Designation: D4130 – 15

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

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 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 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

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, mol/L = $1/2 \sum C_i Z_i^2$,
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 ($BaSO_4$).

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.

[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] 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**

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°C (or –5 to +215°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 ($BaCL_2 \cdot 2H_2O$) 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 $SO_4^{=}$)—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 $SO_4^{=}$) to separate 100 mL graduated mixing cylinders. Add 5.0 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 ± 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. 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 (Note 3).

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 (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 ± 2°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

[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.

TABLE 1 Determination of Precision and Bias

Amount Added, mg/L	Amount Found, mg/L	S_T	S_O	% Bias	Statistically Significant (95 % confidence level)
60.3	61.7	9.35	2.47	+2.32	no
86.3	83.9	6.98	2.45	–2.78	no
128.9	126.1	6.15	2.67	–2.17	no

TABLE 2 Composition of Synthetic Brine Samples

Sample No.	g/L		
	1	2	3
NaCl	47.74	61.04	95.33
$CaCl_2$	27.22	40.85	54.47
$MgCl_2$	3.84	7.68	7.71
$SO_4^{=}$	0.0863	0.1289	0.0603

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 (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 (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:

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

1000 = 1000 mL/L,
W = milligram SO_4^{2-} from the calibration curve, and
V = sample volume, mL.

13. Precision and Bias[4]

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.

13.4 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

NOTE 7—The precision and bias estimates are based on an interlaboratory study on three synthetic brine samples containing various amounts of sulfate and other inorganic compounds as shown in Table 2. One analyst in five laboratories and two analysts in each of two laboratories performed single determinations on each of three days. Practice D2777, was used in developing these precision and bias estimates.

14. Quality Control

14.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing sulfate.

14.2 *Calibration and Calibration Verification:*

14.2.1 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 (see 10.1).

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of sulfate. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

[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.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in 13.1. This study should be repeated until the recoveries are within the limits given in 13.1. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of sulfate with each batch (laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

14.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of sulfate found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of sulfate is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of sulfate and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of sulfate must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV$$

where:

A = analyte known concentration (mg/L) in spiked sample,
B = analyte known concentration (mg/L) in unspiked sample,
C = known concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

14.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Test Method D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 8—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Test Method D5810 for additional information.

14.7 *Duplicate:*

14.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

14.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.8 *Independent Reference Material (IRM):*

14.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

15.1 brackish; brine; seawater; sulfate

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D4130 – 08) that may impact the use of this standard. (Approved Feb. 1, 2015.)

(1) Revised Section 2 to included Specification E2251.
(2) Revised Section 7 to include the thermometer reference.
(3) Revised Section 8 to allow for commercial standards and filter paper information and to correct errors.
(4) Revised Section 9 to allow for pH of the samples in the laboratory.
(5) Revised Section 10 with calibration information, to allow for direct reading instruments or a computer, and to correct errors.
(6) Revised Section 11 to add reagent references, clarify solutions used for blank setting, and correct errors.
(7) Revised 14.2.4 and 14.6.3.