



Plant for making diammonium phosphate fertilizer from wet-process phosphoric acid

to a method described previously (5). The results showed that the granular product made from mixtures of crystals and filter cake remained free flowing after 6 months in five-ply plain paper bags. No loss of ammonia in long-term bag storage could be detected by chemical analysis, nor could the odor of ammonia be detected over the material. The product that was tested was 88% minus 6 plus 35 mesh and 12% minus 35 plus 60 mesh. The moisture was 0.7% on bagging.

The addition of other fertilizer materials such as ammonium nitrate, potassium chloride, or concentrated superphosphate during the mixing of the diammonium phosphate crystals and filter cake offers attractive possibilities of making granular high-analysis fertilizers such as 18-18-18, 15-30-15, and 9-27-27. The compatibility of pure diammonium

phosphate with common fertilizer materials has been discussed in an earlier paper from this laboratory (7). Although the early work indicated that the compatibility with ammonium nitrate was limited to nitrogen-phosphorus pentoxide ratios below 0.75, that point was found to be erroneous. Beeson (2) has discussed the reaction between diammonium phosphate and limestone in the presence of considerable moisture, which results in loss of ammonia. It is planned to make tests of the storage properties of several representative mixtures containing common fertilizer materials and diammonium phosphate made from wet-process acid.

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POTASH DETERMINATION IN FERTILIZERS

Flame Photometric Determination with Ion Exchange Separation of Interfering Anions

THE FLAME PHOTOMETER offers a rapid and inexpensive method for the determination of the potassium content of fertilizers and for this reason several studies have been made on the applicability of flame photometric methods. Schall and Hagelberg (7) adapted the official gravimetric procedure of the Association of Official Agricultural Chemists to flame determination, and reported on the interference of magnesium,

sodium, and phosphate. Several other investigators have studied the flame photometric determination of potassium and observed that various anions affect the intensity of the potassium line (1, 2, 6, 8).

This paper describes a procedure used successfully in the Missouri Agricultural Experiment Station laboratories, in which 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, 1.5M solution.

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

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A rapid, accurate, and inexpensive method has long been needed for the determination of potassium in fertilizers. This study was undertaken to develop a method employing anion exchange resins in conjunction with the flame photometer. Other investigators have reported on the interference of magnesium, sodium, phosphate, and other ions with the line intensity of potassium in the flame determination. A simple, rapid, and accurate method is described in which phosphate and sulfate are exchanged by an anion exchanger, and calcium and magnesium are precipitated as the carbonates. Statistical analyses show that it is as accurate as the AOAC gravimetric methods now in use. This procedure should be of especial value to chemists in state control, commercial, and experiment station laboratories where large numbers of routine determinations on fertilizers are done weekly. Applicability to other agricultural substances is expected.

Standard solutions of reagent grade potassium chloride, containing from 10 to 100 p.p.m. of potassium in steps of 5 p.p.m., 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.

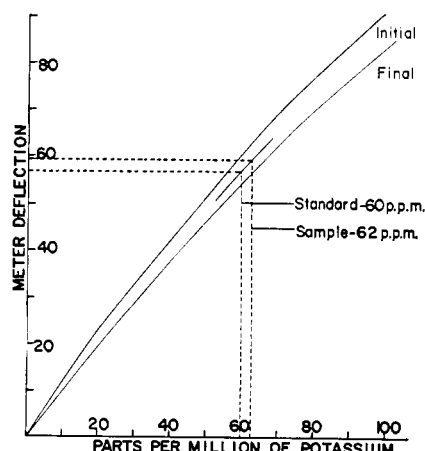


Figure 1. Sample line segment and standard curves

Amberlite IR-4B-C1, an anion exchange resin with a high capacity for phosphate, was used (Rohm & Haas Co., Philadelphia, Pa.). The resin was regenerated by the batch process to the chloride form by first exhausting it with 5% sodium carbonate or sodium hydroxide and washing until all excess base was removed. The resin was then treated with three 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 was set at 4, and the wave length used was 768 m μ . An oxygen-acetylene flame was used with an oxygen pressure of 15 pounds per square inch and an acetylene pressure of 2 pounds per square inch. To

obtain increased sensitivity the 500-megohm resistor was replaced with a 10,000-megohm resistor.

Analytical Procedure

Preparation of Sample

Weigh a 1.5-gram sample of the fertilizer into a 250-ml. borosilicate glass volumetric flask, and add approximately 100 ml. of water and 15 ml. of 1.5M ammonium carbonate. Bring the solution to a boil and allow to boil for 5 minutes. Remove from heat, add 10 ml. of 1 to 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 more 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 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 flask for fertilizers of potash content up to 13%, a 500-ml. flask up to 40%, and a 1000-ml. flask above 40%.

Dilute to the mark and mix thoroughly.

Preparation of Standard Curve

A standard curve of per cent transmittance vs. concentration is made in the conventional manner, using the standard solutions of potassium chloride. This curve is made from a single meter deflection of the photometer for each of the standards, 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 percentage of potash in the unknown, the meter deflection is read first 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 unknown 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 parts per million 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, the potash

Table I. Composition of Solutions^a Used in Studies of Interference and Recovery

Solution No.	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
8	8.03	12	5
9	8.03	24	5
10	4.02	12	5	5	1

^a All solutions prepared from ammonium and chloride salts.

content of which is determined. Figure 1 shows a sample curve.

Results and Discussion

This ion exchange cleanup-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 AOAC gravimetric methods. Since the adoption of the method several hundred determinations have been made, and now the method is used to screen all routine fertilizer samples. All samples were rechecked, when the results fell below the manufacturer's guarantee, and good agreement was obtained between this method and the Perrin or Lindo-Gladding method. The atomizer-burner performed as well with the sample solutions as for the standards. Precision of the meter deflections for the samples was as good as for the standard solutions.

Interference and Recovery

A series of solutions was prepared, similar in composition to common fertilizer samples but without potassium. A like series of solutions containing known amounts of potassium was also prepared (Table I). Aliquots of each of these solutions were carried through the "proposed procedure" and the apparent percentage of potash was determined

(Table II). As may be seen for solutions 1 through 5, the reagents and ion exchange resin did not show a significant blank. Solutions 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 percentage 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 10 contained added potassium chloride equal to that in a fertilizer with 4.02% potash. The results with this sample were not included in the calculation of the standard deviation.

Semiquantitative 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, the calcium and magnesium by the disodium dihydrogen ethylenediaminetetraacetate titration procedure with murexide and Eriochrome Black-T as indicators, and the sulfate content with barium chloride. The tests showed that all the substances were present in concentrations of less than 5 p.p.m. and consequently could not interfere with the flame determination of potassium.

Potash was determined in eight AOAC collaborative samples by the proposed procedure (Table III). As may be seen, the results are in good agreement with the calculated values and with the results of the official Lindo-Gladding gravimetric method. In Table III, sample 1-51 is AOAC collaborative sample 1 for the year 1951. Samples 1-51, 3-51, 2-52, and 6-53 have compositions similar to those encountered in commercial fertilizers. Samples 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 removed enough of these metals to prevent interference.

The data show that the proposed procedure effectively removes the common interfering cations and anions in commercial fertilizers and the average standard deviation of ± 0.15 shows that a good degree of precision is obtained. The method is simple, rapid, and as accurate as the standard AOAC gravimetric procedures.

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Table II. K_2O in Prepared Solutions^a Used in Studies of Interference and Recovery

Solution No.	K_2O Found, %				Av.
	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

Av. % K_2O in solutions 6 through 9, 8.13.

Av. standard deviation of solutions 6 through 9, ± 0.10 .

^a Refer to Table I for composition of solutions.

Table III. K_2O in Eight AOAC Collaborative Samples Found by Proposed Flame Photometric and AOAC Methods

Sample No.	Reference No.	K_2O Found by Proposed Method, %							K_2O Found, %		
		1	2	3	4	5	6	Av.	Official gravimetric method ^a , av.	Calcd. from materials	Standard deviation proposed method
1-51	(3)	16.67	16.95	16.97	16.97	16.77	17.15	16.91	16.84	16.72	0.16
3-51	(3)	8.39	8.23	8.90	8.59	8.43	8.53	8.52	8.44	8.12	0.21
2-52	(4)	9.64	9.50	9.44	9.60	9.70	9.54	9.57	9.40	9.00	0.06
4-52	(4)	17.76	18.03	17.79	18.52 ^b	18.27	18.11	18.08	17.38	18.00	0.19
1-53	(5)	11.81	11.71	12.03	12.11	11.91	12.15	11.96	12.06	12.24	0.15
2-53	(5)	9.50	9.68	9.52	9.72	9.80	9.70	9.66	9.92	10.25	0.14
4-53	(5)	10.06	9.92	10.04	10.18	10.28	10.18	10.19	10.27	10.20	0.14
6-53	(5)	11.61	11.55	11.57	11.37	11.79	11.71	11.60	11.58	11.28	0.13
Av. ± 0.15											

^a Lindo-Gladding official (AOAC) procedure for K_2O . Values given are averages as obtained by collaborators for respective sample and reference number.

^b This value was not used in computing standard deviation.