Standard Test Method for Sulfate Ion in Brackish Water, Seawater, and Brines [1]

This standard is issued under the fixed designation D 4130; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the turbidimetric determination of sulfate ion in brackish water, seawater, and brines. It has been used successfully with synthetic brine grade waters; however, it is the user's responsibility to ensure the validity of this test method to other matrices.

1.2 This test method is applicable to waters having an ionic strength greater than 0.65 mol/L and a sulfate ion concentration greater than 25 mg/L. A concentration less than 25 mg/L sulfate can be determined by using a standard addition method.

1.3 For brines having an ionic strength of less than 0.65 mol/L, refer to Test Methods D 516.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 516 Test Methods for Sulfate Ion in Water [2]
D 1129 Terminology Relating to Water [2]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits [2]
D 1193 Specification for Reagent Water [2]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water [2]
D 3370 Practices for Sampling Water from Closed Conduits [2]
D 5810 Guide for Spiking into Aqueous Samples [2]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis [3]
E 275 Practice for Describing and Measuring Performances of Ultraviolet, Visible, and Near Infrared Spectrophotometers [4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 A sulfate ion is converted to a barium sulfate suspended under controlled conditions. A glycerin-acid solution is added to acidify and stabilize the suspension. A calculated volume of a NaCl solution is added to adjust the ionic strength to a set value of 2 mol/L (Note 1). The turbidity resulting upon addition of barium chloride is determined by a photoelectric colorimeter and compared to a curve prepared from standard sulfate solutions.

NOTE 1—The ionic strength (IS) of the sample is calculated from the concentration of the major ion constituents (Na^+, Ca^{2+}, Mg^{2+}, Cl^-), (K^+ and Sr^{2+} if their concentration exceeds 2000 mg/L) as follows:

where:
IS, mol/L = $1/2\ \Sigma\ C_i Z_i^{\ 2}$,
C_i = g/L ion i/molecular weight ion, *i,* and
Z_i = valence of ion *i*.

5. Significance and Use

5.1 The determination of sulfate and other dissolved constituents is important in identifying the source of brines produced during the drilling and production phases of crude oil or natural gas.

6. Interferences

6.1 Suspended matter in the sample must be removed. Dark colors that cannot be compensated for in the procedure interfere with the measurement of suspended barium sulfate ($BaSO_4$).

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

***A Summary of Changes section appears at the end of this standard.**

7. Apparatus

7.1 *Photometer*—A filter photometer or a spectrophotometer for measurements between 400 to 450 nm, the preferable wavelength being 425 nm. The cell for the instrument must have a light path of 20 ± 2 mm and hold a volume of 25 mL. Filter photometers, spectrophotometers, and photometric practices prescribed in this test method shall conform to Practice E 275.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [5] Other grades may be used, providing it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the precision and bias of the test method. Type III water was specified at the time of round robin testing of this test method. In addition, reagent water used for this test method shall be sulfate-free.

8.3 *Barium Chloride*—Crystals of barium chloride ($BaCL_2{\cdot}2H_2O$) screened to 20 to 70 mesh.

8.4 *Glycerin-Acid Solution*—Mix 250 mL of glycerin and 50 mL of hydrochloric acid (HCl, sp gr 1.19) and dilute to 500 mL with water.

8.5 *Sodium Chloride Solution (5 mol)*—Dissolve 584.4 g of sodium chloride (NaCl) containing less than 0.001% SO_4 in about 1800 mL of water and dilute to 2 L with water.

8.6 *Sulfate Solution, Standard (1 mL = 1.00 mg* $SO_4{}^{=}$*)*—Dissolve 1.479 g of anhydrous sodium sulfate, (Na_2SO_4), in water and dilute to 1 L in a volumetric flask.

9. Sampling

9.1 Collect the sample in accordance with the applicable ASTM standard as follows: Specification D 1192 or Practices D 3370.

9.2 Preserve the samples with high purity hydrochloric acid to a pH of two or less immediately at the time of collection (2 mL/L).

10. Calibration

10.1 Prepare standards by adding 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 mL of sulfate standard solution (1 mL = 1.00 mg $SO_4{}^{=}$) to separate 100 mL graduated mixing cylinders. Add 5.0 mL of glycerin-acid solution and 40.0 mL of sodium chloride solution (5 mol) to each of the cylinders and dilute to 100 mL with water. Adjust the temperature of these solutions to 25 ± 2°C. These solutions will contain 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 mg of sulfate ion, respectively.

10.2 Follow the procedure as given in 11.6-11.8. Prepare a calibration curve showing sulfate ion content in milligrams on the linear axis with the corresponding percent transmittance (%*T*) reading of the photometer on the logarithmic axis of a one cycle semilogarithmic graph paper (Note 2).

NOTE 2—The plot of concentration versus %*T* is not linear but shows a slight s curvature. A separate calibration curve must be prepared for each photometer and a new curve must be prepared if it is necessary to change the photo cell, lamp, filter, or if any other alterations of the instrument or reagents are made. Check the curve with each series of tests by running two or more solutions of known sulfate concentrations.

11. Procedure

11.1 Filter the sample through a 0.45-µm membrane filter. This is necessary to remove nucleating particles.

11.2 Pipet a volume of filtered sample not to exceed 50 mL and 10 mg $SO_4{}^{2-}$ into a 100-mL graduated mixing cylinder. The ionic strength (IS) of the sample when diluted to 100 must not exceed 2.00 mol/L.

11.3 Add 5 mL of glycerin-acid solution.

11.4 Add by a graduated pipet or a buret a volume of sodium chloride solution (5 mol) calculated as follows:

$$mL\ NaCl = (200 - (V \times IS)/5$$

V = volume of sample, and
IS = ionic strength of sample as calculated in Note 1, 4.1.

11.5 Dilute with water to 100 mL, mix well, and adjust the temperature to 25 ± 2°C.

NOTE 3—The temperature of the solution in the mixing cylinder during the development and measurement of the turbidity must be within 2°C of the temperature of the standards when the calibration was performed. A higher temperature will result in a positive error, a lower temperature in a negative error.

11.6 Pipet a 25-mL aliquot of the sample solution into a sample cell and place it in the cell compartment. Set the photometer to 100 % *T* (transmittance) with the wavelength set at 425 nm or blue filter in place.

11.7 Add 0.3 ± 0.01 g of $BaCl_2{\cdot}2H_2O$ crystals to the 75 mL remaining in the mixing cylinder, stopper, set a timer for 5 min, and mix for 30 s by inverting and righting the cylinder 15 times.

NOTE 4—It is important the mixing be performed at a constant rate and duplicated in all determinations.

11.8 Just before 5 min has expired, check the blank setting. Adjust to 100 %*T* if drifting has occurred. Replace the blank with the sample cell and measure turbidity at 5 min. If the % *T* is greater than 80 % or less than 30 % *T,* the determination with a smaller or larger sample volume providing the restrictions in step 11.2 are not violated.

NOTE 5—The most reproducible section of the calibration curve is from 80 to 30 % *T.* Very low concentrations of sulfate ion can be determined by adding 3 mL of sulfate standard (1 mL = 1.00 mg $SO_4{}^{2-}$) before diluting to 100 mL in step 11.5 and then subtracting the 3 mg $SO_4{}^{2-}$ from the final results.

[5] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia*.