SULFATE (COLORIMETRIC, AUTOMATED, METHYLTHYMOL BLUE, AA II)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes.

1.2 Samples in the range of 0.5 to 300 mg SO_4^{-2}/liter 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 is then reacted 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 all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 30 mg SO_4^{-2}/liter; thus the amount of uncomplexed MTB is equal to the sulfate present.

3.0 INTERFERENCES

3.1 The ion-exchange column eliminates interferences from multivalent cations. A mid-scale sulfate standard containing Ca^{++} should be analyzed periodically to ensure that the column is functioning properly.

3.2 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion-exchange resin.

3.3 Turbid samples should be filtered or centrifuged.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 **Sampler.**

4.1.2 **Manifold:** High- or low-level (Figure 1).

4.1.3 **Proportioning pump.**

4.1.4 **Heating bath:** Operable at the temperature specified.

4.1.5 **Colorimeter:** Equipped with 15 mm flowcell and 460 nm interference filters.

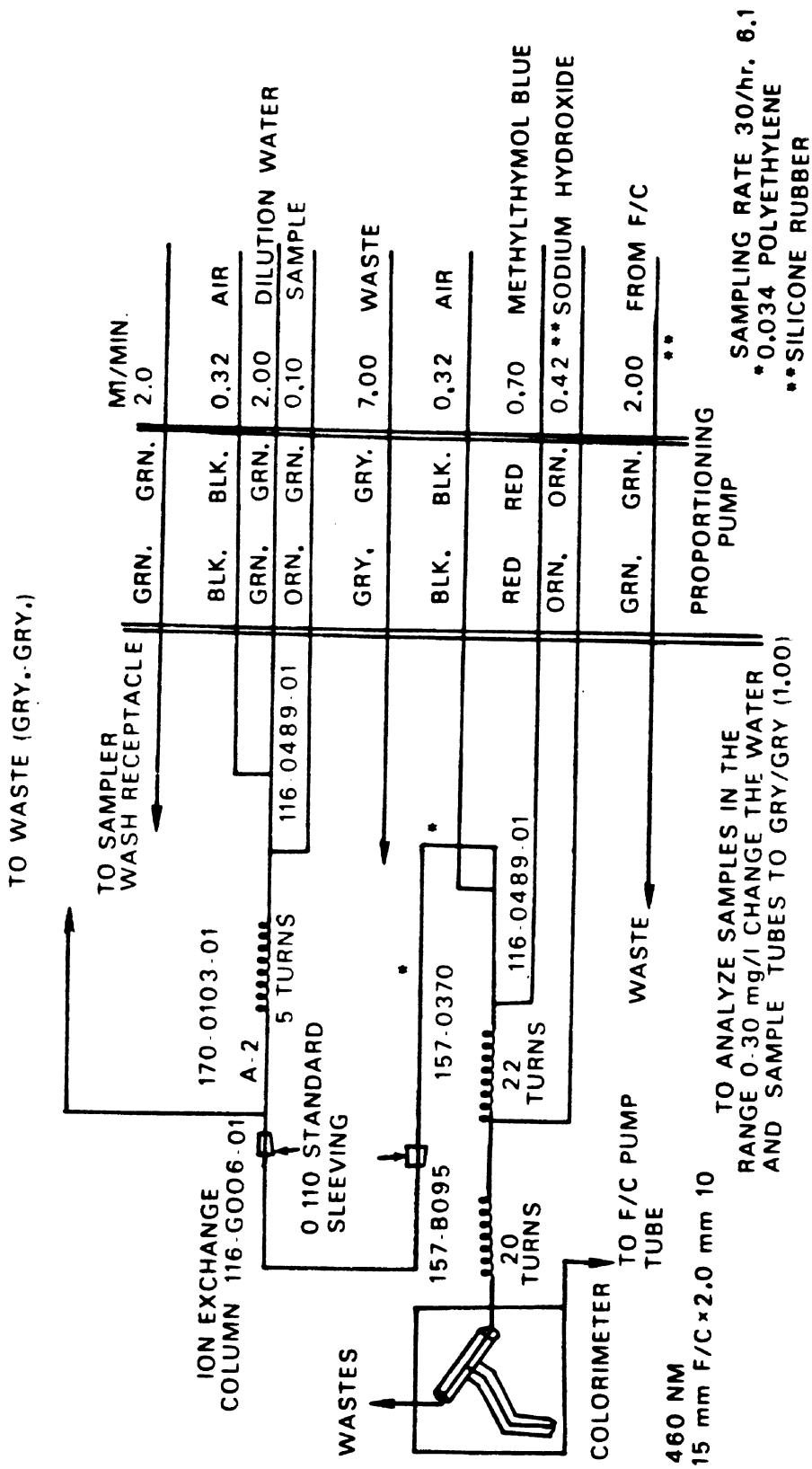


FIGURE 1 SULFATE MANIFOLD AA11

4.1.6 **Filters:** Of specified transmittance.

4.1.7 **Recorder.**

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 500 mL of Type II water and dilute to 1 liter.

5.3 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3'3"-bis-N,N-bis carboxymethyl-amino methylthymolsulfone-phthalein pentasodium salt) in 25 mL of barium chloride solution (Paragraph 5.2). Add 4 mL of 1.0 N hydrochloric acid, which changes the color to bright orange. Add 71 mL of water and dilute to 500 mL with ethanol. The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle in the freezer.

5.4 Buffer, pH 10.5 $\pm$ 0.5: Dissolve 6.75 g of ammonium chloride in 500 mL of Type II water. Add 57 mL of concentrated ammonium hydroxide and dilute to 1 liter with Type II water.

5.5 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (Paragraph 5.4) and dilute to 1 liter with buffer.

5.6 Sodium hydroxide solution (50%): Dissolve 500 g NaOH in 600 mL of Type II water, cool, and dilute to 1 liter.

5.7 Sodium hydroxide, 0.18 N: Dilute 14.4 mL of sodium hydroxide solution (Paragraph 5.6) to 1 liter.

5.8 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 Type II water and decant the supernate before settling is complete.

5.9 Dilution water: Add 0.75 mL of sulfate stock solution (Paragraph 5.10) and 3 drops of Brij-35 (available from Technicon) to 2 liters of Type II water.

5.10 Sulfate stock solution, 1 mL = 1 mg SO_4^{-2}: Dissolve 1.479 g of dried Na_2SO_4 (105°C) in Type II water and dilute to 1 liter.

5.11 Dilute sulfate solution, 1 mL = 0.1 mg SO_4^{-2}: Dilute 100 mL of sulfate stock solution (Paragraph 5.10) to 1 liter.

5.12 High-level working standards, 10-300 mg/L: Prepare high-level working standards by diluting the following volumes of stock standard (Paragraph 5.10) to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
1	10
5	50
10	100
15	150
25	250
30	300

5.13 Low-level working standards, 0.5-30 mg/L: Prepare low-level working standards by diluting the following volumes of dilute sulfate solution (Paragraph 5.11) to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
0.5	0.5
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Refrigerate at 4°C.

7.0 PROCEDURE

7.1 Set up manifold for high- (10-300 mg/L SO_4^{-2}) or low- (0.5-30 mg/L SO_4^{-2}) level samples as described in Figure 1.

7.2 The ion-exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5-in. long, 2.0-mm I.D., and 3.6-mm O.D. This is conveniently done by using a pipet and a loose-fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared again. The column can exchange the equivalent of 35 mg of calcium. For the high-level manifold, this corresponds to about 900 samples with 200 mg/L Ca. The column should be prepared as often as necessary to ensure that no more than 50% of its capacity is used.

7.3 Allow the colorimeter, recorder, and printer to warm up for 30 min. Pump all reagents until a stable baseline is achieved.

7.4 Analyze all working standards in duplicate at the beginning of a run to develop a standard curve. The A and B control standards must be analyzed every hour to ensure that the system remains properly calibrated. Because the chemistry is nonlinear, the 180-mg/L standard is set at 50% on the recorder using the standard calibration control on the colorimeter.

7.5 At the end of each day, the system should be washed with the buffered EDTA solution (Paragraph 5.5). This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 min. Wash the system with water for 15 min before shutting down.

7.6 Prepare a standard curve by plotting peak heights of five processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with the standard curve. Note that this is not a linear curve but a third order curve.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

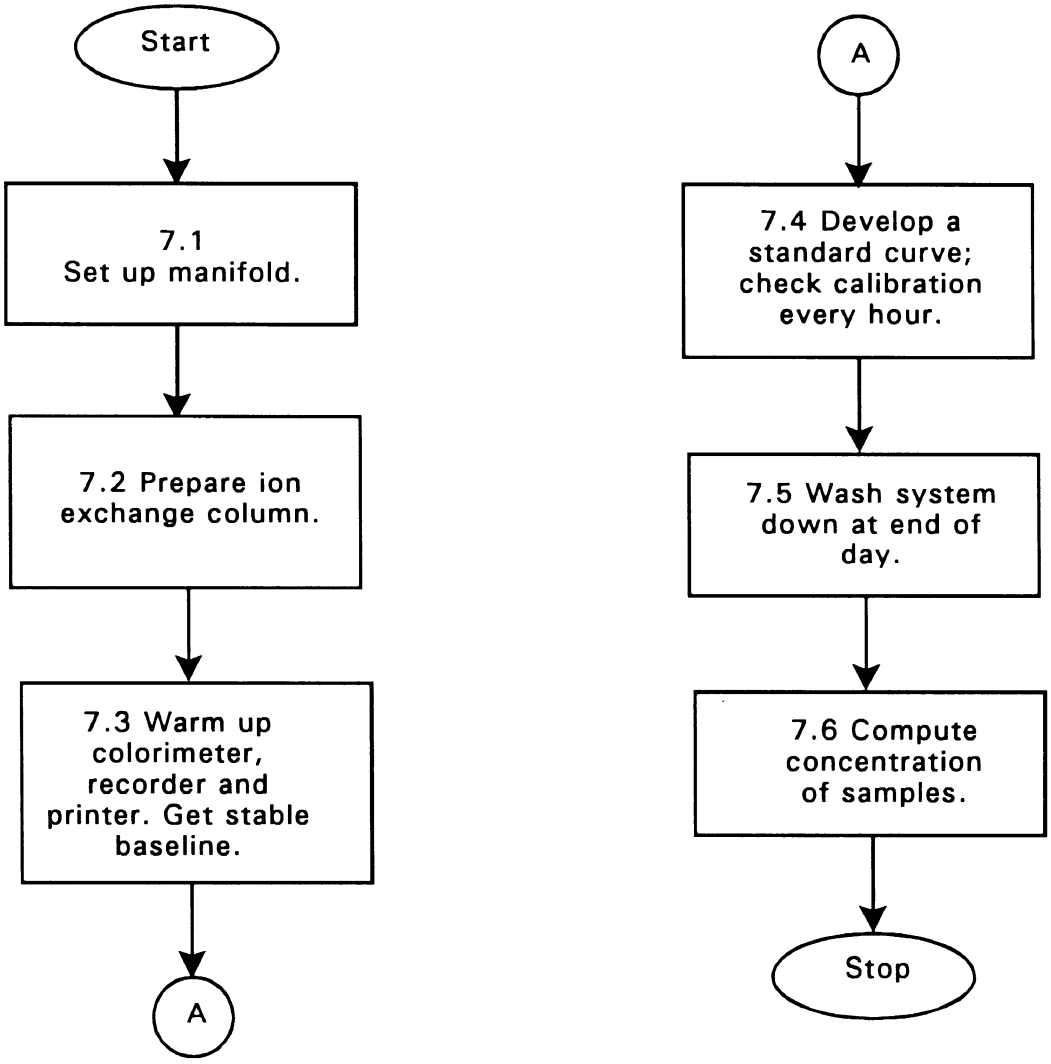
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 375.2 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Coloros, E., M.R. Panesar, and F.P. Parry, "Linearizing the Calibration Curve in Determination of Sulfate by the Methylthymol Blue Method," Anal. Chem. 48, 1693 (1976).

2. Lazrus, A.L., K.C. Hill, and J.P. Lodge, "Automation in Analytical Chemistry," Technicon Symposia, 1965.


Start
7.1
Set up manifold.
7.2 Prepare ion exchange column.
7.3 Warm up colorimeter, recorder and printer. Get stable baseline.
A
A
7.4 Develop a standard curve; check calibration every hour.
7.5 Wash system down at end of day.
7.6 Compute concentration of samples.
Stop