

## METHOD 9038

### SULFATE (TURBIDIMETRIC)

#### 1.0 SCOPE AND APPLICATION

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

1.2 This method is suitable for all concentration ranges of sulfate ( $\text{SO}_4^{-2}$ ); however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg/L of  $\text{SO}_4^{-2}$ .

1.3 The minimum detectable limit is approximately 1 mg/L of  $\text{SO}_4^{-2}$ .

#### 2.0 SUMMARY OF METHOD

2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer, or spectrophotometer and compared with a curve prepared from standard sulfate solution.

#### 3.0 INTERFERENCES

3.1 Color and turbidity due to the sample matrix can cause positive interferences which must be accounted for by use of blanks.

3.2 Silica in concentrations over 500 mg/L will interfere.

#### 4.0 APPARATUS AND MATERIALS

4.1 Magnetic stirrer: Variable speed so that it can be held constant just below splashing. Use identical shapes and sizes of magnetic stirring bars.

4.2 Photometer (one of the following, given in order of preference):

4.2.1 **Nephelometer.**

4.2.2 **Spectrophotometer:** For use at 420 nm with light path of 4 to 5 cm.

4.2.3 **Filter photometer:** With a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.

4.3 Stopwatch: If the magnetic stirrer is not equipped with an accurate timer.

4.4 Measuring spoon: Capacity 0.2 to 0.3 mL.

## 5.0 REAGENTS

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

5.2 Conditioning reagent: Slowly add 30 mL concentrated HCl to 300 mL Type II water, 100 mL 95% ethanol or isopropanol, and 75 g NaCl in solution in a container. Add 50 mL glycerol and mix.

5.3 Barium chloride (BaCl<sub>2</sub>): Crystals, 20 to 30 mesh.

5.4 Sodium carbonate solution: (approximately 0.05 N): Dry 3 to 5 g primary standard Na<sub>2</sub>CO<sub>3</sub> at 250°C for 4 hr and cool in a desiccator. Weigh  $2.5 \pm 0.2$  g (to the nearest mg), transfer to a 1-liter volumetric flask, and fill to the mark with Type II water.

5.5 Proprietary reagents: Such as Hach Sulfaver or equivalent, are acceptable.

5.6 Standard sulfate solution (1.00 mL = 100 ug SO<sub>4</sub><sup>-2</sup>): Prepare by Paragraph 5.6.1 or 5.6.2.

### 5.6.1 Standard sulfate solution from H<sub>2</sub>SO<sub>4</sub>:

5.6.1.1 Standard sulfuric acid, 0.1 N: Dilute 3.0 mL concentrated H<sub>2</sub>SO<sub>4</sub> to 1 liter with Type II water. Standardize against 40.0 mL of 0.05 N Na<sub>2</sub>CO<sub>3</sub> solution (Paragraph 5.4) with about 60 mL Type II water by titrating potentiometrically to a pH of about 5. Lift electrodes and rinse into beaker. Boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate the normality of H<sub>2</sub>SO<sub>4</sub> using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na<sub>2</sub>CO<sub>3</sub> weighed into 1 liter flask (Paragraph 5.4);

B = mL Na<sub>2</sub>CO<sub>3</sub> solution used in the standardization;

C = mL acid used in titration;

5.6.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (Paragraph 5.6.1.1) to 1 liter (use 200.00 mL standard acid if normality is 0.1000 N). Check by standardization against 15 mL of 0.05 N Na<sub>2</sub>CO<sub>3</sub> solution (Paragraph 5.4).

5.6.1.3 Place 10 mL standard sulfuric acid, 0.02 N (Paragraph 5.6.1.2) in a 100-mL volumetric flask and dilute to the mark.

5.6.2 **Standard sulfate solution from Na<sub>2</sub>SO<sub>4</sub>:** Dissolve 147.9 mg anhydrous Na<sub>2</sub>SO<sub>4</sub> in Type II water in a 1-liter volumetric flask and dilute to the mark with Type II water.

## 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 Preserve by refrigerating at 4°C.

## 7.0 PROCEDURE

### 7.1 Formation of barium sulfate turbidity:

7.1.1 Place a 100-mL sample, or a suitable portion diluted to 100 mL, into a 250-mL Erlenmeyer flask.

7.1.2 Add exactly 5.0 mL conditioning reagent (Paragraph 5.2).

7.1.3 Mix in the stirring apparatus.

7.1.4 While the solution is being stirred, add a measured spoonful of BaCl<sub>2</sub> crystals (Paragraph 5.3) and begin timing immediately.

7.1.5 Stir exactly 1.0 min at constant speed.

### 7.2 Measurement of barium sulfate turbidity:

7.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

7.2.2 Measure turbidity at 30-sec intervals for 4 min.

7.2.3 Record the maximum reading obtained in the 4-min period.

### 7.3 Preparation of calibration curve:

7.3.1 Prepare calibration curve using standard sulfate solution (Paragraph 5.6).

7.3.2 Space standards at 5-mg/L increments in the 0-40 mg/L sulfate range.

7.3.3 Above 50 mg/L the accuracy decreases and the suspensions lose stability.

7.3.4 Check reliability of calibration curve by running a standard with every three or four samples.

7.4 Correction for sample color and turbidity:

7.4.1 Run a sample blank using steps 7.1 and 7.2, without the addition of barium chloride (Paragraph 7.1.4).

7.5 Calculation:

7.5.1 Read  $\text{mg SO}_4^{-2}$  from linear calibration curve:

$$\text{mg SO}_4^{-2}/\text{L} = \frac{\text{mg SO}_4^{-2} \times 1,000}{\text{mL sample}}$$

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 spike duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as	
		Bias (%)	Bias (mg/L)
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(Data from: FWPCA Method Study 1, Mineral and Physical Analyses.)

9.2 A synthetic unknown sample containing 259 mg/L sulfate, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 241 mg/L chloride, 0.250 mg/L nitrite N, 1.1 mg/L nitrate N, and 42.5 mg/L total alkalinity (contributed by  $\text{NaHCO}_3$ ), was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

#### 10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D516-68, Method B, p. 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 496, Method 427C, (1975).

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