



Designation: **D4130—08 D4130 – 15**

Standard Test Method for Sulfate Ion in Brackish Water, Seawater, and Brines¹

This standard is issued under the fixed designation D4130; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope—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 **D516**.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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:*²

D516 Test Method for Sulfate Ion in Water

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D3370 Practices for Sampling Water from Closed Conduits

D5810 Guide for Spiking into Aqueous Samples

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids <https://standards.iteh.ai/>

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1129**.

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:

$$IS, \text{ mol/L} = 1/2 \sum C_i Z_i^2,$$

$$C_i = \text{g/L ion } i/\text{molecular weight ion, } i, \text{ and}$$

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. Current edition approved Nov. 15, 2008; Feb. 1, 2015. Published November 2008; April 2015. Originally approved in 1982. Last previous edition approved in 2003, 2008 as **D4130—03; D4130—08**. DOI: 10.1520/D4130-08; 10.1520/D4130-15.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

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).

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 [E275](#).

7.2 *Thermometer*—An ASTM Gravity Thermometer having a range from -20 to $+102^\circ\text{C}$ (or -5 to $+215^\circ\text{F}$), as specified, and conforming to the requirements for Thermometer ASTM 12C (or ASTM 12F), respectively, as prescribed in Specification [E2251](#).

8. Reagents and Materials

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.³ 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 [D1193](#), [D1129](#), 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 ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) screened to 20 to 70 mesh.

8.4 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45- μm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

8.5 *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.

8.6 *Sodium Chloride Solution (5 mol/L)*—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.

8.7 *Sulfate Solution, Standard* (1 mL = 1.00 mg SO_4^{2-})—Dissolve 1.479 g of anhydrous sodium sulfate, (Na_2SO_4), in water and dilute to 1 L in a volumetric flask. Alternatively, certified sulfate stock solutions of appropriate known purity are commercially available through chemical supply vendors and may be used.

9. Sampling

9.1 Collect the sample in accordance with Practices [D3370](#).

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).

NOTE 2—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

10. Calibration

10.1 Analyze at least three working standards containing concentrations of sulfate that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument. 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 ([8.7](#)) solution (1 mL = 1.00 mg SO_4^{2-}) to separate 100 mL graduated mixing cylinders. Add 5.0

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

mL of glycerin-acid (8.5) solution and 40.0 mL of sodium chloride (8.6) solution (5 mol/L) to each of the cylinders and dilute to 100 mL with water. Adjust the temperature of these solutions to $25 \pm 2^\circ\text{C}$. 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~~ Read directly in concentration if this capability is provided with the instrument. Alternatively, prepare a semi-log plot and 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 23).

NOTE 3—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. ~~filter (8.4).~~ 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 (8.5) solution.

11.4 Add by a graduated pipet or a buret a volume of sodium chloride (8.6) solution (5 mol/L) calculated as follows:

$$\text{mL NaCl} = 200 - (V \times IS)5$$

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 $25 \pm 2^\circ\text{C}$.

NOTE 4—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 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals (8.3) 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 5—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. ~~setting (sample from 11.6 without the BaCl_2).~~ 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 6—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.

12. Calculation

12.1 Convert the photometer reading to mg SO_4^{2-} by referring to the calibration curve. Calculate the sulfate ion concentration as follows:

$$\text{Sulfate, mg/L} = W \times 1000/V$$

$\frac{1000}{W} \equiv \frac{1000 \text{ mL/L}}{\text{mL}}$,

W = milligram SO_4^{2-} from the calibration curve, and

V = sample volume, mL.

13. Precision and Bias⁴

13.1 The overall and single-operator precision of this test method within its designated range for brackish water, seawater, and brines varies with the quantity tested in accordance with Table 1.

13.2 These collaborative test data were obtained on synthetic brine waters. For other matrixes, these data may not apply. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

13.3 The bias of the method determined in synthetic brine is presented in Table 1.

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1077. Contact ASTM Customer Service at service@astm.org.