Designation: D 516 – 02

An American National Standard

Standard Test Method for Sulfate Ion in Water[1]

This standard is issued under the fixed designation D 516; 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 turbidimetric test method covers the determination of sulfate in water in the range from 1 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 *This standard does not purport to address 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 1066 Practice for Sampling Steam[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 5847 Practice for Writing Quality Control Specifications for Standard Test Methods of Water Analysis[3]

E 60 Practice for Photometric and Spectrophotometric Methods for the Chemical Analysis of Metals[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[5]

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 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.

6. Interferences

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

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. Silica in excess of 500 mg/L may precipitate along with the barium sulfate causing a positive interference. Chloride in excess of 5000 mg/L will cause a negative interference. Aluminum, polymers, and large quantities of organic material present in the test sample may cause the barium sulfate to precipitate nonuniformly. 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.

6.3 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 Note 2.

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[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 03.05.

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

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 to 5 cm;

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

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

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

7.4 Filter photometers and photometric practices prescribed in this test method shall conform to Practice E 60; spectrophotometer practices 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.[6] 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 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 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.

9. Sampling

9.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, and Practices D 3370, 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 (Note 1). Prepare standards by diluting with water 0.0, 2.0, 5.0, 10.0, 15.0, 20.0, 30.0, 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, 2.0, 5.0, 10.0, 15.0, 20.0, 30.0, and 40.0 mg/L (ppm), respectively.

NOTE 1—A separate calibration curve must be prepared for each photometer and a new curve must be prepared if it is 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 the sample if it is turbid, and adjust the temperature to between 15 and 30°C.

11.2 Pipet into a 250-mL beaker 100 mL or less of the clear sample containing between 0.5 and 4 mg of sulfate ion (Note 2). Dilute to 100 mL with water if required, and add 5.0 mL of conditioning reagent (Note 1).

NOTE 2—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 3—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.

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 [7]

13.1 The precision and bias data presented in this test method meet the requirements of Practice D 2777 – 86.

13.2 The overall and single-operator precision of the test method, within its designated range, varies with the quantity

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[6] *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[7] Supporting data are available from ASTM. Request RR:D-19-1145.

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 D 2777–86, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777–98, 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.

14.1.1 The instrument should be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank should be analyzed at the end of the batch run to ensure contamination ws not a problem during the batch analysis.

14.1.2 An instrument check standard should be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the instrument check standard should fall between 80 and 120 % of the true value.

14.1.3 Two method blanks should be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

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.

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.

14.1.4 A Laboratory Control Sample should be analyzed with each batch of samples at a minimum frequency of 10 %.

14.1.5 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both. (See Practice D 5847.)

14.1.6 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

15. Keywords

15.1 drinking water; ground water; sulfate; surface water; turbidimetric

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF METHODS

X1.1 *Gravimetric:*

X1.1.1 This test method was discontinued in 1988. The test method may be found in the *1988 Annual Book of ASTM Standards*, Vol 11.01. The test method was originally issued in 1938.

X1.1.2 This test method covers the determination of sulfate in water and wastewater. Samples containing from 20 to 100 mg/L of sulfate may be analyzed.

X1.1.3 Sulfate is precipitated and weighted as barium sulfate after removal of silica and other insoluble matter.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

X1.2 *Volumetric:*

X1.2.1 This test method was discontinued in 1988. The test method may be found in the *1988 Annual Book of ASTM Standards*, Vol 11.01. The test method was originally issued in 1959 as a non-referee method, and made the primary method in the 1980 issue of Test Method D 516.

X1.2.2 This test method covers the determination of sulfate in industrial water. Samples containing from 5 to 1000 mg/L of sulfate may be analyzed.

X1.2.3 Sulfate is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution using thorin as the indicator.

X1.2.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.