

## Standard Methods for the Examination of Water and Wastewater

Sample	$\bar{x}$ mg/L	Standard Deviation, $\sigma$ mg/L	Relative Standard Deviation %
Secondary effluent with 0.12 mg $\text{SO}_3^{2-}$ /L	0.12	0.03	25
Secondary effluent with 4.0 mg $\text{SO}_3^{2-}$ /L	3.7	0.30	8.0

### 7. References

1. STEPHENS, B.G. & F. LINDSTROM. 1964. Spectrophotometric determination of sulfur dioxide suitable for atmospheric analysis. *Anal. Chem.* 36:1308.
2. WEST, P. W. & G.C. GAEKE. 1956. Fixation of sulfur dioxide as sulfitomercurate and subsequent colorimetric determination. *Anal. Chem.* 28:1816.

**4500-SO<sub>4</sub><sup>2-</sup>      SULFATE\*#(89)**

**4500-SO<sub>4</sub><sup>2-</sup> A.      Introduction**

### 1. Occurrence

Sulfate ( $\text{SO}_4^{2-}$ ) is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute large amounts of  $\text{SO}_4^{2-}$  through pyrite oxidation. Sodium and magnesium sulfate exert a cathartic action.

### 2. Selection of Method

The ion chromatographic method (4110) and capillary ion electrophoresis (CIE—see Section 4140) are suitable for sulfate concentrations above 0.1 mg/L. The gravimetric methods (C and D) are suitable for  $\text{SO}_4^{2-}$  concentrations above 10 mg/L. The turbidimetric method (E) is applicable in the range of 1 to 40 mg  $\text{SO}_4^{2-}$  /L. The automated methylthymol blue methods (F and G) are the procedures for analyzing large numbers of samples for sulfate alone when the equipment is available; over 30 samples can be analyzed per hour. Methods C, D, F, G, 4110, or

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CIE (4140) are preferred for accurate results.

### 3. Sampling and Storage

In the presence of organic matter certain bacteria may reduce  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$ . To avoid this, store samples at 4°C.

### 4500-SO<sub>4</sub><sup>2-</sup> B. (Reserved)

### 4500-SO<sub>4</sub><sup>2-</sup> C. Gravimetric Method with Ignition of Residue

#### 1. General Discussion

*a. Principle:* Sulfate is precipitated in a hydrochloric acid (HCl) solution as barium sulfate ( $\text{BaSO}_4$ ) by the addition of barium chloride ( $\text{BaCl}_2$ ).

The precipitation is carried out near the boiling temperature, and after a period of digestion the precipitate is filtered, washed with water until free of  $\text{Cl}^-$ , ignited or dried, and weighed as  $\text{BaSO}_4$ .

*b. Interference:* The gravimetric determination of  $\text{SO}_4^{2-}$  is subject to many errors, both positive and negative. In potable waters where the mineral concentration is low, these may be of minor importance.

1) Interferences leading to high results—Suspended matter, silica,  $\text{BaCl}_2$  precipitant,  $\text{NO}_3^-$ ,  $\text{SO}_3^{2-}$  and occluded mother liquor in the precipitate are the principal factors in positive errors. Suspended matter may be present in both the sample and the precipitating solution; soluble silicate may be rendered insoluble and  $\text{SO}_3^{2-}$  may be oxidized to  $\text{SO}_4^{2-}$  during analysis. Barium nitrate [ $\text{Ba}(\text{NO}_3)_2$ ],  $\text{BaCl}_2$ , and water are occluded to some extent with the  $\text{BaSO}_4$  although water is driven off if the temperature of ignition is sufficiently high.

2) Interferences leading to low results—Alkali metal sulfates frequently yield low results. This is true especially of alkali hydrogen sulfates. Occlusion of alkali sulfate with  $\text{BaSO}_4$  causes substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfates of alkali metals act similarly and, in addition, decompose on being heated. Heavy metals, such as chromium and iron, cause low results by interfering with the complete precipitation of  $\text{SO}_4^{2-}$  and by formation of heavy metal sulfates.  $\text{BaSO}_4$  has small but significant solubility, which is increased in the presence of acid. Although an acid medium is necessary to prevent precipitation of barium carbonate and phosphate, it is important to limit its concentration to minimize the solution effect.

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### 2. Apparatus

- a. *Steam bath.*
- b. *Drying oven*, equipped with thermostatic control.
- c. *Muffle furnace*, with temperature indicator.
- d. *Desiccator.*
- e. *Analytical balance*, capable of weighing to 0.1 mg.
- f. *Filter*: Use one of the following:
  - 1) *Filter paper*, acid-washed, ashless hard-finish, sufficiently retentive for fine precipitates.
  - 2) *Membrane filter*, with a pore size of about 0.45  $\mu\text{m}$ .
- g. *Filtering apparatus*, appropriate to the type of filter selected. (Coat membrane filter holder with silicone fluid to prevent precipitate from adhering.)

### 3. Reagents

- a. *Methyl red indicator solution*: Dissolve 100 mg methyl red sodium salt in distilled water and dilute to 100 mL.
- b. *Hydrochloric acid*, HCl, 1 + 1.
- c. *Barium chloride solution*: Dissolve 100 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 L distilled water. Filter through a membrane filter or hard-finish filter paper before use; 1 mL is capable of precipitating approximately 40 mg  $\text{SO}_4^{2-}$ .
- d. *Silver nitrate-nitric acid reagent*: Dissolve 8.5 g  $\text{AgNO}_3$  and 0.5 mL conc  $\text{HNO}_3$  in 500 mL distilled water.
- e. *Silicone fluid*. \*#(90)

### 4. Procedure

- a. *Removal of silica*: If the silica concentration exceeds 25 mg/L, evaporate sample nearly to dryness in a platinum dish on a steam bath. Add 1 mL HCl, tilt, and rotate dish until the acid comes in complete contact with the residue. Continue evaporation to dryness. Complete drying in an oven at 180°C and if organic matter is present, char over flame of a burner. Moisten residue with 2 mL distilled water and 1 mL HCl, and evaporate to dryness on a steam bath. Add 2 mL HCl, take up soluble residue in hot water, and filter. Wash insoluble silica with several small portions of hot distilled water. Combine filtrate and washings. Discard residue.
- b. *Precipitation of barium sulfate*: Adjust volume of clarified sample to contain approximately 50 mg  $\text{SO}_4^{2-}$  in a 250-mL volume. Lower concentrations of  $\text{SO}_4^{2-}$  may be tolerated if it is impracticable to concentrate sample to the optimum level, but in such cases limit total volume to 150 mL. Adjust pH with HCl to pH 4.5 to 5.0, using a pH meter or the orange color of methyl red indicator. Add 1 to 2 mL HCl. Heat to boiling and, while stirring gently,

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slowly add warm  $\text{BaCl}_2$  solution until precipitation appears to be complete; then add about 2 mL in excess. If amount of precipitate is small, add a total of 5 mL  $\text{BaCl}_2$  solution. Digest precipitate at 80 to 90°C, preferably overnight but for not less than 2 h.

*c. Filtration and weighing:* Mix a small amount of ashless filter paper pulp with the  $\text{BaSO}_4$ , quantitatively transfer to a filter, and filter at room temperature. The pulp aids filtration and reduces the tendency of the precipitate to creep. Wash precipitate with small portions of warm distilled water until washings are free of  $\text{Cl}^-$  as indicated by testing with  $\text{AgNO}_3\text{-HNO}_3$  reagent. Place filter and precipitate in a weighed platinum crucible and ignite at 800°C for 1 h. Do not let filter paper flame. Cool in desiccator and weigh.

### 5. Calculation

$$\text{mg SO}_4^{2-}/\text{L} = \frac{\text{mg BaSO}_4 \times 411.6}{\text{mL sample}}$$

### 6. Precision and Bias

A synthetic sample containing 259 mg  $\text{SO}_4^{2-}/\text{L}$ , 108 mg  $\text{Ca}^{2+}/\text{L}$ , 82 mg  $\text{Mg}^{2+}/\text{L}$ , 3.1 mg  $\text{K}^+/\text{L}$ , 19.9 mg  $\text{Na}^+/\text{L}$ , 241 mg  $\text{Cl}^-/\text{L}$ , 0.250 mg  $\text{NO}_2^-/\text{N/L}$ , 1.1 mg  $\text{NO}_3^-/\text{N/L}$ , and 42.5 mg total alkalinity/L (contributed by  $\text{NaHCO}_3$ ) was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

### 7. Bibliography

HILLEBRAND, W.F. et al. 1953. Applied Inorganic Analysis, 2nd ed. John Wiley & Sons, New York, N.Y.

KOLTHOFF, I.M., E.J. MEEHAN, E.B. SANDELL & S. BRUCKENSTEIN. 1969. Quantitative Chemical Analysis, 4th ed. Macmillan Co., New York, N.Y.

## 4500-SO<sub>4</sub><sup>2-</sup> D. Gravimetric Method with Drying of Residue

### 1. General Discussion

See Method C, preceding.

### 2. Apparatus

With the exception of the filter paper, all of the apparatus cited in Section 4500-SO<sub>4</sub><sup>2-</sup>.C. is required, plus the following:

*a. Filters:* Use one of the following:

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1) *Fritted-glass filter*, fine (“F”) porosity, with a maximum pore size of 5 µm.

2) *Membrane filter*, with a pore size of about 0.45 µm.

b. *Vacuum oven*.

### 3. Reagents

All the reagents listed in Section 4500-SO<sub>4</sub><sup>2-</sup>.C. are required.

### 4. Procedure

a. *Removal of interference*: See Section 4500-SO<sub>4</sub><sup>2-</sup>.C..

b. *Precipitation of barium sulfate*: See Section 4500-SO<sub>4</sub><sup>2-</sup>.C..

c. *Preparation of filters*:

1) Fritted glass filter—Dry to constant weight in an oven maintained at 105°C or higher, cool in desiccator, and weigh.

2) Membrane filter—Place filter on a piece of filter paper or a watch glass and dry to constant weight\*#(91) in a vacuum oven at 80°C, while maintaining a vacuum of at least 85 kPa or in a conventional oven at a temperature of 103 to 105°C. Cool in desiccator and weigh membrane only.

d. *Filtration and weighing*: Filter BaSO<sub>4</sub> at room temperature. Wash precipitate with several small portions of warm distilled water until washings are free of Cl<sup>-</sup>, as indicated by testing with AgNO<sub>3</sub>-HNO<sub>3</sub> reagent. If a membrane filter is used add a few drops of silicone fluid to the suspension before filtering, to prevent adherence of precipitate to holder. Dry filter and precipitate by the same procedure used in preparing filter. Cool in a desiccator and weigh.

### 5. Calculation

$$\text{mg SO}_4^{2-}/\text{L} = \frac{\text{mg BaSO}_4 \times 411.6}{\text{mL sample}}$$

### 6. Bibliography

See Section 4500-SO<sub>4</sub><sup>2-</sup>.C.

## 4500-SO<sub>4</sub><sup>2-</sup> E. Turbidimetric Method

### 1. General Discussion

a. *Principle*: Sulfate ion (SO<sub>4</sub><sup>2-</sup>) is precipitated in an acetic acid medium with barium

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chloride ( $\text{BaCl}_2$ ) so as to form barium sulfate ( $\text{BaSO}_4$ ) crystals of uniform size. Light absorbance of the  $\text{BaSO}_4$  suspension is measured by a photometer and the  $\text{SO}_4^{2-}$  concentration is determined by comparison of the reading with a standard curve.

*b. Interference:* Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. If both are small in comparison with the  $\text{SO}_4^{2-}$  concentration, correct for interference as indicated in ¶ 4d below. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate  $\text{BaSO}_4$  satisfactorily.

In potable waters there are no ions other than  $\text{SO}_4^{2-}$  that will form insoluble compounds with barium under strongly acid conditions. Make determination at room temperature; variation over a range of  $10^\circ\text{C}$  will not cause appreciable error.

*c. Minimum detectable concentration:* Approximately 1 mg  $\text{SO}_4^{2-}$ /L.

### 2. Apparatus

*a. Magnetic stirrer:* Use a constant stirring speed. It is convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate stirring speed. Use magnets of identical shape and size. The exact speed of stirring is not critical, but keep it constant for each run of samples and standards and adjust it to prevent splashing.

*b. Photometer:* One of the following is required, with preference in the order given:

1) *Nephelometer.*

2) *Spectrophotometer*, for use at 420 nm, providing a light path of 2.5 to 10 cm.

3) *Filter photometer*, equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 2.5 to 10 cm.

*c. Stopwatch or electric timer.*

*d. Measuring spoon*, capacity 0.2 to 0.3 mL.

### 3. Reagents

*a. Buffer solution A:* Dissolve 30 g magnesium chloride,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 5 g sodium acetate,  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , 1.0 g potassium nitrate,  $\text{KNO}_3$ , and 20 mL acetic acid,  $\text{CH}_3\text{COOH}$  (99%), in 500 mL distilled water and make up to 1000 mL.

*b. Buffer solution B* (required when the sample  $\text{SO}_4^{2-}$  concentration is less than 10 mg/L): Dissolve 30 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 5 g  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , 1.0 g  $\text{KNO}_3$ , 0.111 g sodium sulfate,  $\text{Na}_2\text{SO}_4$ , and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

*c. Barium chloride*,  $\text{BaCl}_2$ , crystals, 20 to 30 mesh. In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

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*d. Standard sulfate solution:* Prepare a standard sulfate solution as described in 1) or 2) below;  $1.00 \text{ mL} = 100 \text{ } \mu\text{g SO}_4^{2-}$ .

1) Dilute 10.4 mL standard 0.0200N  $\text{H}_2\text{SO}_4$  titrant specified in Alkalinity, Section 2320B.3c, to 100 mL with distilled water.

2) Dissolve 0.1479 g anhydrous  $\text{Na}_2\text{SO}_4$  in distilled water and dilute to 1000 mL.

### 4. Procedure

*a. Formation of barium sulfate turbidity:* Measure 100 mL sample, or a suitable portion made up to 100 mL, into a 250-mL erlenmeyer flask. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add a spoonful of  $\text{BaCl}_2$  crystals and begin timing immediately. Stir for  $60 \pm 2 \text{ s}$  at constant speed.

*b. Measurement of barium sulfate turbidity:* After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at  $5 \pm 0.5 \text{ min}$ .

*c. Preparation of calibration curve:* Estimate  $\text{SO}_4^{2-}$  concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying  $\text{SO}_4^{2-}$  standards through the entire procedure. Space standards at 5-mg/L increments in the 0- to 40-mg/L  $\text{SO}_4^{2-}$  range. Above 40 mg/L accuracy decreases and  $\text{BaSO}_4$  suspensions lose stability. Check reliability of calibration curve by running a standard with every three or four samples.

*d. Correction for sample color and turbidity:* Correct for sample color and turbidity by running blanks to which  $\text{BaCl}_2$  is not added.

### 5. Calculation

$$\text{mg SO}_4^{2-}/\text{L} = \frac{\text{mg SO}_4^{2-} \times 1000}{\text{mL sample}}$$

If buffer solution A was used, determine  $\text{SO}_4^{2-}$  concentration directly from the calibration curve after subtracting sample absorbance before adding  $\text{BaCl}_2$ . If buffer solution B was used subtract  $\text{SO}_4^{2-}$  concentration of blank from apparent  $\text{SO}_4^{2-}$  concentration as determined above; because the calibration curve is not a straight line, this is not equivalent to subtracting blank absorbance from sample absorbance.

### 6. Precision and Bias

With a turbidimeter,\*#(92) in a single laboratory with a sample having a mean of 7.45 mg  $\text{SO}_4^{2-}/\text{L}$ , a standard deviation of 0.13 mg/L and a coefficient of variation of 1.7% were obtained.

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Two samples dosed with sulfate gave recoveries of 85 and 91%.

### 7. Bibliography

SHEEN, R.T., H.L. KAHLER & E.M. ROSS. 1935. Turbidimetric determination of sulfate in water. *Ind. Eng. Chem., Anal. Ed.* 7:262.

THOMAS, J.F. & J.E. COTTON. 1954. A turbidimetric sulfate determination. *Water Sewage Works* 101:462.

ROSSUM, J.R. & P. VILLARRUZ. 1961. Suggested methods for turbidimetric determination of sulfate in water. *J. Amer. Water Works Assoc.* 53: 873.

## 4500-SO<sub>4</sub><sup>2-</sup> F. Automated Methylthymol Blue Method

### 1. General Discussion

*a. Principle:* Barium sulfate is formed by the reaction of the SO<sub>4</sub><sup>2-</sup> with barium chloride (BaCl<sub>2</sub>) at a low pH. At high pH excess barium reacts with methylthymol blue to produce a blue chelate. The uncomplexed methylthymol blue is gray. The amount of gray uncomplexed methylthymol blue indicates the concentration of SO<sub>4</sub><sup>2-</sup>.

*b. Interferences:* Because many cations interfere, use an ion-exchange column to remove interferences.

Molybdenum, often used to treat cooling waters, has been shown to cause a strong positive bias with this method, even with as little as 1 mg Mo/L.

*c. Application:* This method is applicable to potable, ground, surface, and saline waters as well as domestic and industrial wastewaters over a range from about 10 to 300 mg SO<sub>4</sub><sup>2-</sup>/L.

### 2. Apparatus

*a. Automated analytical equipment:* An example of the required continuous-flow analytical instrument consists of the interchangeable components shown in Figure 4500-SO<sub>4</sub><sup>2-</sup>:1.

*b. Ion-exchange column:* Fill a piece of 2-mm-ID glass tubing about 20 cm long with the ion-exchange resin.\*#(93) To simplify filling column put resin in distilled water and aspirate it into the tubing, which contains a glass-wool plug. After filling, plug other end of tube with glass wool. Avoid trapped air in the column.

### 3. Reagents

*a. Barium chloride solution:* Dissolve 1.526 g BaCl<sub>2</sub>·2H<sub>2</sub>O in 500 mL distilled water and dilute to 1 L. Store in a polyethylene bottle.

*b. Methylthymol blue reagent:* Dissolve 118.2 mg methylthymol blue†#(94) in 25 mL BaCl<sub>2</sub> solution. Add 4 mL 1N HCl and 71 mL distilled water and dilute to 500 mL with 95% ethanol.



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Store in a brown glass bottle. Prepare fresh daily.

*c. Buffer solution, pH 10.1:* Dissolve 6.75 g  $\text{NH}_4\text{Cl}$  in 500 mL distilled water. Add 57 mL conc  $\text{NH}_4\text{OH}$  and dilute to 1 L with distilled water. Adjust pH to 10.1 and store in a polyethylene bottle. Prepare fresh monthly.

*d. EDTA reagent:* Dissolve 40 g tetrasodium ethylenediaminetetraacetate in 500 mL pH 10.1 buffer solution. Dilute to 1 L with pH 10.1 buffer solution and store in a polyethylene bottle.

*e. Sodium hydroxide solution, 0.36N:* Dissolve 7.2 g  $\text{NaOH}$  in 250 mL distilled water. Cool and make up to 500 mL with distilled water.

*f. Stock sulfate solution:* Dissolve 1.479 g anhydrous  $\text{Na}_2\text{SO}_4$  in 500 mL distilled water and dilute to 1000 mL; 1.00 mL = 1.00 mg  $\text{SO}_4^{2-}$ .

*g. Standard sulfate solutions:* Prepare in appropriate concentrations from 10 to 300 mg  $\text{SO}_4^{2-}$ /L, using the stock sulfate solution.

### 4. Procedure

Set up the manifold as shown in Figure 4500- $\text{SO}_4^{2-}$ :1 and follow the general procedure described by the manufacturer.

After use, rinse methylthymol blue and  $\text{NaOH}$  reagent lines in water for a few minutes, rinse them in the EDTA solution for 10 min, and then rinse in distilled water.

### 5. Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against  $\text{SO}_4^{2-}$  concentrations in standards. Compute sample  $\text{SO}_4^{2-}$  concentration by comparing sample peak height with standard curve.

### 6. Precision and Bias

In a single laboratory a sample with an average concentration of about 28 mg  $\text{SO}_4^{2-}$ /L had a standard deviation of 0.68 mg/L and a coefficient of variation of 2.4%. In two samples with added  $\text{SO}_4^{2-}$ , recoveries were 91% and 100%.

### 7. Bibliography

- LAZRUS, A.L., K.C. HILL & J.P. LODGE. 1965. A new colorimetric microdetermination of sulfate ion. *In Automation in Analytical Chemistry*. Technicon Symposium.
- COLOROS, E., M. R. PANESAR & F.P. PERRY. 1976. Linearizing the calibration curve in determination of sulfate by the methylthymol blue method. *Anal. Chem.* 48:1693.

## 4500- $\text{SO}_4^{2-}$ G. Methylthymol Blue Flow Injection Analysis (PROPOSED)

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## 1. General Discussion

*a. Principle:* At pH 13.0 barium forms a blue complex with methylthymol blue (MTB). This gives a dark blue base line. The sample is injected into a low, but known, concentration of sulfate. The sulfate from the sample then reacts with the ethanolic barium-MTB solution and displaces the MTB from the barium to give barium sulfate and uncomplexed MTB. Uncomplexed MTB has a grayish color. The pH is raised with NaOH and the color of the gray uncomplexed MTB is measured at 460 nm. The intensity of gray color is proportional to the sulfate concentration.

Also see Section 4500-SO<sub>4</sub><sup>2-</sup>.A and Section 4500-SO<sub>4</sub><sup>2-</sup>.F, and Section 4130, Flow Injection Analysis (FIA).

*b. Interferences:* Remove large or fibrous particulates by filtering sample through glass wool. Guard against nitrate and nitrite contamination from reagents, water, glassware, and the sample preservation process.

A cation-exchange column removes multivalent cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup>. A midrange sulfate standard containing a typical level of hardness as CaCO<sub>3</sub> can be run periodically to check the performance of the column. Any decrease in peak height from that of a sulfate standard without added CaCO<sub>3</sub> indicates the need to regenerate or replace the resin.

Neutralize samples that have pH less than 2. High acid concentrations can displace multivalent cations from the column.

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

Also see Section 4500-SO<sub>4</sub><sup>2-</sup>.F..

## 2. Apparatus

*Flow injection analysis equipment* consisting of:

*a. FIA injection valve* with sample loop or equivalent.

*b. Multichannel proportioning pump.*

*c. FIA manifold* (Figure 4500-SO<sub>4</sub><sup>2-</sup>:2) with cation-exchange column and flow cell. Relative flow rates only are shown in Figure 4500-SO<sub>4</sub><sup>2-</sup>:2. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE.

*d. Absorbance detector*, 460 nm, 10-nm bandpass.

*e. Injection valve control and data acquisition system.*

## 3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas

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carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

a. *Carrier solution*, 0.30 mg  $\text{SO}_4^{2-}$ /L: To a tared 1-L container, add 0.30 g 1000 mg/L stock sulfate standard (§ 3h) and 999.7 g water. Shake or stir to mix. Degas with helium.

b. *Barium chloride solution*, 6.24mM: To a tared 1-L container, add 1.526 g barium chloride dihydrate,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , and 995 g water. Shake or stir until dissolved. Degas with helium.

c. *Hydrochloric acid*, HCl, 1.0M: To a tared 1-L container, add 913 g water and 99.6 g conc HCl (specific gravity 1.20, 37%). CAUTION: *Fumes*. Shake or stir to mix well. Degas with helium.

d. *Barium—MTB color reagent*: NOTE: The purity of the methylthymol blue and the denaturants in the alcohol are critical. Use the sources specified below, or test the material from alternative sources for suitability before using.

To a tared 500-mL dry brown plastic bottle, place 0.236 g methylthymol blue, 3,3'-bis[*N,N*-di(carboxymethyl)amino-methyl]-thymol-sulfonephthalein, pentasodium salt. Add 50 g barium chloride solution (§ 3b), which may be used to aid in transfer of the dye. Swirl to dissolve. Add 4.0 g of 1.0M HCl (§ 3c) and mix. The solution should turn orange. Add 71 g water and 321 g ethanol (ethyl alcohol, specially denatured anhydrous alcohol\*#(95)). Stir or shake to mix well. The pH should be 2.5. Prepare solution the day before use and store, refrigerated, in a brown plastic bottle. Let warm to room temperature before using, then degas with helium.

e. *Stock sodium hydroxide solution*, NaOH, 50% (w/v) solution: To a glass 1-L container add 500 g water and 500.0 g NaOH. Dilute to 1 L. CAUTION: *The solution becomes very hot*. Shake or stir until dissolved. Cool to ambient. Store in a plastic bottle.

f. *Working sodium hydroxide solution*, NaOH, 0.18M: To a tared plastic 1-L container add 982 g water and 19.8 g stock NaOH solution (§ 3e). Shake or stir to mix. Degas with helium.

g. *Cation exchange column preparation*: Prepare approximately 0.5 g ion exchange resin,†#(96) 50 to 100 mesh, by mixing with sufficient water to make a slurry. Remove one end fitting from the threaded glass column. Fill column with water and aspirate slurry into column or let it settle into column by gravity. Take care to avoid trapping air bubbles in column or fittings at this point and during all subsequent operations. When resin has settled, replace end fitting. To ensure a good seal, remove any resin particles from the threads of glass, column end, and end fitting. To store column, join ends of the TFE tubing.

To test column effectiveness, make up two midrange standards, one of only sodium sulfate and the other with an identical concentration of sodium sulfate but with hardness typical of the samples. If the column is depleted, the standard with hardness will give a lower response because the divalent  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations are complexing with the free MTB. If depletion has occurred, repack column with fresh resin.

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*h. Stock sulfate standard, 1000 mg SO<sub>4</sub><sup>2-</sup>/L:* Dry approximately 2 g sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, at 105° overnight. Cool in a desiccator. In a 1-L volumetric flask, add 1.479 g of dried sodium sulfate to about 800 mL water. Dissolve by swirling, dilute to mark, and mix by inversion.

*i. Standard solutions:* Prepare sulfate standards in desired concentration range, using the stock standard (§ 3h), and diluting with water.

### 4. Procedure

Set up a manifold equivalent to that in Figure 4500-SO<sub>4</sub><sup>2-</sup>:2 and follow method supplied by manufacturer or laboratory standard operating procedure. Follow quality control protocols outlined in Section 4020.

### 5. Calculations

Prepare standard curves by plotting adsorbance of standards processed through the manifold versus sulfate concentration.

### 6. Precision and Bias

*a. Recovery and relative standard deviation:* Table 4500-SO<sub>4</sub><sup>2-</sup>:I gives results of single-laboratory studies.

*b. MDL:* A 180-μL sample loop was used in the method described above. Using a published MDL method,<sup>1</sup> analysts ran 21 replicates of a 5.00-mg SO<sub>4</sub><sup>2-</sup>/L standard. These gave a mean of 4.80 mg SO<sub>4</sub><sup>2-</sup>/L, a standard deviation of 0.69 mg SO<sub>4</sub><sup>2-</sup>/L, and MDL of 1.8 mg SO<sub>4</sub><sup>2-</sup>/L.

### 7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 rev. 1.11 amended June 30, 1986. 49 CFR 43430.

## Figures

**Figure 4110:1. Typical inorganic anion separation.** Eluent: 1.7 mM NaHCO<sub>3</sub>, 1.8 mM Na<sub>2</sub>CO<sub>3</sub>; sample loop: 50 μL; flow: 2.0 mL/min; column: Dionex AG4A plus AS4A.

Anion	Time	Conc mg/L
Fluoride	1.15	2
Chloride	1.72	20