

**ESS Method 370.2:
Sulfates Colorimetric,
Automated, Methylthymol Blue**

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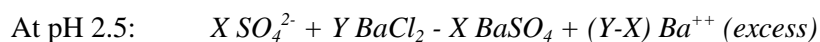
ESS Method 370.2: Sulfates Colorimetric, Automated, Methylthymol Blue

1.0 Scope and Application

- 1.1 This method is applicable to the determination of sulfate in drinking and surface waters, domestic and industrial wastes.
- 1.2 Samples with concentrations in the range of 10 to 100 mg SO₄/L can be analyzed directly. However, the range may be extended by diluting samples prior to analysis. The sensitivity can be increased to analyze samples in the range of 1.0 to 30 mg SO₄/L. Approximately 30 samples per hour can be analyzed.

2.0 Summary of Method

- 2.1 The sample is first passed through a sodium form cation exchange column to remove multivalent metal ions. The sample containing sulfate then reacts with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5-3.0 to form barium sulfate. The combined solution is raised to a pH of 12.5-13.0 so that excess barium reacts with MTB. The uncomplexed MTB color is gray; if it is at all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 300 mg SO₄/L; thus the amount of uncomplexed MTB is equal to the sulfate present.
- 2.2 The reactions are:



3.0 Sample Handling and Preservation

All samples should be refrigerated at 4°C.

4.0 Interferences

- 4.1 The ion exchange column eliminates interferences from multivalent cations, e.g. Ca, Al, Fe. A mid-scale sulfate standard containing Ca⁺⁺ should be analyzed periodically to insure the column's performance.
- 4.2 Turbid samples should be filtered to remove particulates.
- 4.3 Samples with a pH below 2 should be neutralized because high acid concentrations elute cations from the ion exchange resin.

5.0 Apparatus

- 5.1 Technicon AutoAnalyzer consisting of:
 - 5.1.1 Sampler IV with a 30/h (2:1) Cam for both concentration ranges
 - 5.1.2 Analytical manifold - for both ranges
 - 5.1.3 Proportioning pump III
 - 5.1.4 Colorimeter equipped with 15 mm flowcells and solvaflex tubing and 460 nm interference filters.
 - 5.1.5 Printer/Plotter
- 5.2 Column glass, 7.5" long with a 2.0 mm ID and 3.6 mm OD. Alternatively a 7.5 in piece of purple-purple pump tube may be used.

6.0 Reagents

- 6.1 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 500 mL of Milli-Q water and dilute to 1 L.
- 6.2 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3',3'-bis-N, N-bis (carboxymethyl)-amino methylthymolsulfonephthalein pentasodium salt) in 25.0 mL of barium chloride solution (6.1). Add 4 mL of 1.0 N hydrochloric acid, which changes the color to bright orange. Add 71 mL of Milli-Q water and dilute to 500 mL with ethyl alcohol (Aldrich Chemical Co., spectrophotometric grade). The pH of this solution is 2.6. Store in a brown glass bottle overnight at 4 °C. Prepare new reagent for each use.
- 6.3 Buffer, pH 10.5 ± 0.5 : Dissolve 6.75 g of ammonium chloride in 500 mL of Milli-Q water. Add 57 mL of concentrated ammonium hydroxide and dilute to 1 L with Milli-Q water.
- 6.4 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (Section 6.3), and dilute to 1 L with buffer.
 - 6.4.1 Alternative method for making Buffered EDTA: Dissolve 6.75 g NH_4Cl and 40 g tetrasodium EDTA in 500 mL Milli-Q water and 57 mL concentrated NH_4OH . Dilute to 1 L with Milli-Q water.
- 6.5 Sodium hydroxide, 0.18N: Dissolve 7.2 g sodium hydroxide in 900 mL of Milli-Q water. Allow to cool and dilute to 1 L with Milli-Q water.
- 6.6 Dilution water
 - 6.6.1 High range: Add 0.75 mL of 1000 mg/L sulfate standard and 1.0 mL Brij-35 (30%) to 2 L of Milli-Q water.

- 6.6.2 Low range: Add 4 mL of 1000 mg/L sulfate standard and 0.5 mL Brij-35 to 1 L of Milli-Q water.
- 6.7 Ion exchange resin: Bio-Rex 70, 20-50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of Milli-Q water and decanting the supernatant before settling is complete.
- 6.8 Sulfate stock solution, 1000 mg/L: Dissolve 1.479 g of anhydrous sodium sulfate (Na_2SO_4) (dried at 105°C for one hour) in Milli-Q water and dilute to 1 L.
- 6.9 High level working standards, 10-100 mg SO_4/L : Prepare the high level working standards by diluting the following volumes of stock standard solution (Section 6.8) to 100 mL with Milli-Q water. Use 10 mL buret.

Conc. mg SO_4/L	mL Stock Standard/100 mL
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10.0	1.0
30.0	3.0
40.0	4.0
50.0	5.0
60.0	6.0
70.0	7.0
80.0	8.0
90.0	9.0
100.0	10.0

- 6.10 Low level working standards, 1.0-30 mg SO_4/L : Prepare the low level working standards by diluting the following volumes of stock standard solution (Section 6.8) to 500 mL with Milli-Q water:

Conc. mg SO_4/L	mL Stock Standard/500 mL
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1.0	0.5
3.0	1.5
6.0	3.0
10.0	5.0
15.0	7.5
18.0	9.0
22.0	11.0
26.0	13.0
30.0	15.0

- 6.11 Calcium hardness solution for column efficiency check, approximately 1000 mg/L as CaCO_3 : Dissolve 1.5 g calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$) in 1 L with Milli-Q water. (Illinois EPA Method).

7.0 Procedure

- 7.1 Set up the manifold for high level (10-100 mg SO₄/L) or low level (1.0-30 mg SO₄/L) as described in Figure 1. Be sure to use silicone tubing and silicone pump tubing where noted **.
- 7.2 Prepare the ion exchange column by dropping a room temperature slurry of the resin into the column. This is conveniently done by using a small funnel attached with tubing to the glass U-shaped column. Place a glass wool plug at the end of the column to prevent the resin from passing through the column. Fill the column with water and pour the resin slurry into the funnel. Care should be taken to avoid air bubbles entering the column. If air bubbles become trapped, prepare the column over again. Insert the column in the manifold after the dilution water reagent has been pumped through the system. The column can exchange the equivalent of 35 mg of calcium. The column should be prepared as often as necessary to assure that no more than 50% of its capacity is used. To check the column efficiency: analyze as Reagent Blank a 1:1 mixture of mid-range standard (50 mg SO₄/L) and calcium hardness solution (6.11).
- 7.3 Allow the colorimeter and printer to warm up for 30 minutes while pumping a Brij-35 solution (5 mL Brij-35 (30%)/200 mL) through the NaOH and MTB reagent lines. This coats the tubing and helps prevent BaCl₂ from precipitating inside the system. Pump the reagents until a stable baseline is achieved and allow to run about 30 minutes. Follow an air segment from sampler to mixing coil. If it breaks up, replace tubing and clean connections.
- 7.4 Load the sampler according to the CFDA Tray Protocol.
- 7.5 Analyze according to procedures described in the LIMS-CFDA Methods manual and General AutoAnalyzer Procedures.
- 7.6 At the end of each day, wash the system by placing the methylthymol blue and sodium hydroxide lines in water for a few minutes and then in the buffered EDTA solution (6.4) for at least 15 minutes. The dilution water line should be in Milli-Q water. Insert all waste lines in 10% (v/v) HCl while washing with the EDTA solution to prevent NH₃ gas from being evolved into the laboratory. After washing with the EDTA solution, place all lines in Milli-Q water and rinse for 15 minutes before shutting down.

Note: The system must be thoroughly cleaned with the EDTA solution and rinsed to prevent hydrolic problems on subsequent analytical runs.

8.0 Calculations

The sulfate concentration is obtained directly from the LIMS plotter.

9.0 Precision and Accuracy

Precision and accuracy data are available in the Inorganic Chemistry Unit Methods file.

10.0 References

- 10.1 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA 600/4-79-020, p 375.2, (1979).
- 10.2 Sulfate (Automated Methylthymol Blue Method), U.S. Environmental Protection Agency, Central Region Laboratory, Region V, Chicago, IL, (1978).
- 10.3 Sulfate in Water and Wastewater, Technicon Industrial Systems, Tarrytown, NY. Industrial Method No. 118-71W/TENTATIVE.
- 10.4 Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U.S. Geological Survey Techniques of Water Resources Inv. Book #5, Ch. A1, p 501 (1979).

