DETERMINATION OF TOTAL SULFUR IN WHEAT WITH EDTA AND EGTA AFTER NITRIC-PERCHLORIC ACID OXIDATION[1]

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ABSTRACT

A rapid method for the determination of sulfur in plant material is proposed. EDTA and EGTA are used as chelating agents for the Ba^{++} in $BaSO_4$. Correlation between these results and the standard AOAC method was good.

Because the available methods for the determination of total sulfur in plant tissue were either cumbersome or of a low degree of precision, a simple procedure developed by W. M. Shaw (1), utilizing nitric and perchloric acid oxidation, was used. This method gave precise and accurate results comparable with those obtained by the AOAC magnesium nitrate method (2).

This paper reports the results of an investigation carried out on whole-wheat samples using ethylene diamine tetraacetic acid (EDTA) or ethylene glycol bis(-aminoethyl ether)-N,N′ tetraacetic acid (EGTA) as chelating agents for the barium ions in the barium sulfate precipitate and determination of excess EDTA or EGTA. The use of EGTA was investigated on account of the higher stability constant of the EGTA-Ba^{++} complex in comparison with the EDTA-Ba^{++} complex; that is, a value of 8.4 (3) in the former and 7.76 (4) in the latter case, indicated a higher degree of complexation with the EGTA.

Materials and Methods

Reagents. 1. Nitric-perchloric acid solution: Mix equal parts of nitric and 70% perchloric acid by volume.

2. Standard (about 0.01*M*) EDTA. Dissolve 1.861 g. of AR disodium dihydrogen ethylene diamine tetraacetic acid in distilled water and dilute to 1 liter. Standardize with a standard Mg^{++} solution and with Eriochrome Black T as indicator. Store in polyethylene containers.

3. Standard (about 0.01*M*) EGTA. Dissolve 3.8035 g. EGTA in distilled water and dilute to 1 liter. Standardize with a standard Zn^{++} solution and with Eriochrome Black T as indicator. Store in polyethylene containers.

4. Buffer solution, pH 10. Dissolve 90 g. of reagent grade ammonium chloride in 560 ml. concentrated ammonium hydroxide solution and dilute to 950 ml. with distilled water.

5. Buffer solution, pH 8. Saturated solution of borax, adjusted to pH 8 with hydrocholoric acid.

6. Standard (about 0.01*M*) magnesium solution.

7. Standard (about 0.01*M*) zinc solution.

8. Ammonia solution by volume, 1:1.

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9. Hydrochloric acid by volume, 1:1.
10. Barium chloride solution, 10%.
11. Sodium hydroxide, 0.5*M*.
12. Eriochrome Black T indicator (Merck reagent, cat. No. 3170).

Procedure. Grind four wheat samples finely and analyze for total sulfur content according to the procedure set out below.

Weigh out accurately 1 g. of the finely ground wheat and transfer to a 150-ml. Erlenmeyer flask. Add 10 ml. of the nitric-perchloric acid solution and place on an electric hot plate, guarding against excessive fuming. Increase the heat and maintain digestion at active but not excessive boiling until white fumes appear, and continue to boil for 1 hr. after the solution has attained a pale greenish-yellow color. Remove the flask and cool; add 40 ml. distilled water and heat at boiling temperature for 15 min. Filter the solution and wash the residue with hot water. Neutralize the filtrate with 1:1 ammonia solution using methyl red as indicator; acidify with 2 ml. 1:1 hydrochloric acid and dilute to 200 ml. Bring the solution to the boil and add dropwise from a buret or pipet an excess (10–12 ml.) of warm 10% $BaCl_2$ solution. Stir the solution constantly during addition of the $BaCl_2$. Allow the precipitate to settle for a minute or two and then test the supernatant liquid for complete precipitation of the sulfate by adding a few drops of $BaCl_2$ solution. When an excess of $BaCl_2$ has been added, cover the beaker with a watch glass and keep the solution hot, but not boiling, on a water bath for 1 hr. When the watch glass is removed, the lower side must be rinsed off into the beaker by means of a jet of water from a wash bottle. The precipitate should settle readily and a clear supernatant liquid should be obtained.

Filter by means of suction through a filter paper disk (Whatman No. 42) supported on a porcelain Gooch crucible or through a sintered glass crucible (porosity 4). Wash the precipitate thoroughly with cold distilled water and transfer the precipitate to the original beaker. Add 20 ml. of the standard EDTA solution and 2–3 ml. 0.5*M* NaOH solution and boil gently for 10–15 min. Add a further 2 ml. of 0.5*M* NaOH solution and cool. Add 10 ml. of buffer solution, pH 10, Eriochrome Black T indicator, and titrate the excess EDTA with the standard magnesium solution (color change: blue to wine-red).

With EGTA follow the same procedure as above, except: add 10 ml. pH 8 buffer solution instead of 10 ml. pH 10 buffer solution. Titrate the excess EGTA with standard zinc solution and Eriochrome Black T indicator.

Calculations. Calculate the sulfur content of the sample as follows:

$$\% \text{ Sulfur} = \frac{T \times M \times 1.603}{W}$$

where:

T = calculated ml. EDTA or EGTA in the complexing of the Ba^{++};
M = molarity of EDTA or EGTA;
W = weight of sample, moisture-free basis.

Results and Discussion

The results of the tests on the four wheat samples, and a statistical analysis thereof, are reported in Tables I and II.

TABLE I

COMPARISON OF AOAC METHOD AND EDTA TITRATION PROCEDURE FOR DETERMINATION OF TOTAL SULFUR IN WHEAT FLOUR

Sample No.	A AOAC Method		B Nitric-Perchloric Acid Oxidation-EDTA Titration		Difference between the means (B minus A)	t at 5% Probability Level	
	N	S ± St. Dev.	N	S ± St. Dev.		Calculated Value	Critical Value
		%		%	%		
1	5	0.1328 ± 0.0092	5	0.1404 ± 0.0051	0.0076	1.346	2.306
2	5	0.09998 ± 0.0098	5	0.1067 ± 0.0063	0.00672	1.263	2.306
3	5	0.1267 ± 0.0110	5	0.1368 ± 0.0055	0.0081	1.473	2.306
4	5	0.1496 ± 0.0100	5	0.1570 ± 0.0069	0.0074	1.335	2.306

TABLE II

COMPARISON OF AOAC METHOD AND EGTA TITRATION PROCEDURE FOR DETERMINATION OF TOTAL SULFUR IN WHEAT FLOUR

Sample No.	A AOAC Method		B Nitric-Perchloric Acid Oxidation-EDTA Titration		Difference between the means (B minus A)	t at 5% Probability Level	
	N	S ± St. Dev.	N	S ± St. Dev.		Calculated Value	Critical Value
		%		%	%		
1	5	0.1328 ± 0.0092	5	0.1418 ± 0.0061	0.0090	1.822	2.306
2	5	0.09998 ± 0.0098	5	0.1094 ± 0.0084	0.00942	1.592	2.306
3	5	0.1267 ± 0.0110	5	0.1348 ± 0.0056	0.0081	1.518	2.306
4	5	0.1496 ± 0.0100	5	0.1569 ± 0.0051	0.0073	1.442	3.306

In a comparison of the results obtained by means of the proposed EDTA and EGTA methods and the AOAC method, it was found that the two former methods gave higher figures. The differences were, however, not significant at the 5% probability level.

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