

METHOD #: 375.4 Approved for NPDES (Editorial Revision 1978)

TITLE: Sulfate (Turbidimetric)

ANALYTE: Sulfate, SO₄

INSTRUMENTATION: Spectrophotometer

STORET No. Total 00945

1.0 Scope and Application

- 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
- 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO₄/L.
- 1.3 The minimum detectable limit is approximately 1 mg/L sulfate.

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 to a curve prepared from standard sulfate solutions.
- 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
- 2.3 Silica in concentrations over 500 mg/L will interfere.

3.0 Comments

- 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
- 3.2 Preserve by refrigeration at 4°C.

4.0 Apparatus

- 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
- 4.2 Photometer: one of the following which are 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 Conditioning reagent: Place 30 mL conc. HCl, 300 mL distilled water, 100 mL 95% ethanol or isopropanol and 75 g NaCl in solution in a container.

- Add 50 mL glycerol and mix.
- 5.2 Barium chloride, BaCl₂, crystals, 20 to 30 mesh.
 - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na₂CO₃ at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.
 - 5.4 Standard sulfate solution (1.00 mL = 100 μg SO₄): Prepare by either 5.4.1 or 5.4.2.
 - 5.4.1 Standard sulfate solution from H₂SO₄
 - 5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 mL conc. H₂SO₄ to 1 liter with distilled water. Standardize versus 40.00 mL of 0.05 N Na₂CO₃ solution (5.3) with about 60 mL distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3-5 minutes under a watchglass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

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

where:

A = g Na₂CO₃ weighed into 1 liter

B = mL Na₂CO₃ solution

C = mL acid used to inflection point

- 5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 mL if 0.1000 N). Check by standardization versus 15 mL of 0.05 N Na₂CO₃ solution (5.3).
- 5.4.1.3 Place 10.41 mL standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 mL volumetric and dilute to the mark.
- 5.4.2 Standard sulfate solution from Na₂SO₄: Dissolve 147.9 mg anhydrous Na₂SO₄ in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6.0 Procedure

- 6.1 Formation of barium sulfate turbidity
 - 6.1.1 Place 100 mL sample, or a suitable portion diluted to 100 mL, into a 250 Erlenmeyer flask.
 - 6.1.2 Add exactly 5.0 mL conditioning reagent (5.1).
 - 6.1.3 Mix in the stirring apparatus.
 - 6.1.4 While the solution is being stirred, add a measuring spoonful of BaCl₂ crystals (5.2) and begin timing immediately.
 - 6.1.5 Stir exactly 1.0 minutes at constant speed.
- 6.2 Measurement of barium sulfate turbidity
 - 6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.
 - 6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

- 6.2.3 Record the maximum reading obtained in the 4 minute period.
- 6.3 Preparation of calibration curve.
 - 6.3.1 Prepare calibration curve using standard sulfate solution (5.4).
 - 6.3.2 Space standards at 5 mg/L increments in the 0-40 mg/L sulfate range.
 - 6.3.3 Above 50 mg/L the accuracy decreases and the suspensions lose stability.
 - 6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.
- 6.4 Correction for sample color and turbidity.
 - 6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7.0 Calculations

- 7.1 Read mg SO₄ from calibration curve

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

8.0 Precision and Accuracy

- 8.1 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/liter	Precision as Standard Deviation mg/liter	Bias, %	Accuracy as Bias mg/liter
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

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

- 8.2 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 NaHCO₃) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

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 Edition, p 496, Method 427C, (1975).