

Conclusions

The TVA process for the production of granular diammonium phosphate can be used in conventional ammoniation-granulation plants with the addition of only a preneutralizer tank and an ammonia scrubber. Recycle requirement for grades such as 18-46-0 and 21-53-0 is relatively low, about 2.5 pounds per pound of product, because the process takes advantage of the change in solubility of ammonium phosphate with the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio to assist in control of granulation. The preneutralizer is operated near the $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio giving maximum solubility of ammonium phosphate to obtain the most concentrated slurry with satisfactory fluidity, and the am-

moniator-granulator is operated at an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio giving low solubility to further reduce the amount of liquid phase present. With operation of the preneutralizer at an $\text{NH}_3:\text{H}_3\text{PO}_4$ mole ratio of about 1.4, the temperature of the slurry can be as high as 245° F. without excessive loss of ammonia, and effective use can be made of the heat of reaction to evaporate water. The process also is applicable to the production of N-P-K fertilizers.

Acknowledgment

The authors acknowledge the assistance of F. P. Achorn, TVA Division of Agricultural Development, who suggested the basic ideas of the process. They are indebted also to A. B. Phillips,

Chief of the Process Engineering Branch, whose advice helped direct the course of the work.

Literature Cited

- (1) Brosheer, J. C., Anderson, J. F., Jr., *J. Am. Chem. Soc.* **68**, 902-4 (1946).
- (2) Phillips, A. B., Hicks, G. C., Jordon, J. E., Hignett, T. P., *J. Agr. Food Chem.* **6**, 449-53 (1958).
- (3) Shepherd, H. H., Mahan, J. N., Graham, C. A., *Farm. Chem.* **124** (No. 4), 32, 34, 36 (1961).
- (4) Yates, L. D., Nielsson, F. T., Hicks, G. C., *Ibid.*, **117** (No. 7), 38, 41, 43, 45, 47-8; (No. 8), 34, 36-8, 40-1 (1954).

Received for review November 3, 1961. Accepted January 8, 1962. *Fertilizer and Soil Chemistry, 140th Meeting, ACS, Chicago, September 1961.*

FERTILIZER MATERIALS ANALYSIS

Determination of Calcium in Phosphate Materials by Titration with EDTA in the Presence of Calcein Indicator

H. G. GRAHAM, Jr., T. C. McRIGHT, and E. D. FREDERICK
Tennessee Valley Authority,
Wilson Dam, Ala.

A routine analytical control procedure was developed for the determination of calcium in phosphate materials by an EDTA method. Interferences from P, Fe, Al, or Mn and from ions of salts of acids or bases used to decompose the samples were avoided by addition of triethanolamine and/or dilution of the aliquot to be titrated. Continuous stirring and back titration with a standard calcium carbonate solution were also employed. The indicator was a mixture of Calcein and thymolphthalein; the titration was carried out at pH 12.0 or above. With the phosphates tested, the procedure appeared to be about as accurate as the calcium oxalate-potassium permanganate method and required less than half the time.

THE DETERMINATION of calcium is required in many phases of the manufacture of phosphorus or phosphates from natural ores. In nature, phosphorus usually occurs as calcium phosphate associated with various contaminants. The proportion of calcium in these ores affects the process used to recover the phosphate. In the wet process for making phosphoric acid, calcium oxide in the ore reacts with sulfuric acid, and this affects the amount of acid consumed. In the electric furnace process for making phosphorus or phosphoric acid, silica must be added to the phosphate to combine with the calcium oxide present to form a calcium silicate slag which can be removed from the furnace. Many phosphate fertilizers and food-grade phosphates contain calcium. The proportions of calcium to phosphorus in these materials affect the manufacturing processes used, as well as the quality of the products. Therefore, improvements in the analytical method for determining calcium in

phosphate materials contribute to more efficient phosphate manufacturing processes.

The calcium oxalate-potassium permanganate method is used ordinarily to determine calcium in phosphate materials. This method involves time-consuming steps of precipitating and filtering calcium oxalate to separate the calcium from the phosphorus. But the direct determination of calcium in the presence of phosphates would significantly reduce the time required for such a determination. In view of this, the application of an EDTA (the disodium salt of ethylenedinitrilotetraacetic acid) method for this purpose was investigated.

Within the last two decades, the use of EDTA in the determination of calcium has gained wide acceptance because of the accuracy, speed, and convenience with which such an analysis can be made. The development of EDTA methods has been summarized by Borchert (1), Reilley *et al.* (13), Verma and Theratitil (15), and Welcher (16).

The theories upon which these methods are based, together with the factors affecting the methods, have been discussed in detail by Flaschka (7, 8) and Reilley *et al.* (13). In general, EDTA methods involve the stoichiometric formation of a complex between the calcium ions and the EDTA in the presence of an indicator which is specific for free calcium ions under the titration conditions. Obviously, the indicator must exhibit a definite color change when all the calcium ions have been complexed by the EDTA; yet the indicator must not form such a stable complex with the calcium that the calcium cannot be removed by the EDTA.

The feasibility of applying an EDTA method to analysis of calcium in phosphate materials used in production of phosphorus and phosphate fertilizers was investigated. The materials tested were:

Phosphate rock (consisting mostly of colophane but containing some clay, silica, and limestone as impurities).

Table I. Typical Analyses of Phosphate Materials

Constituent	Percentage of Constituent in Phosphate Material				
	Phosphate rock ^a	Nodulized phosphate	Calcium silicate slag	Calcium metaphosphate	Concd. superphosphate
P ₂ O ₅	35.5	27.5	1.2	64.6	55.0
CaO	49.8	39.5	46.0	26.5	23.6
SiO ₂	7.4	24.1	38.0	6.3	2.1
Fe ₂ O ₃	0.7	3.3	0.3	1.1	0.6
Al ₂ O ₃	0.9	4.2	9.2	1.3	0.3
Na ₂ O	0.07	0.3	0.3	..	0.2
K ₂ O	0.09	0.8	1.2	..	0.04
MgO	0.04	0.3	0.3	..	0.2
MnO ₂	0.006	0.6	0.2	..	0.03
F	3.95	2.2	2.8	0.3	..
SO ₃	0.4	0.5
Ba	0.1
Sr	0.1

^a Florida phosphate used in the production of calcium metaphosphate and concentrated superphosphate. A mixture of Florida and Tennessee phosphates is used to produce nodules.

Table II. Analyses of Calcium Carbonate Solution by EDTA and by Calcium Oxalate-Potassium Permanganate Methods

Sample	Added	CaO, %			
		Recovered by EDTA		Recovered by Oxalate	
		Observations	Range	Observations	Range
1	48.0	4	48.0-48.0	9	47.8-48.6
2	48.0	6	48.1-48.2	13	47.8-48.2
3	48.0	6	48.1-48.1	3	48.0-48.4
Av.			48.09		48.07
Std. dev.			0.05		0.18

Nodulized phosphate. (This is phosphate ore that has been partially fused to form agglomerates of suitable size for furnace charging. The principal mineral phase of the fused portion is a cryptocrystalline material approaching fluorapatite.)

Calcium silicate slag (a fused mixture of calcium silicate and calcium aluminate).

Calcium metaphosphate (a glass made by reacting P₂O₅ with phosphate rock; the product contains a small amount of crystalline pyrophosphate).

Concentrated superphosphate (an impure mixture of mono-, di-, and tricalcium phosphates with the monocalcium phase predominating).

Analyses of these materials are given in Table I.

The method was first used to analyze a standard calcium carbonate solution. Then various chemicals were added to the calcium carbonate solution; these chemicals were those expected to interfere when the EDTA method is used with phosphate materials. Finally, the modified procedure was used to analyze the phosphates, and the values obtained using this procedure were compared with those obtained with the calcium oxalate-potassium permanganate method.

Experimental

Adaptation of an EDTA method to the determination of calcium in the phosphates mentioned above required

some changes in previously reported procedures.

Since calcium is only one of several determinations ordinarily made on these materials, the concentration of the EDTA solution had to give a reasonable titer when used to titrate an aliquot equivalent to 0.05 gram of sample. Because such an aliquot normally contains 12 to 24 mg. of calcium oxide, the concentration of the EDTA solution was adjusted so that each milliliter was equivalent to approximately 0.7 mg. of calcium oxide.

Three indicators—Murexide, Pontachrome Blue Black R, and Calcein—were tested for their end-point color change during a typical EDTA titration of the phosphates being analyzed. With Murexide, the color change was so gradual that the end point was difficult to detect. With Pontachrome Blue Black R, the end point could be satisfactorily detected. However, Calcein indicator in the presence of an alcoholic solution of thymolphthalein gave a sharper color change.

This sharpness of color change at the end point, along with other advantages described by Diehl and Ellingboe (5) and Tucker (74), resulted in the selection of Calcein. Diehl and Ellingboe reported that when Calcein is used as the indicator, calcium can be titrated with EDTA, even in the presence of large amounts of magnesium, and that sodium, chlorine, nitrate, acetate, and sulfate ions do not interfere with this titration. They observed that, whenever present, barium and strontium are titrated along with the

calcium under the test conditions. However, these two elements are also titrated as calcium when the calcium oxalate-potassium permanganate method is used. But the percentages of barium and strontium in the phosphate materials are so small that their effect upon the amount of calcium determined by either method can be ignored for practical purposes.

To determine the accuracy of the EDTA titration of calcium solutions free of possible interfering elements, samples of reagent-grade calcium carbonate were titrated with EDTA solution, and these values were compared with analyses obtained by the calcium oxalate-potassium permanganate method. As shown in Table II, data obtained by the two methods indicate that the EDTA method gives more precise results than the oxalate-permanganate method. The average values obtained by both methods were slightly higher than the quantity added, but they were essentially the same.

The phosphate samples are solubilized by fusing with sodium hydroxide and/or digesting with perchloric acid or a mixture of hydrochloric and nitric acids. The solution is subsequently treated with potassium hydroxide to bring its pH to 12.5. Therefore, any aliquot titrated would normally contain a relatively high concentration of sodium chlorate, potassium chlorate, potassium nitrate, or potassium chloride. The effects of the above salts upon the EDTA titration were determined by adding each or a combination of them to an aliquot of the standard calcium carbonate solution and titrating. The amounts of salts added were in excess of that expected in the digested sample. Analyses of these samples and visual observations indicated that no interference occurred from the addition of these salts in the concentrations tested—that is, 10 mg. of salt per ml. of solution titrated.

Previous investigators, Brooke and Hollbrook (2), Collier (3), Diehl, Goetz, and Hach (6), and Mason (9), concluded that it is usually necessary to remove the phosphate ions when calcium is being titrated with EDTA to avoid large negative errors which they attribute to the precipitation of calcium phosphate at the high pH ordinarily used. However, Collier (4) later reported that although calcium phosphate may precipitate, the titration can still be carried out because the precipitate is redissolved when EDTA solution is added.

During the present study, some false end points were observed in the titration of samples containing phosphate. This obstacle was overcome by adding an excess of EDTA solution, stirring for 5 minutes and back-titrating with standard calcium carbonate solution. Various amounts of potassium acid phosphate were added to aliquots of standard calcium carbonate and the mixture was ti-

trated. The ratios of phosphorus pentoxide to calcium oxide in these treated aliquots were as great as 2.5, which is the maximum ratio expected in the materials to be analyzed. No interference from the phosphates was encountered at concentrations up to 52 mg. of P_2O_5 in the portion titrated.

EDTA forms complexes with most metal ions under certain conditions, so any analytical procedure for a specific cation must be designed to prevent interferences from other cations. The typical analyses of the phosphate materials (Table I) show the cations present in the materials. After the acid digestion of any of these materials, the solution contains phosphate, calcium, iron, aluminum, potassium, magnesium, manganese, sodium, and sulfate ions. Results of tests made by the authors indicate that the phosphate, potassium, sodium, and sulfate ions do not interfere with the titration when the aliquot is diluted to a 300-ml. volume. Tucker (14) reported that magnesium does not interfere with the determination of calcium by the EDTA titration under these conditions. Pribil (12), Nielsch (10), and Podlaha and Ullmann (11) reported that interference from the ions of iron, aluminum, and manganese can be eliminated by the addition of triethanolamine. Therefore, the effectiveness of the triethanolamine was determined. Samples of the standard calcium carbonate solution were prepared so that they contained the equivalent of 48 mg. of calcium oxide and various amounts of compounds of iron, aluminum, and manganese either separately or in combination. The amounts of iron, aluminum, and manganese added were as much as four times the amounts normally found in the samples of phosphate materials. The amounts of triethanolamine added were as much as 20 ml. in the 300-ml. volume to which the aliquot had been diluted. At the lower concentrations of these metals, no interference was observed, even without the addition of any triethanolamine. (This lack of interference was attributed to the effects of dilution.) At higher concentrations, even 20 ml. of triethanolamine did not completely eliminate interferences; some titrations showed off-color or indistinct end points. However, results of these tests indicated that 5 ml. of triethanolamine satisfactorily prevented interference when the concentrations of these metals were twice that ordinarily found in the phosphate materials—that is, 3.5 mg. of ferric oxide, 6.2 mg. of aluminum oxide, and 0.6 mg. of manganese dioxide in 300 ml. of solution.

Analytical Procedures

Reagents. EDTA SOLUTION. Dissolve 4.775 grams of reagent-grade EDTA in distilled water and dilute to 1

Table III. Calcium Oxide Contents of Phosphate Materials as Determined by EDTA and Calcium Oxalate-Potassium Permanganate Methods

Sample	CaO, %			
	EDTA Method		Oxalate Method	
	Observations	Range	Observations	Range
Phosphate rock	10	44.0-44.3	5	44.0-44.4
Nodulized phosphate	10	38.8-39.1	6	38.8-39.0
Calcium silicate slag	6	48.9-49.0	6	48.8-49.2
Calcium metaphosphate	10	28.3-28.6	6	28.4-28.8
Concentrated superphosphate	10	23.1-23.3	6	23.0-23.4

liter. Each milliliter of this solution is equivalent to approximately 0.7 mg. of calcium oxide. Standardize this solution against a standard calcium carbonate solution.

STANDARD CALCIUM CARBONATE SOLUTION. Dissolve 2 grams of reagent-grade calcium carbonate in 15 ml. of hydrochloric acid and dilute to 1 liter.

CALCEIN INDICATOR SOLUTION. Dissolve 2 grams of reagent-grade potassium hydroxide in 100 ml. of distilled water and dissolve 0.85 gram of Calcein dye in this solution.

THYMOLPHTHALEIN INDICATOR SOLUTION. Dissolve 1 gram of thymolphthalein powder in ethanol and dilute to 1 liter with ethanol.

Dissolution of Sample. Dissolve 1-gram samples of the different phosphate materials in reagent-grade chemicals as follows:

PHOSPHATE ROCK. Fume with 30 ml. of 72% perchloric acid or a mixture of 30 ml. of hydrochloric acid and 10 ml. of nitric acid.

NODULIZED PHOSPHATE FURNACE FEED. Fuse with 6 grams of sodium hydroxide and then fume with 65 ml. of 72% perchloric acid.

CALCIUM SILICATE SLAG. Fume with 20 ml. of 72% perchloric acid.

CALCIUM METAPHOSPHATE. Digest in a mixture of 30 ml. of hydrochloric acid and 10 ml. of nitric acid.

CONCENTRATED SUPERPHOSPHATE. Digest in a mixture of 30 ml. of hydrochloric acid and 10 ml. of nitric acid.

Filtration, Dilution, and Titration. After all samples have been dissolved, dilute, filter, and make them up to a volume of 500 ml. with distilled water. Take a 25-ml. aliquot (equivalent to 0.05 gram of the original sample), transfer to a 600-ml. beaker, and dilute to 300 ml. with distilled water. Add 5 ml. of triethanolamine. Adjust the pH of the solution to about 12.5 with approximately 12*N* potassium hydroxide solution. Add three drops of Calcein indicator and 13 drops of thymolphthalein indicator. Place the solution on a magnetic stirrer under a fluorescent lamp having a black base and back. While the sample is being stirred, titrate it with EDTA solution; add at least 5 ml. of excess EDTA solution. Continue stirring for 5 minutes, and then back-titrate the solution with standard calcium carbonate solution until a bright, clear, green color appears.

Analyses of Phosphate Materials

Samples of five phosphate materials—phosphate rock, nodulized phosphate, calcium silicate slag, calcium metaphosphate, and concentrated superphosphate—were analyzed for their calcium contents by both the EDTA and the calcium oxalate-potassium permanganate methods. A comparison of these analyses, shown in Table III, indicates good agreement.

Conclusions

The EDTA method described in this article is used routinely for the control of processes to produce phosphorus, calcium metaphosphate, and calcium superphosphate. Considerable savings in analysts' time are realized; after the sample has been solubilized, the time required for calcium determination is about 15 minutes by the EDTA method as compared with 1 hour for the calcium oxalate - potassium permanganate method. Possibly the EDTA method can be applied to the determination of calcium in other phosphate materials, but such an application would require additional investigation similar to that described in this article.

Literature Cited

- (1) Borchert, Otto, *Chem. Tech. (Berlin)* **12**, 332 (1960).
- (2) Brooke, M., Holbrook, M., *Chemist-Analyst* **41**, 80 (1952).
- (3) Collier, R. E., *Ibid.*, **43**, 41 (1954).
- (4) Collier, R. E., *Chem. Ind. (London)* **1955**, 587.
- (5) Diehl, H., Ellingboe, J. L., *Anal. Chem.* **28**, 882 (1956).
- (6) Diehl, H., Goetz, C. A., Hach, C. C., *J. Am. Water Works Assoc.* **42**, 40 (1950).
- (7) Flaschka, H., "EDTA Titrations: An Introduction to the Theory and Practice," Chap. 2, Pergamon Press, New York, 1959.
- (8) Flaschka, H., Barnard, A. J., Jr., Broad, W. C., *Chemist-Analyst* **47**, 109 (1958).
- (9) Mason, A. C., *Analyst* **77**, 529 (1952).
- (10) Nielsch, W., *Glas-Email-Keramot. Tech.* **6**, 73 (1955).
- (11) Podlaha, O., Ullmann, J., *Cesk. Epidemiol. Mikrobiol. Imunol.* **4**, 260 (1955).
- (12) Pribil, H., *Chem. Listy* **47**, 1333 (1953).

- (13) Reilley, Charles N., Schmid, R. W., Sadek, Fawzy S., *J. Chem. Educ.* **36**, 555 (1959).
- (14) Tucker, B. M., *Analyst* **82**, 284 (1957).
- (15) Verma, M. R., Therattil, K. J., *J. Sci. Ind. Res. India*, **15A**, Suppl. No. 9, 1-41 (1956).
- (16) Welcher, F. J., "The Analytical Uses of Ethylenediaminetetraacetic

Acid," pp. 103-47, Van Nostrand, New York, 1958.

Received for review September 22, 1961. Accepted February 5, 1962. Division of Fertilizer and Soil Chemistry, 140th Meeting, ACS, Chicago, September 1961.

FERTILIZER EFFECTS ON PLANT COMPOSITION

Influence of K, Ca, and Mg Application on Acid Content, Composition, and Yield of Tomato Fruit

DONALD B. BRADLEY¹

Agricultural Research Department,
Campbell Soup Co., Riverton, N. J.

Two field experiments involving various rates of K, Ca, and Mg were conducted to determine the influence of these cations on titratable acidity, total acidity, acid composition, and yield of tomato fruit. Potassium applications induced significant increases in titratable acidity, total acidity, citric acid content, and tomato yields. Neither Ca nor Mg applications produced significant differences in acid content or yield of fruit. Acids normally present as salts were converted to the hydrogen form by passing filtered tomato puree through the cation exchange resin, Dowex 50. Titratable and total acidity were determined by titrating aliquots of filtered tomato puree before and after resin treatment, respectively. Ion exchange and partition chromatographic techniques were employed to determine acid composition.

PATTERSON (9) in 1890 reported that K fertilization tended to produce tomato fruit with less sugar and more acid than where no K had been applied. Lee and Sayre (7) presented evidence which indicated an inverse relationship between soil moisture and acidity levels in tomato fruit. They further noted that the acid content of tomatoes varied during the season. In 1946, Lee and Sayre (8) reported that K fertilizers produced tomato fruit that were higher in total acid than where no K was applied. This was noted particularly where relatively large amounts of K were used.

Carangal *et al.* (3) observed that variations in the content of individual acids in tomato fruits grown under greenhouse conditions were not caused by an individual ion, such as NO_3^- , NH_4^+ , or K^+ , but rather by an interaction of ions.

Iljin (5) observed that plants affected with lime-induced chlorosis contained more citric acid than healthy plants. The amount was directly correlated with severity of the disease. Large increases in citric acid concentration were noted before symptoms of chlorosis became visible.

Bear and Toth (7) concluded that conditions approach optimum for cation nutrition of alfalfa when 65% of the exchange complex is occupied by Ca, 10% by Mg, 5% by K, and 20% by H.

¹ Present address: Campbell Soup Co., Davis, Calif.

Lambeth (6) obtained similar results with a variety of vegetable crops.

The objective of this study was to determine the influence of K, Ca, and Mg applications on yield, titratable acidity, and acid composition of tomato fruit.

Experimental

Experiment 1. A split plot factorial experiment with 12 treatments and three replications was established on a Freehold sandy loam soil at Riverton, N. J. Each plot consisted of five rows, 5 feet apart and 30 feet long. Tomato plants were set 3 feet apart in the rows. Main plot treatments were 0 and 930 pounds of Ca per acre. Three rates of K application and two of Mg were superimposed in random arrangement on the main plots. Rates of K and Mg were 0, 166, and 332 pounds per acre and 0 and 152 pounds per acre, respectively. The Ca, Mg, and K were applied as calcite limestone, kieserite, and muriate of potash, respectively.

The Ca, Mg, $\frac{1}{3}$ of the N, and $\frac{1}{2}$ of the K were broadcast and thoroughly disked before planting. The remaining portion of the K and N were sidedressed. No P was applied because laboratory soil tests indicated a high level in the plot area. The pH of the soil was 5.9. The soil contained 477, 58, and 86 pounds per acre of Ca, Mg, and K, respectively, as determined by methods outlined by Hester and Shelton (4).

Southern grown Improved Garden State plants were set in the field on May 14 under ideal conditions. Ripe tomatoes

were picked at 10-day intervals. Fruits from the August 24 picking were pureed and canned for subsequent analysis. Acid anions in the puree samples were separated by partition chromatographic techniques (2).

Experiment 2. A split factorial design with 18 treatments and four replications was used. Plots consisted of four rows spaced 5 feet apart and 30 feet long. Plants were set $2\frac{1}{2}$ feet apart in the row. The main plots included two rates of Mg. Sub-plots were made up of three rates of K and three of Ca and were superimposed in random arrangement on the main plots.

The K, Mg, and Ca treatments were based on the cation exchange capacity (C.E.C.) of the soil and its initial percentage saturation with these cations including H. The C.E.C. of the Evesboro sandy loam soil at Riverton, N. J., averaged 4.3 meq. per 100 grams as determined by the method of Peech *et al.* (10). The pH of the soil was 5.3. The initial percentages of K, Ca, Mg, and H on the exchange complex were 1.9, 26.1, 5.8, and 66.2%, respectively. The applications of 150 and 365 pounds per acre were calculated to adjust the C.E.C. from 1.9% K to 6 and 12%, respectively. Similarly, Ca was applied at rates of 600 and 1650 pounds per acre which were equivalent to increasing the exchangeable Ca from 26.1 to 61 and 122%, respectively. Magnesium applications of 24 and 108 pounds per acre were made to regulate exchangeable Mg levels at 8 and 16%, respectively.

Calcium as calcite limestone was