ESS Method 370.3: Sulfates Colorimetric, Automated Flow Injection, Methylthymol Blue

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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 SO_4/L can be analyzed directly. However, the range may be extended by diluting samples prior to analysis.

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 SO_4/L; thus the amount of uncomplexed MTB is proportional to the sulfate concentration present.

2.2 The reactions are:

At pH 2.5: $X\ SO_4^{2-} + Y\ BaCl_2 - X\ BaSO_4 + (Y\text{-}X)\ Ba^{++}$ *(excess)*

At pH 12.5: $(Y\text{-}X)\ Ba^{++} + Y\ MTB - (Y\text{-}X)\ MTB \bullet Ba + X\ MTB$

3.0 Sample Handling and Preservation

All samples should be refrigerated at 4°C.

4.0 Interferences

4.1 The cation 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.

4.4 Orthophosphate: Orthophosphate forms a precipitate with barium at high pH. If samples are known to be high in orthophosphate, a recovery study, using added amounts of sulfate, should be done, or a sample blank containing only the orthophosphate matrix should be run.

5.0 Apparatus

Lachat QuikChem Automated Flow Injection Ion Analyzer which includes:

5.1 Automatic Sampler

5.2 Proportioning Pump

5.3 Injection Module with a 20 cm x 0.8 mm i.d. sample loop

5.4 Colorimeter

5.4.1 Flow Cell, 10 mm, 80 µL

5.4.2 Interference Filter, 460 nm

5.5 Reaction Module 10-116-10-2-C

5.6 Automated Digital Diluter

5.7 QuikCalc II Software System or Recorder

5.8 QuikChem AE System Unit

5.9 IBM Personal System 12 Computer

6.0 Reagents

Use deionized water (10 megohm) for all solutions.

6.1 Degassing with Helium: To prevent bubble formation, degas all solutions except the standards with helium. Use He at 20 lb/in^2 through a gas dispersion tube. Bubble He vigorously through the solution for at least one minute.

6.2 Barium chloride (6.24 mm): Dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of Milli-Q water and dilute to 1 L.

6.3 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 (6.2). 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. Allow to warm to room temperature before using, then degas with helium.

6.4 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.

6.5 Buffered EDTA: For cleaning manifold. Dissolve 40 g of tetrasodium EDTA in pH 10.5 Buffer (6.4), and dilute to 1 L with buffer.

Alternative method for making Buffered EDTA: Dissolve 6.75 g ammonium chloride (NH_4Cl) and 40 g tetrasodium EDTA in 500 mL Milli-Q water and 57 mL concentrated ammonium hydroxide (NH_4OH). Dilute to 1 L with Milli-Q water. *(Caution: Fumes!)*

6.6 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. Store in plastic bottle. Degas with helium.

6.7 Carrier - 0.30 mg SO_4^{-2}/L

To a 1 L volumetric flask, add 0.30 mL of 1000 mg/L stock sulfate solution. Dilute to 1 L with Milli-Q water. Degas with Helium.

6.8 Hydrochloric Acid, 1.0 M: Add 83 mL of concentrated Hydrochloric Acid (HCl) (specific gravity 1.20, 37%) to 800 mL Milli-Q water. Dilute to 1 L. (*Caution: Fumes!*)

6.9 Calcium hardness solution (1000 mg/L $CaCO_3$) for column efficiency check. Dissolve 1.5 g calcium chloride dihydrate ($CaCl_2 \cdot 2\ H_2O$) in 1 L with Milli-Q water. (Illinois EPA Method).

6.10 Cation Exchange Column Preparation:

6.10.1 Prepare approximately 0.5 g of BioRex 70 ion exchange resin, 50 - 100 mesh, by mixing with sufficient water to make a slurry.

6.10.2 Remove one end fitting and foam plug from the glass column (Lachat part no. 5000-232). Fill the column with water then add the slurry and allow it to settle by gravity to pack the column. Take care to avoid trapping air bubbles in the column or its fittings at this point and during all subsequent operations.

6.10.3 When the resin has settled, replace the end fitting and foam plug. To ensure a good seal take care to remove any resin particles from the threads of the glass, the column end, and the end fitting. To store the column, the ends of the Teflon tubing may be joined with a union.

6.10.4 If desired, the spent resin may be regenerated using the following procedure: Collect the used resin in a small beaker or flask. Wash with dilute HCl until the wash tests free of calcium and magnesium: a calmagite solution will be wine-red in the presence of these cations and a lighter red in their absence. This procedure removes the divalent cations by protonating the carboxylate exchange group (-COOH). Convert the resin back to the sodium form by neutralizing with washes of 0.5 M NaOH until the wash has a pH of 9 or greater. Rinse with water and store.

7.0 Standards

7.1 Sulfate stock solution, 1000 mg SO_4/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.

7.2 Intermediate stock standard, 100 mg SO_4^{2-}/L: In a 500 mL volumetric flask, dilute 50.0 mL of the stock sulfate solution (7.1) to the mark with Milli-Q water.

7.3 High Level working standards, 20-100 mg SO_4/L: Prepare the high level working standards by diluting the following volumes of stock standard solution (7.1) to 200 mL with Milli-Q water. Use 25 mL buret.

Conc. mg SO_4/L	mL Stock Standard/200 mL
20.0	4.0
60.0	12.0
80.0	16.0
100.0	20.0

Conc. mg SO_4/L	mL Stock Standard/500 mL
50.0	25 mL

7.4 Low level working standards, 2.0-10.0 mg SO_4/L: Prepare the low level working standards by diluting the following volumes of stock standard solution (7.2) to 200 mL with Milli-Q water. Use 25 mL buret.

Conc. mg SO_4/L	mL Stock Standard/200 mL
2.0	4.0 mL
5.0	10.0 mL
10.0	20.0 mL

8.0 Injection Timing

Cycle period:	50 s
Load period:	30 s
Inject period:	30 s
Inject to peak start period	17 s
Inject to peak end period:	54 s
Sample loop length:	20 cm

9.0 System Operation

9.1 Inspect modules for proper connections.

9.2 Turn on power to all modules and check diagnostics.

9.3 Follow directions in General Operating Procedures.

9.4 Pump the reagents onto the manifold with a short piece of manifold tubing in place of the column. When all air has passed and the baseline is steady, turn off the pump and place the column in line. To prevent air from entering the column when it is added to the manifold, always connect the column to the valve first and to the manifold second. When the column is in place, resume pumping.

9.5 Pump system until a stable baseline is attained.

9.6 To check the column efficiency, analyze as Reagent Blank a 1:1 mixture of mid-range standard (50 mg SO_4/L) an calcium hardness solution (6.9). Calculate the percent

$$\frac{\textit{True Value - 25 mg/L}}{\textit{25 mg/L}} \textit{ x 100 = Percent Recovery.}$$

9.7 Include in your run a Reagent Blank (Milli-Q water) and a known reference sample.

9.8 At end of run, turn the pump off and remove the column. To prevent air bubbles from entering the column when removing the column from the manifold, disconnect the column from the manifold first, then disconnect it from the valve and reconnect the column ends with a union. Replace the column with a short piece of manifold tubing.

9.9 Rinse the manifold with water, then with buffered EDTA, then water, and finally pump dry.

9.10 Turn off pump, all modules, and release pump tube cassettes.

10.0 System Notes

10.1 If the baseline is noisy even without the column in line, degas all reagents thoroughly, especially the carrier (see 1. Reagents, above). Also check to see that the back-pressure coil (255 cm on a 4" coil support) is in place on the outlet of the flow cell. If these measures do not solve the problem, check all hydraulic connections on the manifold and valve module for blockages, leaks, etc.

The red silicone pump tube used for the color reagents wears faster than the standard PVC tubes and should be changed once a week.

If the baseline is good without the column in line but noisy with the column, repack the column. Even small air bubbles in the column can cause pulsing and noise. Also check the column fittings for blockages and leaks.

If the baseline drifts badly, clean the manifold with the buffered EDTA (8. Reagents, above).

10.2 If the sensitivity of the method is poor as indicated by the need for an extremely high gain, check to see that the pump tube for the color reagent is silicone and not the standard PVC. Also, be sure that the transmission line for this tube is Teflon and not the standard tygon tube. The alcohol in the color reagent extracts plasticizer from the PVC pump tubes and transmission lines which then produces marked turbidity when mixed with the sodium hydroxide on the manifold. This turbidity

results in a high baseline and lack of sensitivity.

10.3 The balance between the MTB concentration and that of the Ba^{2+} ion is critical to the proper operation of this method. If the barium concentration is too high, the detection limit will be adversely affected, while if the MTB concentration is too high, the baseline will be raised and the signal from the sulfate ions will be lowered. Thus the purity of the MTB used must either be known or be determined for each lot of material used. As a service to our users, Lachat makes available preassayed MTB (Part No. 5000-237) with a lot-specific recipe for the Barium-MTB Color Reagent (5. Reagents, above).

11.0 Precision and Accuracy

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

12.0 References

12.1 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA 600/4-79-020, p 375.2, (1979).

12.2 Sulfate (Automated Methylthymol Blue Method), U.S. Environmental Protection Agency, Central Region Laboratory, Region V, Chicago, IL, (1978).

12.3 Sulfate in Water and Wastewater, Technicon Industrial Systems, Tarrytown, NY. Industrial Method No. 118-71W/TENTATIVE.

12.4 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).

12.5 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 375.2.

12.6 Standard Methods for the Examination of Water and Wastewater (1985) 16 Edition, APHA-AWWA-WPCF, Part 426D, pp. 468-470.

12.7 Colovos, G., et al., Anal. Chem. (1976) 48, 1693-1696 (1976).