

## Rapid Determination of Magnesium in Mixed Fertilizers

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Application of the chelation principle to magnesium in mixed fertilizer necessitates elimination of phosphate ions, which interfere in the ethylenediaminetetraacetic acid titration. A method by which the phosphate ions are precipitated by ferric ions at a pH low enough to prevent coprecipitation of magnesium ions gives fast, accurate, and reliable results for the samples tested, and eliminates the long periods of evaporation, filtration, washing, and weighing of the Association of Official Agricultural Chemists' method.

THE DETERMINATION OF either acid-soluble or water-soluble magnesium in mixed fertilizers, by official methods (7), necessitates certain tedious and time-consuming operations which are a distinct disadvantage when reliable results are needed quickly. Separations, evaporation, precipitation, drying periods, ignition, and weighing detract from the attractiveness of the methods for use in control work.

Reports by many investigators, particularly Cheng, Kurtz, and Bray on their work with limestone (2), caused the authors of this paper to investigate the application of (ethylenedinitrilo)tetraacetic acid [ethylenediaminetetraacetic acid (EDTA)] procedures to magnesium in fertilizers.

In order to apply the chelation or complexing power of EDTA in fertilizer analysis, however, the phosphate ions, which interfere in the EDTA titration, must be eliminated. Apparently, phosphate interference has delayed this approach to magnesium in mixed fertilizer.

The procedure outlined here provides one method of overcoming this interference by the precipitation of phosphate with ferric ions at a pH low enough to prevent coprecipitation of magnesium.

### Reagents

**Iron solution.** Dissolve 136 grams of c.p. ferric ammonium sulfate [ $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ] in distilled water with 5 ml. of concentrated sulfuric acid. Dilute to volume in a 1-liter volumetric flask.

**Standard magnesium solution.** Weigh approximately 1 gram ( $\pm 0.1$  mg.) of pure magnesium turnings. Dissolve in a calculated amount of hydrochloric acid and dilute to 1 liter.

**EDTA solution.** Dissolve approximately 4 grams of the disodium salt of ethylenediaminetetraacetic acid in water and dilute to 1 liter. Standardize against the standard magnesium solution.

**Calcium indicator powder.** Mix thoroughly 40 grams of powdered potassium sulfate and 0.2 gram of Eastman Kodak murexide.

**F241 indicator.** Dissolve 0.15 gram of Eriochrome Black T (F241) (Eastman Kodak) and 0.5 gram of sodium borate in 25 ml. of methanol.

**Buffer solution.** Dissolve 60 grams of ammonium chloride in 200 ml. of water, add 570 ml. of concentrated ammonium hydroxide, and dilute to 1 liter with water.

**Potassium hydroxide, 20% aqueous solution.**

**Potassium cyanide, 10% aqueous solution.**

**Sodium hydroxide, 10% aqueous solution.**

**Sodium hydroxide, approximately 0.5N.**

### Samples

**Water-Soluble Magnesium.** Weigh a 1-gram sample of fertilizer and transfer the sample to a 250-ml. beaker. Add 150 ml. of distilled water, cover with a watch glass, and boil for 30 minutes on a hot plate. Filter, while hot, into a 250-ml. beaker through Whatman No. 30 paper. Use hot water to effect a quantitative transfer and wash the filter to a volume not exceeding 200 ml. Cool to room temperature.

Using a pH meter, immerse the electrodes and magnetic or mechanical stirrer in the solution. If the pH is 3.0 or lower, add sodium hydroxide (10% or 0.5N) dropwise until the pH reads 4.0. Precipitate phosphate by adding the iron solution at the rate of 0.5 ml. for each 1% of expected available phosphorus pentoxide in the sample. Bring the pH back to 5.0 with 0.5N sodium hydroxide. The sodium hydroxide must be added slowly to avoid local high alkalinity and possible coprecipitation of magnesium. Remove and wash down

the electrodes with distilled water and transfer the contents of the beaker quantitatively to a 250-ml. volumetric flask. Dilute to the mark with water. Mix well and filter through dry Whatman No. 30 paper. Proceed as directed under determination of magnesium.

**Acid-Soluble Magnesium.** Weigh a 1-gram sample of fertilizer and transfer the sample to a 250-ml. beaker. Cover with a watch glass and add, slowly, 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid. Place on an asbestos mat on a hot plate and evaporate to near dryness. Cool and add about 150 ml. of distilled water, washing down the watch glass and sides of the beaker. Continue as in the water-soluble procedure beginning with the use of the pH meter. The iron solution should be added in an amount equal to 0.5 ml. for each 1% of expected available phosphorus pentoxide plus an additional 1 ml.

### Determination of Magnesium

Pipet a 25-ml. aliquot of the sample solution to be analyzed into a 250-ml. beaker. Add 2.5 ml. of buffer solution from a graduated pipet, a few drops of 10% potassium cyanide solution and 5 to 8 drops of F241 indicator. Stir and titrate with the EDTA solution, using a fluorescent titration lamp. The end point is reached when the color changes from wine-red to pure blue. Let the titration volume be designated as *A* ml.

Pipet a second 25-ml. aliquot into a 100-ml. porcelain dish; add 1 ml. of 20% potassium hydroxide and 20 to 30 mg. of calcium indicator powder. Stir and titrate using the titration lamp. The end point is the change from pink to violet. Let this titration volume be designated *B* ml.

Calculate as follows:

$$\frac{(A \text{ ml.} - B \text{ ml.}) \times (\text{EDTA equivalence in mg. MgO/ml.}) \times 100}{\text{mg. sample in aliquot}} = \% \text{ MgO}$$

**Table I. Comparison of EDTA and AOAC MgO Determinations**

Fertilizer Grade	Water-Soluble MgO, Mg.						Acid-Soluble MgO, Mg.					
	EDTA			AOAC (Titr.)			EDTA			AOAC (Grav.)		
	Calcd.	Found	Diff.	Calcd.	Found	Diff.	Calcd.	Found	Diff.	Calcd.	Found	Diff.
23-21-17	1.66	1.64	-0.02	1.66	1.72	+0.06	1.66	1.64	-0.02			
		1.65	-0.01		1.77	+0.11		1.63	-0.03			
	4.15	4.09	-0.06				4.15	4.11	-0.04	4.15	4.48	+0.33
		4.10	-0.05					4.07	-0.08		4.30	+0.15
10-10-10	1.76	1.74	-0.02	1.76	1.81	+0.05	1.86	1.81	-0.05			
		1.74	-0.02		1.82	+0.06		1.82	-0.04			
	4.25	4.23	-0.02				4.35	4.26	-0.09	4.65	4.68	+0.03
		4.23	-0.02					4.28	-0.07		4.73	+0.08
8-16-16	1.72	1.66	-0.06				1.87	1.84	-0.03	2.19	2.02	-0.17
		1.67	-0.05					1.84	-0.03			
	4.21	4.12	-0.09	4.21	4.39	+0.18	4.36	4.24	-0.12			
		4.13	-0.08		4.46	+0.25		4.24	-0.12			
4-8-12	1.78	1.78	0				1.86	1.87	+0.01	2.16	2.11	-0.05
		1.76	-0.02					1.86	0		2.11	-0.05
	4.27	4.27	0	4.27	4.49	+0.22	4.35	4.32	-0.03			
		4.27	0		4.56	+0.29		4.31	-0.04			
	Average		-0.033			+0.153			-0.049			+0.046

**Table II. Determination of Magnesium Oxide in Mixed Fertilizers by EDTA Method**

Fertilizer Grade	Water-Soluble MgO, Mg.			Acid-Soluble MgO, Mg.		
	Calcd.	Found	Diff.	Calcd.	Found	Diff.
23-21-17	0.83	0.82	-0.01	0.83	0.86	+0.03
	2.49	2.50	+0.01	2.49	2.59	+0.10
	4.15	4.19	+0.04	4.15	4.19	+0.04
	8.30	8.19	-0.11	8.30	8.35	+0.05
10-10-10	0.93	0.96	+0.03	0.96	1.08	+0.12
	2.59	2.61	+0.02	2.62	2.67	+0.05
	4.25	4.29	+0.04	4.28	4.36	+0.08
	8.40	8.43	+0.03	8.43	8.51	+0.08
8-16-16	0.95	0.92	-0.03	1.17	1.15	-0.02
	2.61	2.57	-0.04	2.83	2.76	-0.07
	4.27	4.25	-0.02	4.49	4.45	-0.04
	8.42	8.34	-0.08	8.64	8.62	-0.02
4-8-12	0.90	0.93	+0.03	1.18	1.25	+0.07
	2.56	2.59	+0.03	2.84	2.90	+0.06
	4.22	4.30	+0.08	4.50	4.51	+0.01
	8.37	8.42	+0.05	8.65	8.73	+0.08
	Average		+0.004			+0.039

**Discussion**

Four standard fertilizer samples of different grades and ratios were analyzed to establish the validity of the method.

These samples were a completely soluble 23-21-17, containing no magnesium, and samples of 10-10-10, 8-16-16, and 4-8-12, all three of which contained small amounts of acid-soluble as well as water-soluble magnesium oxide, the exact amounts of which were determined. The high, medium, and low amounts of available phosphorus pentoxide present were favorable for testing the phosphate removal part of the procedure.

Specific amounts of a standard magnesium chloride solution were added to the weighed samples taken for analysis prior to proceeding with either the water-soluble or acid-soluble extracting procedures. The results obtained show the precision and accuracy of the procedure in measuring the amounts of magnesium present. These results are shown in Tables I and II.

In establishing the details of the

procedure, the following considerations served as guideposts.

In order to be of maximum value the procedure should be as short as possible, consistent with acceptable accuracy and precision.

To avoid lengthy evaporation, the amount of water used for extracting the magnesium oxide in the water-soluble procedure was set at 150 ml. and the boiling time at 30 minutes. The sample-water ratio and the boiling time differ from the official (7) procedure for extracting water-soluble magnesium. However, in fertilizer formulations made up with neutral water-soluble magnesium salts, no significant differences in results were encountered.

Following the initial extraction and filtration, phosphate ion is removed. Most trivalent metals precipitate phosphate ions at a low pH (2 to 3). In this instance, a ferric iron solution was chosen for the precipitation. The iron solution is acidified to prevent hydrolysis and to bring the sample solution to about pH 2 after the addition of this reagent.

The danger of coprecipitation of magnesium with the phosphate appears to be minimized by this procedure. Similarly, in eliminating the excess ferric ions by a final upward adjustment to pH 5.0, the coprecipitation of magnesium was not encountered.

Nevertheless, the amount of iron precipitant used should be kept to as small an excess as is required to ensure complete precipitation of phosphate, thus avoiding filtration difficulties. The difference in color of ferric phosphate (yellow-white) and ferric hydroxide (red-brown) enables the direct observation of the presence of this excess ferric ion.

The amount of iron solution to be used in the water-soluble magnesium determination should be based on the amount of water-soluble phosphorus pentoxide present. As there is no way of obtaining this figure short of an actual determination, a fair estimate can be derived from the available phosphorus pentoxide figure as suggested. Therefore, a variable excess of iron is added, but the results show no appreciable error in the magnesium

determination. In preliminary experiments, even a 50% excess of iron produced a loss of magnesium within the limits of error which could be tolerated in analytical control work. If an insufficient amount of iron is added to precipitate all the phosphate present, considerable difficulty in end point determination in the titration step is encountered and reliable results cannot be obtained.

Likewise, in the acid-soluble procedure the total phosphorus pentoxide figure should theoretically be used in calculating the amount of iron to be added. It can be assumed that the total phosphorus pentoxide in any given grade will not in most cases exceed the guaranteed available phosphorus pentoxide value by more than 2%. (A 10% sample will not normally have a total phosphorus pentoxide content of more than 12%.) So here again the figure can serve as a guide. When samples have been analyzed for total and water-soluble phosphorus pentoxide before magnesium analysis is started, the iron excess can be held to an absolute minimum by using these figures rather than estimating from the expected available phosphorus pentoxide as suggested here.

A pH meter is used in the neutralization step. The 0.5*N* sodium hydroxide is

normally used in the water-soluble procedure to make pH adjustments before and after the addition of the iron solution. Because of the initial high degree of acidity in the acid-soluble procedure, the pH adjustment to pH 4.0, prior to the addition of the iron solution, is made with the stronger 10% sodium hydroxide solution. If an indicator were used instead of a pH meter, the indicator color would mask the end point in the final titration with murexide and Eriochrome Black T. Buffering the solution to pH 5 is not feasible because the final titration has to be made in a medium buffered to pH 10 for the titration with Eriochrome Black T, and in an alkaline solution of pH 12 for the calcium titration with murexide. As the amount of sodium hydroxide necessary for neutralization depends on the amount of iron solution used and the original acidity of the fertilizer solution, a pH meter is most convenient for this step.

The final titration procedure is nearly identical with that described by Cheng, Kurtz, and Bray (2) for limestone analysis.

#### Interference

During more than a year of actual use of this method in the laboratory under

routine conditions the following interferences were observed:

**Manganese.** Manganese present in fertilizer in amounts greater than a few hundredths of 1% influences the indicator color of both murexide and Eriochrome Black T, making the end points very indefinite and unreliable.

**Organic matter.** As a completely clear uncolored solution is desirable in the final titration, the lightly colored solutions, resulting from organic fertilizers, might interfere with a proper end point determination. However, in this laboratory such samples have not been encountered. A moderate amount of organic matter does not cause a coloring severe enough to interfere.

#### Literature Cited

- (1) Assoc. Offic. Agr. Chemists, Washington, D. C., "Official Methods of Analysis," 8th ed., pp. 21-3, 1955.
- (2) Cheng, K. L., Kurtz, T., Bray, R. H., *Anal. Chem.* **24**, 1640-1 (1952).

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## PESTICIDE DETERMINATION

### Critical Points in the Schechter-Hornstein Colorimetric Method for Lindane

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The Schechter-Hornstein colorimetric procedure for lindane was studied to determine its critical points and to improve its precision and accuracy. Careful attention in the analytical method must be given to cleanliness, contamination, moisture, removal of ether solvent, and timing. Low and erratic results were obtained when small amounts (20 mg.) of phosphoric acid lubricant were placed in the reaction pot. The precision of the Schechter-Hornstein method was improved significantly with acetic and dichloroacetic acid lubricants. Average deviation for phosphoric was 16.1%, acetic was 3.6%, and dichloroacetic was 5.3%. The method was applied to determine the residual concentration of lindane on finished pickles.

**C**HEMICAL RESIDUES DETERMINATIONS on plant and animal tissues have become a necessity because of the increased use of the newer insecticides. In many cases the toxic level to man and animals has been undetermined. The Schechter-Hornstein colorimetric method (7, 8) has been collaboratively studied (3, 5, 6) and used for the estimation of the residual amount of lindane on plant tissues and in foods (4). This method is probably the best in use

today, but it is lengthy and has a number of critical points at which losses of lindane or interference may occur. The objective of this article is to present findings on extensive studies on the reproducibility and accuracy of the method and its application to the determination of lindane residues on pickles.

The sample of lindane used in all the work was a referee sample obtained from the Association of Official Agricultural Chemists in 1953 and contained

99%+ of the gamma isomer. All other chemical reagents used were of the highest purity—reagent quality.

#### Application of Method to Lindane Residues on Pickles

This investigation resulted from a cooperative project with the Departments of Entomology and Horticulture of the Agricultural Experiment Station, in which a series of experiments was