Designation: D516 – 22

Standard Test Method for Sulfate Ion in Water[1]

This standard is issued under the fixed designation D516; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 This turbidimetric test method covers the determination of sulfate in water in the range from 5 mg/L to 40 mg/L of sulfate ion (SO_4^{--}).

1.2 This test method was used successfully with drinking, ground, and surface waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 Former gravimetric and volumetric test methods have been discontinued. Refer to Appendix X1 for historical information.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
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 Flowing Process Streams
D4327 Test Method for Anions in Water by Suppressed Ion Chromatography
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

4. Summary of Test Method

4.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. A solution containing glycerin and sodium chloride is added to stabilize the suspension and minimize interferences. The resulting turbidity is determined by a nephelometer, spectrophotometer, or photoelectric colorimeter and compared to a curve prepared from standard sulfate solutions.

5. Significance and Use

5.1 The determination of sulfate is important because it has been reported that when this ion is present in excess of about 250 mg/L in drinking water, it causes a cathartic action (especially in children) in the presence of sodium and magnesium, and gives a bad taste to the water.

5.2 Test Method D4327 ("Test Method of Anions in Water by Suppressed Ion Chromatography") may be used.

6. Interferences

6.1 Insoluble 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.

Current edition approved Dec. 1, 2022. Published March 2023. Originally approved in 1938. Last previous edition approved in 2016 as D516 – 16. DOI: 10.1520/D0516-22.

[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**

6.2 Polyphosphates as low as 1 mg/L will inhibit barium sulfate precipitation causing a negative interference. Phosphonates present in low concentrations, depending on the type of phosphonate, will also cause a negative interference.

6.3 Silica in excess of 500 mg/L may precipitate along with the barium sulfate causing a positive interference.

6.4 Chloride in excess of 5000 mg/L will cause a negative interference.

6.5 Aluminum, polymers, and large quantities of organic material present in the test sample may cause the barium sulfate to precipitate nonuniformly.

6.6 In the presence of organic matter certain bacteria may reduce sulfate to sulfide. To minimize the action of sulfate reducing bacteria, samples should be refrigerated at 4 °C when the presence of such bacteria is suspected.

6.7 Although other ions normally found in water do not appear to interfere, the formation of the barium sulfate suspension is very critical. Determinations that are in doubt may be checked by a gravimetric method in some cases, or by the procedure suggested in 11.2.1.

7. Apparatus

7.1 *Photometer*—One of the following which are given in order of preference.

7.1.1 Nephelometer or turbidimeter;

7.1.2 Spectrophotometer for use at 420 nm with light path of 4 cm to 5 cm;

7.1.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 cm to 5 cm.

7.2 *Stopwatch,* if the magnetic stirrer is not equipped with an accurate timer.

7.3 *Measuring Spoon,* capacity 0.2 mL to 0.3 mL.

7.4 Filter photometers and photometric practices prescribed in this test method shall conform to Practice E60; spectrophotometer practices shall conform to Practice E275.

7.5 *Laboratory Glassware*—All glassware should be in good condition, clean, and free of contaminating substances.

7.5.1 If the testing is for regulatory purposes, volumetric flasks should be of Type A precision and serialized for quality control tracking.

7.6 *Stirring Apparatus*—A magnetic stirrer should be used along with a magnetic stir bar appropriately sized for the labware in use.

7.7 *Weighing Apparatus*—A scale or analytical balance of the appropriate accuracy and precision should be used. It should be calibrated and within its calibration interval.

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.[3] Other grades may be used, provided 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, 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 II water was specified at the time of round robin testing of this test method.

8.3 *Barium Chloride*—Crystals of barium chloride ($BaCl_2 \cdot 2H_2O$) screened to 20 to 30 mesh. To prepare in the laboratory, spread crystals over a large watch glass, desiccate for 24 h, screen to remove any crystals that are not 20 to 30 mesh, and store in a clean, dry jar.

8.4 *Conditioning Reagent*—Place 30 mL of concentrated hydrochloric acid (HCl, sp gr 1.19), 300 mL reagent water, 100 mL 95 % ethanol or isopropanol and 75 g sodium chloride (NaCl) in a container. Add 50 mL glycerol and mix.

8.5 *Sulfate Solution, Standard* (1 mL = 0.100 mg SO_4^{--})—Dissolve 0.1479 g of anhydrous sodium sulfate (Na_2SO_4) in water, and dilute with water to 1 L in a volumetric flask. A purchased stock solution of adequate purity is also acceptable.

8.6 *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.

9. Sampling

9.1 Collect the sample in accordance with Practice D1066, and Practices D3370, as applicable.

10. Calibration

10.1 Follow the procedure given in Section 11, using appropriate amounts of the standard sulfate solution prepared in accordance with 8.5 and prepare a calibration curve showing sulfate ion content in milligrams per litre plotted against the corresponding photometer readings (10.2).

10.2 Prepare standards by diluting with water 0.0 mL, 5.0 mL, 10.0 mL, 15.0 mL, 20.0 mL, 30.0 mL, and 40.0 mL of standard sulfate solution to 100 mL volumes in volumetric flasks. These solutions will have sulfate ion concentrations of 0.0 mg/L, 5.0 mg/L, 10.0 mg/L, 15.0 mg/L, 20.0 mg/L, 30.0 mg/L, and 40.0 mg/L (ppm), respectively.

10.2.1 A separate calibration curve must be prepared for each photometer and a new curve must be prepared if it is

[3] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, 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 and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

necessary to change the cell, lamp, or filter, or if any other alterations of 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 (8.6) the sample if it is turbid through a 0.45 µm membrane and adjust the temperature to between 15 °C and 30 °C.

11.2 Pipette into a 250 mL beaker 100 mL or less of the clear sample containing between 0.5 mg and 4 mg of sulfate ion (11.2.1). Dilute to 100 mL with water if required, and add 5.0 mL of conditioning reagent (10.2.1).

11.2.1 The solubility of $BaSO_4$ is such that difficulty may be experienced in the determination of sulfate concentrations below about 5 mg/L (ppm). This can be overcome by concentrating the sample or by adding 5 mL of standard sulfate solution (1 mL = 0.100 mg SO_4^{--}) to the sample before diluting to 100 mL. This will add 0.5 mg SO_4 to the sample, which must be subtracted from the final result.

11.3 Mix in the stirring apparatus.

11.4 While the solution is being stirred, add a measured spoonful of $BaCl_2$ crystals (0.3 g) and begin timing immediately.

11.5 Stir exactly 1.0 min at constant speed.

NOTE 1—The stirring should be at a constant rate in all determinations. The use of a magnetic stirrer has been found satisfactory for this purpose.

11.6 Immediately after the stirring period has ended, pour solution into the cell and measure the turbidity at 30-s intervals for 4 min. Record the maximum reading obtained in the 4-min period.

11.7 If the sample contains color or turbidity, run a sample blank using the procedure 11.2 through 11.6 without the addition of the barium chloride.

11.8 If interferences are suspected, dilute the sample with an equal volume of water, and determine the sulfate concentration again. If the value so determined is one half that in the undiluted sample, interferences may be assumed to be absent.

11.8.1 After dilution, if interferences are still determined to be present alternate methods should be used. It is up to the user to determine appropriate alternate methods.

12. Calculation

12.1 Convert the photometer readings obtained with the sample to milligrams per litre sulfate ion (SO_4^{--}) by use of the calibration curve described in Section 10.

13. Precision and Bias[4]

13.1 The precision and bias data presented in this test method meet the requirements of Practice D2777 – 86.

13.2 The overall and single-operator precision of the test method, within its designated range, varies with the quantity being tested according to Table 1 for reagent water and Table 2 for drinking, ground, and surface waters.

13.2.1 Seven laboratories participated in the round robin at three levels in triplicate, making a total of 21 observations at each level for reagent water and for matrix water (drinking, ground, and surface water).

13.3 Recoveries of known amounts of sulfate from reagent water and drinking, ground, and surface waters are as shown in Table 3.

13.3.1 A table for estimating the bias of the test method through its applicable concentration range can be found in Table 4.

13.3.2 These collaborative test data were obtained on reagent grade water and natural waters. For other matrices, these data may not apply.

13.4 Precision and bias for this test method conforms to Practice D2777 – 86, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control (QC)

14.1 The following quality control information is recommended for the determination of sulfate ion in water.

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 Section 11). The calibration correlation coefficient shall be equal to or greater than 0.990.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

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.

TABLE 1 Overall (S_T) and Single-Operator (S_O) Standard Deviations Against Mean Concentration for Interlaboratory Recovery of Sulfate from Reagent Water[A]

Mean Concentration ($\bar{x}$), mg/L	Standard Deviation, mg/L	
	S_T	S_O
6.6	0.5	0.1
20.4	1.0	0.4
63.7	2.5	1.3

[A] The test method is linear to 40 mg/L. Testing at the 63.9 level was accomplished through dilution as described in 11.2.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1145. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Overall (S_T) and Single-Operator (S_O) Standard Deviations Against Mean Concentration for Interlaboratory Recovery of Sulfate from Drinking, Ground, and Surface Water[A]

Mean Concentration ($\bar{x}$), mg/L	Standard Deviation, mg/L	
	S_T	S_O
6.9	0.7	0.5
20.2	2.2	1.8
63.3	4.5	1.6

[A] The test method is linear to 40 mg/L. Testing at the 63.9 level was accomplished through dilution as described in 11.2.

TABLE 3 Determination of Bias[A]

	Amount Added, mg/L	Amount Found, mg/L	±Bias	±% Bias	Statistically Significant at 5 % Level (at ±0.05)
Reagent water	20.8	20.4	−0.4	−1.9 %	no
	63.9[A]	63.7[A]	−0.2	−0.2 %	no
	7.0	6.6	−0.4	−5.3 %	no
Drinking, ground and surface water	20.8	20.2	−0.6	−2.7 %	no
	63.9[A]	63.3[A]	−0.6	−0.9 %	no
	7.0	6.9	−0.1	−1.8 %	no

[A] The test method is linear to 40 mg/L. Testing at the 63.9 level was accomplished through dilution as described in 11.2.

TABLE 4 Mean Sulfate Recovery Against Concentration Added with Overall Standard Deviation Shown for Interlaboratory Experimental Recovery of Sulfate from Reagent Water and Drinking, Ground, and Surface Water[A]

Sulfate Added, mg/L	Mean Sulfate Recovery ($\bar{x}$), mg/L	
	Reagent Water (S_T)	Matrix Water (S_O)
7.0	6.6 (0.5)	6.9 (0.7)
20.8	20.4 (1.0)	20.2 (2.2)
63.9	63.7 (2.5)	63.3 (4.5)

[A] The test method is linear to 40 mg/L. Testing at the 63.9 level was accomplished through dilution as described in 11.2.

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, and so forth, 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 midrange 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.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 3. This study should be repeated until the recoveries are within the limits given in Table 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 known concentration of sulfate with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range 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 formula:

$$P = [A\ (V_s + V) - BV_s]/CV \quad (1)$$

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 Guide 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