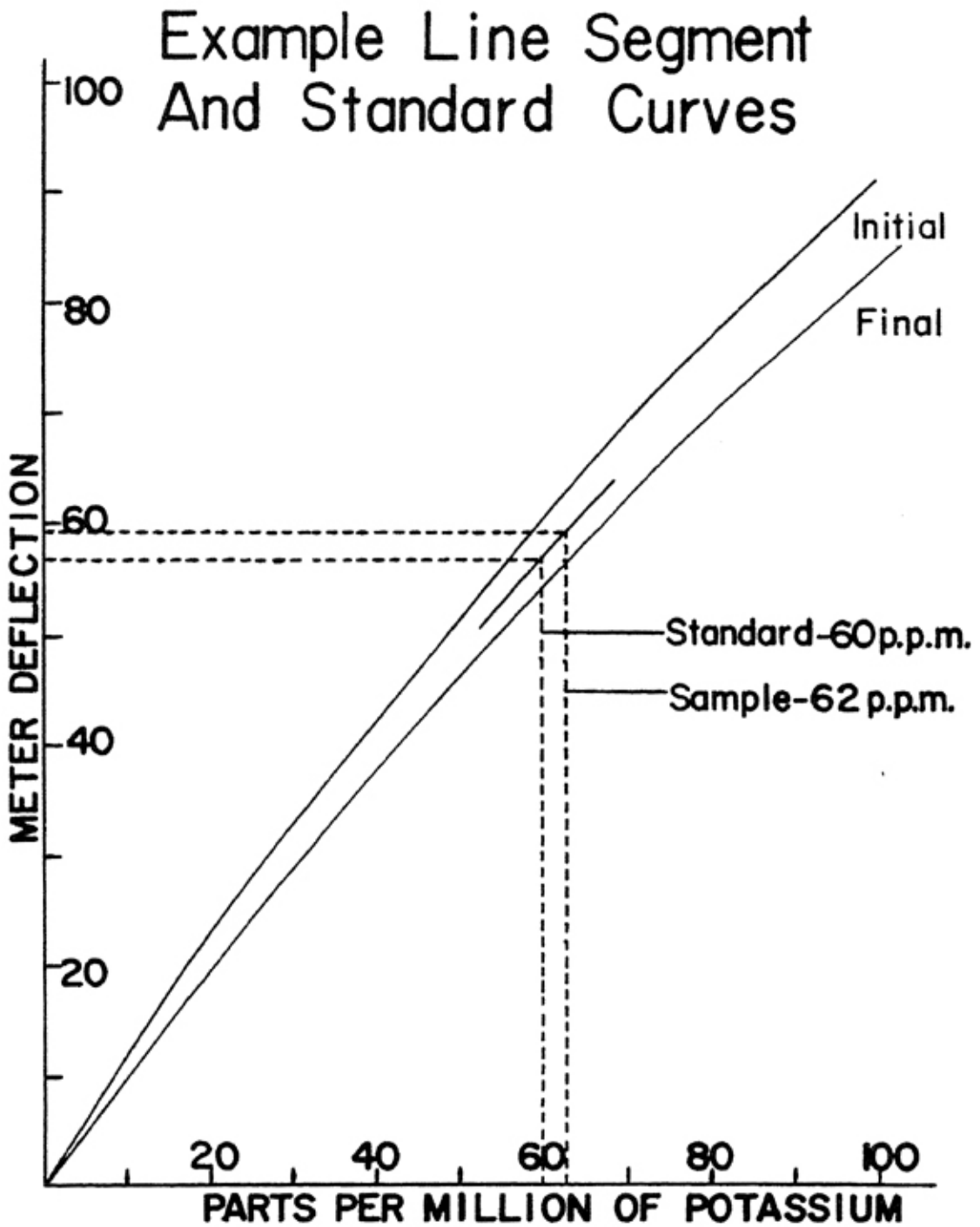


Fig. 1.—Example line segment and standard curves.

Preparation of the Standard Curve and the Determination of the Percent Potash

A standard curve of meter deflection versus concentration is made in the conventional manner using the standard solutions of potassium chloride of 10 to 100 p.p.m. of potassium. This curve is made from a single meter deflection of the photometer for each of the standards and is made both at the beginning and at the end of a series of determinations. It is best not to adjust the oxygen or acetylene pressure during this series of readings.

To determine the percent potash in the unknown, the meter deflection is first read for the unknown and then for the standard whose deflection is closest to that of the unknown. This procedure is repeated three times, alternating with the unknown and the standard. More readings of each are taken if the photometer is not performing satisfactorily. In this way three closely agreeing readings are obtained for the unknowns and the standards.

The averages of the three independent meter deflections for the samples and standards are then computed. The point determined by the average of the deflections of the standard is located on the graph and a "line segment" is drawn parallel to the standard curves through this point. The p.p.m. of potassium in the unknown is then read from this new standard curve or "line segment" using the average value for the deflection of the unknown. With this procedure the slit width may be kept constant and in effect a standard curve is obtained for each sample whose potash content is determined. Figure 1 shows a sample curve.

RESULTS AND DISCUSSION

This ion exchange clean up—flame photometric procedure was first adopted on the basis of the agreement of results of a number of analyses made on commercial fertilizer samples by this method and the official A.O.A.C. gravimetric methods. Data on a series of routine results are given in Table 1. These results were obtained on samples which were so high or so low with respect to the manufacturer's guarantee that they were rerun with either the official Lindo-Gladding or Perrin methods.

These data give a good idea of what might be expected in routine work—especially during a training period as the personnel who made the determinations were in training at the time. Since the adoption of the method several hundred determinations have been made, and now all routine fertilizer samples are screened using this method. Also, for all samples, the results of which fell below the manufacturer's guarantee a recheck was made using either the Perrin or Lindo-Gladding methods, and good agreement was obtained between the results for the two methods.

TABLE 1--COMPARISON OF A.O.A.C. GRAVIMETRIC AND FLAME RESULTS
ON ROUTINE FERTILIZER SAMPLES. AN ION EXCHANGE RESIN
WAS USED TO CLEAN THE SOLUTION PRIOR TO
FLAME ANALYSIS.

Sample Nos.	Guar- antee	Flame Method			Percent K ₂ O		
		1	2	3	1	2	3
1	30	33.12			32.00	33.12	
2	20	22.53			21.44		
3	20	19.79			19.32		
4	30	29.13			28.76		
5	27	25.76			25.62		
6	4	6.93			6.24	6.96	
7	6.2	6.11			6.24		
8	20	18.50			18.84		
9	8	10.14			9.58		
10	8	7.79			7.88		
11	8	6.34			7.10		
12	8	7.49			7.96		
13	9	8.11			9.07		
14	10	9.80			10.22		
15	10	9.16			9.73		
16	10	9.53			9.86		
17	10	9.58			9.88		
18	12	11.70			12.35		
19	12	11.40			11.98		
20	30	28.88			28.54	28.38	
21	12	11.29			11.28	11.42	
22	16	15.96			15.69	15.73	
23	12	11.44			11.28	11.32	
24	8	7.06			7.30	7.21	
25	4	4.70			4.63	4.62	
26	8	8.36			8.46	8.33	
27	20	16.48			16.28	16.17	16.46
28	12	14.77			13.57	13.62	
29	18	16.85			16.23	16.16	
30	16	14.15			14.15	14.29	
31	8	12.85			12.17	12.28	
32	10	8.72			8.37	8.26	
33	12	14.05			13.27	13.52	
34	12	11.69			11.18	11.19	
35	12	8.70			8.74	8.33	
36	12	9.98			9.91	9.71	
37	12	14.03			13.41	13.55	
38	12	9.83			9.80	9.54	
39	20	26.35			25.87	25.34	
40	6	9.50			9.42	9.22	
41	27	26.23			25.87	25.46	
42	12	9.72			9.32	9.53	
43	12	14.63			13.84	13.86	
44	12	13.83			13.50		
45	16	18.00			17.50		
46	12	15.06			14.56	14.49	
47	20	19.02			19.02		
48	8	7.48	7.66	7.72	7.34	7.45	
49	8	10.08			9.34		
50	8	7.31			7.15		
51	8	7.61			7.54		
52	8	10.13	10.11		9.78	9.61	

TABLE 1 (cont.)

Sample Nos.	Guar-antee	Percent K ₂ O					
		Flame Method			Official A.O.A.C.		
		1	2	3	1	2	3
53	10	9.93			9.68		
54	10	11.79			11.53		
55	10	9.27			9.21		
56	10	13.08			12.67	12.50	
57	12	13.83	14.22		13.12		
58	12	13.83	14.05		12.88		
59	8	7.76			7.98		
60	8	10.74			10.29	10.26	
61	60	58.69	61.03		59.96		
62	20	23.10	22.39		21.88	22.02	
63	20	21.30	21.10		21.33		
64	16	17.81	18.07		17.38		
65	8	7.97	8.17		8.04		
66	10	11.35	11.16		10.62		
67	10	11.22	11.56		10.96		
68	12	13.12	12.99		12.40		
69	60	56.14	57.40		55.46	55.60	
70	12	13.15	12.76		12.23		
71	12	13.45	13.17		12.83		
72	20	19.55			19.69		
73	8	10.72			10.63		
74	8	7.98			7.98		
75	8	9.88			9.68		
76	18	16.62			16.64	16.80	
77	12	11.10			11.00	10.86	
78	4	6.50			6.58		
79	18	17.19			17.32		
80	8	10.15			9.92		
81	8	9.75			9.68		
82	4	5.58			5.46		
83	60	59.97			60.16		
84	19	18.07			18.05		
85	20	18.40			18.42	18.43	
86	4	6.15			6.06		
87	4	6.73			6.69	6.72	
88	4	5.86			5.76		
89	16	14.94			14.88		
90	8	6.89			6.86		
91	8	10.11			10.10		
92	8	11.13			11.10	11.04	

The atomizer-burner performed as well with the sample solutions as for the standards. The precision of the meter deflections for the samples was as good as for the standard solutions.

It is best to work in the concentration range of 10 to 50 p.p.m., and usually not over 100 p.p.m. Where high concentrations are involved, it is necessary to dilute to this range, since the atomizer design is such that it does not perform satisfactorily when aspirating concentrated solutions. This is one of the disadvantages of using interference buffers which are added to standards and samples alike. In the "proposed method" the sample

weights and initial dilutions are such that the final solution concentrations are in the above given range. Also, the composition of the final sample solutions which are aspirated into the flame is essentially a solution of potassium chloride containing some ammonium chloride, since all of the major interfering cations and anions have been removed.

Interference and Recovery Study

A series of solutions were prepared whose composition were similar to that of common fertilizer samples but which did not contain potassium. A like series of solutions containing known amounts of potassium were also prepared. The composition of these solutions is given in Table 2. Ali-

TABLE 2--COMPOSITION OF THE SOLUTIONS* USED IN INTERFERENCE AND RECOVERY STUDIES

Solution No.	Percent of				
	K ₂ O	P ₂ O ₅	SO ₄	Ca	Mg
1	Distilled Water				
2	---	8	5	---	---
3	---	12	5	---	---
4	---	24	5	---	---
5	---	12	5	5	1
6	8.03	---	---	---	---
7	8.03	8	5	---	---
8	8.03	12	5	---	---
9	8.03	24	5	---	---
10	4.02	12	5	5	1

* All solutions were prepared from the ammonium and chloride salts.

quots of each of these solutions were carried through the "proposed procedure" and the apparent percent potash determined. The results are given in Table 3. As may be seen for solutions 1 through 5, the reagents and ion

TABLE 3--PERCENT K₂O FOUND IN THE PREPARED SOLUTIONS* USED IN INTERFERENCE AND RECOVERY STUDIES

Solution No.	Percent K ₂ O Found**			Avg.
	1	2	3	
1	0.08	0.01	0.18	0.12
2	0.25	0.16	0.20	0.20
3	0.13	0.10	0.23	0.15
4	0.03	0.06	0.06	0.05
5	0.16	0.16	0.16	0.16
6	8.23	8.23	8.16	8.21
7	8.12	8.12	8.20	8.15
8	8.31	8.08	8.10	8.16
9	8.00	7.93	8.12	8.02
10	3.84	3.81	3.84	3.83

Avg. Standard deviation of solutions 6 through 9=+0.10.

* Refer to Table 1 for composition of solutions.

** Average percent K₂O in solutions 6 through 9=8.13.

exchange resin did not show a significant blank. Solutions numbered 6 through 9 contained added potassium chloride equal to that of a fertilizer

containing 8.03% potash. Three independent determinations were made on each sample. The average percent of potash recovered was $8.13 \pm 0.10\%$. In each case the recovery of the added potassium chloride was considered to be good. The average standard deviation was calculated from the results of 12 determinations. Solution number 10 contained added potassium chloride equal to that in a fertilizer with 4.02% potash. The results of this sample were not included in the calculation of the standard deviation.

Semi-quantitative analyses were made for residual phosphate, sulfate, calcium, and magnesium on 10 solutions prepared by the "proposed procedure" from commercial fertilizers. The phosphate was determined by the molybdenum blue colorimetric method (10), the calcium and magnesium by the disodium dihydrogen ethylenediaminetetraacetate titration procedure with murexide and Eriochrome Black-T as indicators (3), and the sulfate content was determined with barium chloride (4). The tests showed that all the substances analyzed for were in concentrations of less than 5 p.p.m. and consequently would not significantly enhance or repress the intensity of the potassium line.

Eight A.O.A.C. collaborative samples selected from the 1951-1953 groups were analyzed for their potash content by the "proposed procedure." The data are presented in Table 4. As may be seen from Table 4, the results are in good agreement with the values calculated from the materials and with the results of the official Lindo-Gladding gravimetric method. The numbering system for the A.O.A.C. samples is such that their detailed compositions may be found by examining the appropriate reference which is given in Table 4; for example, number 1-51 is A.O.A.C. collaborative sample number 1 for the year 1951.

Samples numbered 1-51, 3-51, 2-52, 4-52, and 6-53 have compositions similar to those encountered in commercial fertilizers. Samples numbered 1-53, 2-53, and 4-53 contained large quantities of added metals such as copper and manganese which are necessary to plants as trace elements. The "proposed procedure" was effective in removing enough of these metals to remove any interference which they might have brought about. Also, a comparative study was made on the A.O.A.C. collaborative samples submitted to referees in 1954. These data are shown in Tables 5 and 6.

The data show that the "proposed procedure" effectively removes the common interfering cations and anions in commercial fertilizers. The following average standard deviations were calculated from results obtained by the "proposed method."

- a. ± 0.10 for 12 analyses on 4 synthetic fertilizers,
- b. ± 0.15 for 48 analyses on 8 A.O.A.C. collaborative samples, and
- c. ± 0.18 for 38 analyses on 8 (1954) A.O.A.C. collaborative samples.

These data show that a good degree of precision was obtained using the

TABLE 4--COMPARISON OF THE K₂O RESULTS OF EIGHT A.O.A.C. COLLABORATIVE SAMPLES
BY "PROPOSED FLAME PHOTOMETRIC" AND A.O.A.C. METHODS

Percent K ₂ O Found											
A.O.A.C. Sample No.	Reference No.	"Proposed Method"							Official Gravimetric Method*	Calcu- lated from	Standard Deviation
		1	2	3	4	5	6	Avg.	Avg.	Materials	"Proposed Method"
1-51	5	16.67	16.95	16.97	16.97	16.77	17.15	16.91	16.84	16.72	0.16
3-51	5	8.39	8.23	8.90	8.59	8.43	8.53	8.52	8.44	8.12	0.21
2-52	6	9.64	9.50	9.44	9.60	9.70	9.54	9.57	9.40	9.00	0.06
4-52	6	17.76	18.03	17.79	18.52**	18.27	18.11	18.08	17.38	18.00	0.19
1-53	7	11.81	11.71	12.03	12.11	11.91	12.15	11.96	12.06	12.24	0.15
2-53	7	9.50	9.68	9.52	9.72	9.80	9.70	9.66	9.92	10.25	0.14
4-53	7	10.06	9.92	10.04	10.18	10.28	10.18	10.11	10.27	10.20	0.12
6-53	7	11.61	11.55	11.57	11.37	11.79	11.71	11.60	11.58	11.28	0.13
										Average	+0.15

* Lindo-Gladding official (A.O.A.C.) procedure for K₂O. The values given are averages as obtained by the collaborators for the respective sample and reference number.

** This value was not used in computing the standard deviation.

TABLE 5--A COMPARISON OF THE K₂O RESULTS ON EIGHT 1954 A.O.A.C. COLLABORATIVE
SAMPLES OBTAINED BY THE "PROPOSED" AND OFFICIAL METHODS.

Percent K ₂ O Found											
A.O.A.C. Sample No.	Lindo-Gladding Method					"Proposed Method"					
	1	2	3	4	Avg.	1	2	3	4	5	Avg.
1*	25.34	25.18	24.95	25.22	25.17	22.83	23.33	23.01	23.17	-----	23.09
2	13.05	13.32	12.85	12.84	13.02	13.50	13.67	13.60	13.52	13.60	13.58
3	17.37	17.40	17.38	17.25	17.35	17.38	17.25	17.23	18.02	17.68	17.51
4	17.00	17.00	17.02	16.98	17.00	16.98	17.33	16.36	17.47	17.35	17.20
5	6.98	6.93	6.68	6.79	6.85	6.92	6.78	7.03	7.00	7.05	6.96
6	63.53	63.53	63.32	63.30	63.42	63.64	64.45	63.91	63.96	-----	63.99
7	10.81	10.55	10.51	10.52	10.60	11.24	11.04	11.46	11.20	11.13	11.21
8	29.58	30.88	29.68	29.87	30.00	30.29	29.97	30.38	30.12	29.98	30.15

* Difficulty was encountered in placing this sample in solution.

TABLE 6--COMPARISON OF STANDARD DEVIATIONS FOR RESULTS OBTAINED BY "PROPOSED" AND OFFICIAL METHODS ON 1954 A.O.A.C. COLLABORATIVE SAMPLES

Sample Number	Standard Deviation	
	"Proposed Method"	Official Method
1	0.19	0.14
2	0.06	0.20
3	0.30	0.06
4	0.24	0.01
5	0.09	0.12
6	0.29	0.11
7	0.15	0.12
8	0.18	0.52
Average	± 0.18	± 0.16

"proposed procedure." For group (c) an average standard deviation of ± 0.16 (32 determinations) was calculated from the Lindo-Gladding results, this value compares favorably with the average standard deviations for the "proposed method." The method is simple, rapid, and as accurate and precise as the standard A.O.A.C. gravimetric procedures.

SUMMARY

In summary it may be said that: a) A simple, rapid, accurate and precise method is described for the flame photometric determination of potash in fertilizers. b) The common interfering substances which affect the intensity of the potassium line, such as phosphate and sulfate, are almost completely removed by contact with an anion exchanger, and the carbonate-hydroxide precipitation effectively removes interfering cations (Ca^{++} , Mg^{++}). c) The calculated standard deviations show the method to be precise, and the accuracy is increased by comparing each sample with a particular standard so that in effect a standard curve is obtained for each sample. d) Analyses made on 16 A.O.A.C. collaborative samples show that the "proposed method" is as accurate as the standard gravimetric methods now in use.

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