



Designation: D 859 – 9400

## Standard Test Method for Silica in Water <sup>1</sup>

This standard is issued under the fixed designation D 859; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

### 1. Scope

1.1 This test method covers the determination of silica in water and waste water; however, the analyst should recognize that the precision and accuracy statements for reagent water solutions may not apply to waters of different matrices.

1.2 This test method is a colorimetric method that determines molybdate-reactive silica. It is applicable to most waters, but some waters may require filtration and dilution to remove interferences from color and turbidity. This test method is useful for concentrations as low as 20  $\mu\text{g/L}$ .

1.3 This test method covers the photometric determination of molybdate-reactive silica in water. Due to the complexity of silica chemistry, the form of silica measured is defined by the analytical method as molybdate-reactive silica. Those forms of silica that are molybdate-reactive include dissolved simple silicates, monomeric silica and silicic acid, and an undetermined fraction of polymeric silica.

1.4 The useful range of this test method is from 20 to 1000  $\mu\text{g/L}$  at the higher wavelength (815 nm) and 0.1 to 5 mg/L at the lower wavelength (640 nm). It is particularly applicable to treated industrial waters. It may be applied to natural waters and wastewaters following filtration or dilution, or both. For seawater or brines, this test method is applicable only if matched matrix standards or standard addition techniques are employed.

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.*

NOTE 1—For many natural waters, a measurement of molybdate-reactive silica by this test method provides a close approximation of total silica, and, in practice, the colorimetric method is frequently substituted for other more time-consuming techniques. This is acceptable when, as frequently occurs, the molybdate-reactive silica is in the *milligram* per litre concentration range while the nonmolybdate-reactive silica, if present at all, is in the microgram per litre concentration range.

1.6 Former Test Method A (Gravimetric—Total Silica) was discontinued. Refer to Appendix X1 for historical information.

### 2. Referenced Documents

2.1 *ASTM Standards:*

---

<sup>1</sup> 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 ~~May 15, 1994~~; June 10, 2000. Published ~~July 1994~~; September 2000. Originally published as D 859 – 45 T. Last previous edition D 859 – 8894.

- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>2</sup>
- D 5810 Standard Guide for Spiking into Aqueous Samples<sup>2</sup>
- D 5847 Standard Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>2</sup>
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals<sup>3</sup>
- E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers<sup>3</sup>

### 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 This test method is based on the reaction of the soluble silica with molybdate ion to form a greenish-yellow complex, which in turn is converted to a blue complex by reduction with 1-amino-2-naphthol-1-sulfonic acid.

### 5. Significance and Use

5.1 Silicon comprises about 28 % of the lithosphere and is, next to oxygen, the most abundant element. It is found as the oxide in crystalline forms, as in quartz; combined with other oxides and metals in a variety of silicates; and in amorphous forms. Silicon is the most abundant element in igneous rocks and is the characteristic element of all important rocks except the carbonates. It is the skeletal material of diatoms but is not known to play a significant role in the structure of processes of higher life forms.

5.2 Silica is only slightly soluble in water. The presence of most silica in natural waters comes from the gradual degradation of silica-containing minerals. The type and composition of the silica-containing minerals in contact with the water and the pH of the water are the primary factors controlling both the solubility and the form of silica in the resulting solution. Silica may exist in suspended particles, as a colloid, or in solution. It may be monomeric or polymeric. In solution it can exist as silicic acid or silicate ion, depending upon pH. The silica content of natural waters is commonly in the 5 to 25 mg/L range, although concentrations over 100 mg/L occur in some areas.

5.3 Silica concentration is an important consideration in some industrial installations such as steam generation and cooling water systems. Under certain conditions, silica forms troublesome silica and silicate scales, particularly on high-pressure steam turbine blades. In cooling water systems, silica forms deposits when solubility limits are exceeded. In contrast, silica may be added as a treatment chemical in some systems, for example, in corrosion control. Silica removal is commonly accomplished by ion exchange, distillation, reverse osmosis, or by precipitation, usually with magnesium compounds in a hot or cold lime softening process.

### 6. Interferences

6.1 Color and turbidity will interfere if not removed by filtration or dilution.

6.2 The only specific substance known to interfere in the color reaction is phosphate. Phosphate interference is eliminated by the addition of oxalic acid.

6.3 A high dissolved salts concentration, such as in seawater or brine samples, can affect color development. This can be compensated for by preparing standards in a matrix similar to that of samples or by using a standard additions technique.

6.4 Strong oxidizing and reducing agents that may be found in some industrial waste waters may interfere in the reduction step of the reaction. Such waste waters may also contain organic compounds that may interfere in the color formation.

### 7. Apparatus

7.1 *Spectrophotometer or Filter Photometer* (see Note 2)— To obtain maximum sensitivity and reproducibility, a spectrophotometer suitable for measurements at 815 nm is required. Measurements may be made at 640 nm with a spectrophotometer, or 640 to 700 nm with a filter photometer if less sensitivity is preferred. Precision and bias information on this test method (see Section 14) is based on data obtained at 815 nm.

NOTE 2—Photometers and photometric practices shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

7.2 *Sample Cells*— The cell size to be used depends on the range covered and the particular instrument used. The higher concentration range should be attainable with 10-mm path length cells. Longer path length cells (40 to 50 mm) are recommended for concentrations below 0.1 mg/L.

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 03.05.

## 8. Reagents and Materials

NOTE 3—Store all reagents to be used in this test method in polyethylene or other suitable plastic bottles.

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.<sup>4</sup> 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, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II. In addition, the water shall be made silica-free by distillation or demineralization and determined as such in accordance with the method of test being used. The collecting apparatus and storage containers for the reagent water must be polyethylene or other suitable plastic.

8.3 *Amino-Naphthol-Sulfonic Acid-Solution*—Dissolve 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in 50 mL of a solution containing 1 g of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ). After dissolving, add the solution to 100 mL of a solution containing 30 g of sodium hydrogen sulfite ( $\text{NaHSO}_3$ ). Make up to 200 mL and store in a dark, plastic bottle. Shelf life of this reagent may be extended by refrigeration. Solution should be adjusted to room temperature,  $25 \pm 5^\circ\text{C}$ , before use. Discard when the color darkens or a precipitate forms.

8.4 *Ammonium Molybdate Solution (75 g/L)* (Note 4)—Dissolve 7.5 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) in 100 mL of water.

NOTE 4—Batch to batch variations in ammonium molybdate have been found to affect results at low concentrations (below 0.1 mg/L). High blanks, nonlinear calibration curves, and poor reproducibility have been observed with some batches of this compound. When working with low concentrations of silica, a batch of ammonium molybdate known to produce reasonable blanks, linearity, and reproducibility should be set aside for this purpose.

8.5 *Hydrochloric Acid (1 + 1)*—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

8.6 *Oxalic Acid Solution (100 g/L)*—Dissolve 10 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) in 100 mL of water.

8.7 *Silica Solution, Standard (1 mL = 0.1 mg  $\text{SiO}_2$ )*— Dissolve 0.473 g of sodium metasilicate ( $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ ) in water and dilute to 1 L. Check the concentration of this solution gravimetrically.<sup>5</sup>

NOTE 5—This solution may require filtration to remove fine particulate matter containing silica. This filtration, if needed, should precede standardization gravimetrically.<sup>5</sup> This step was not included as a requirement in the collaborative tests from which precision and bias determined.

## 9. Sampling

9.1 Collect the samples in accordance with Practice D 1066 or Practices D 3370, as applicable.

9.2 Use plastic or stainless steel sample bottles, provided with rubber or plastic stoppers.

9.3 If the water being sampled is at elevated temperature, cool to less than  $35^\circ\text{C}$  but *do not freeze*.

9.4 The holding time for the samples may be calculated in accordance with Practice D 4841.

## 10. Quality Control (QC)

10.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test.

### 10.2 Calibration and Calibration Verification

10.2.1 When beginning use of this method, an initial Calibration Verification Standard (CVS) should be used to verify the calibration standards and acceptable instrument performance. This verification should be performed on each analysis day. The CVS is a solution of method analytes of known concentration (mid-calibration range) used to fortify reagent water. If the determined CVS concentrations are not within  $\pm 15\%$  of the known values, the analyst should reanalyze the CVS. If the values still fall outside acceptable limits, a new calibration curve is required which must be confirmed by a successful CVS before continuing with on-going analyses.

10.2.2 One CVS should then be run with each sample batch (maximum of 20 samples) to verify the previously established calibration curves. If the determined analyte concentrations fall outside acceptable limits ( $\pm 15\%$ ) that analyte is judged out of control, and the source of the problem should be identified before continuing with on-going analyses.

### 10.3 Initial Demonstration of Laboratory Capability

10.3.1 The laboratory using this test should perform an initial demonstration of laboratory capability. Analyze seven replicates of an Initial Demonstration of Performance (IDP) solution. The IDP solution contains method analytes of known concentration, prepared from a different source to the calibration standards, used to fortify reagent water. Ideally, the IDP solution should be prepared by an independent source from reference materials. The level 2 spiking solution used for the precision and bias study is a suitable IDP solution.

<sup>4</sup> *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.

<sup>5</sup> Refer to former Test Method A (Gravimetric—Total Silica) last published in the 1988 *Annual Book of ASTM Standards* for complete description of procedure.

The mean and standard deviation of the seven values should then be calculated and compared, according to Standard D 5847, to the single operator precision and recovery established for this Test Method. The upper limit for acceptable precision and the range of acceptable recoveries are detailed below:

Analyte	IDP Solution Amount	Method $S_0$	Acceptable IDP Precision, $n = 7$
Silica	115 µg/L	1.0 µg/L	≤ 1.7 µg/L

  

Analyte	Method Mean Recovery	Lower Acceptable IDP Recovery	Upper Acceptable IDP Recovery
Silica	112.2 µg/L	97.0 µg/L	127.4 µg/L

#### 10.4 Laboratory Control Sample

10.4.1 One Laboratory Control Sample (LCS) should be run with each sample batch (maximum of 20 samples). The LCS is a solution of method analytes of known concentration added to a matrix which sufficiently challenges the Test Method. A synthetic “water” matrix of relevance to the user (e.g., drinking water or wastewater) spiked with the method analytes at the level of the IDP solution would be an example of an appropriate LCS.

The analyte recoveries for the LCS should fall within the control limits of  $x \pm 3S$ , where  $x$  is the IDP amount and ( $S$ ) is the standard deviation of the mean recovery established from the interlaboratory precision and bias study data at the IDP levels, as shown below:

Analyte	LCS Amount	Lower Recovery Limit	Upper Recovery Limit
Silica	115 µg/L	112 µg/L	118 µg/L

#### 10.5 Method Blank

10.5.1 A reagent blank should be run when generating the initial calibration curves. A blank should also be run with each sample batch (maximum of 20 samples) to check for sample or system contamination.

#### 10.6 Matrix Spike

10.6.1 One Matrix Spike (MS) should be run with each sample batch (maximum of 20 samples) to test method recovery. The MS should be prepared in accordance with Guide D 5810. Spike a portion of a water (or other) sample from each batch with the method analytes at the level of the IDP solution. The % recovery of the spike should fall within limits established from the interlaboratory precision and bias study data (assuming a background level of zero), according to Standard D 5847, as shown below:

Analyte	MS Amount	Lower Recovery Limit (%)	Upper Recovery Limit (%)
Silica	115 µg/L	82.5%	112.7%

#### 10.7 Duplicate

10.7.1 One Matrix Duplicate (MD) should be run with each sample batch (maximum of 20 samples) to test method precision. If non-detects are expected in all the samples to be analyzed, a Matrix Spike Duplicate should be run instead. The precision of the duplicate analysis should be compared, according to Standard D 5847, to the nearest tabulated  $S_0$  value established from the interlaboratory precision and bias study data for each analyte.

#### 10.8 Independent Reference Material

10.8.1 In order to verify the quantitative values produced by the test method, an Independent Reference Material (IRM), submitted to the laboratory as a regular sample (if practical), should be analyzed once per quarter. The concentration of the IRM should be within the scope of the method, as defined in 1.4. The values obtained must fall within the limits specified by the outside source.

### 11. Calibration and Standardization

101.1 Prepare a series of at least four standards covering the desired concentration range by proper dilution of the standard silica solution (see 8.7). Treat 50.0-mL aliquots of the standards in accordance with 1+2.1-1+2.3. Prepare a blank using a 50.0-mL aliquot of water that has been similarly treated.

101.2 For standards in the 20 to 1000 µg/L range, set the spectrophotometer at 815 nm and read the absorbance of each standard against the reagent blank. For standards in the 0.1 to 5 mg/L range, set the spectrophotometer at 640 nm (filter photometer 640 to 700 nm).

**TABLE 1 Overall ( $S_T$ ) and Single-Operator ( $S_0$ ) Interlaboratory Precision for Silica**

Mean Concentration (X), µg/L	$S_T$ , µg/L	$S_0$ , µg/L
38.6	3.4	0.8
112.2	5.8	1.0
381.8	10.0	1.7
941.8	30.0	5.9

**TABLE 2 Recovery**

Amount Added, µg SiO <sub>2</sub> /L	Amount Found, µg SiO <sub>2</sub> /L	Bias, %	Statistically Significant 95 % Level
951	941.8	-1.0	no
381	381.8	+ 0.2	no
115	112.2	-2.4	no
39	38.6	- 1.0	no

101.3 Prepare a calibration curve for measurements at 815 nm by plotting absorbance versus micrograms SiO<sub>2</sub> per litre on linear graph paper. For measurements at 640 nm, plot absorbance versus milligrams SiO<sub>2</sub> per litre.

### 11. Procedure

11.1 Transfer quantitatively 50.0 mL (or an aliquot diluted to 50 mL) of the sample that has been filtered through a 0.45-µm membrane filter, if necessary, to remove turbidity, to a polyethylene or other suitable plastic container and add, in quick succession, 1 mL of HCl (1 + 1) and 2 mL of the ammonium molybdate solution. Mix well.

11.2 After exactly 5 min, add 1.5 mL of oxalic acid solution and again mix well.

11.3 After 1 min, add 2 mL of amino-naphthol-sulfonic acid solution. Mix well and allow to stand for 10 min.

11.4 Prepare a reagent blank by treating a 50.0-mL aliquot of water as directed in 11.1-11.3.

11.5 Measure the absorbance of the sample at 815 nm against the reagent blank (or at 640 nm for higher concentrations).

### 12. Procedure

12.1 Transfer quantitatively 50.0 mL (or an aliquot diluted to 50 mL) of the sample that has been filtered through a 0.45-µm membrane filter, if necessary, to remove turbidity, to a polyethylene or other suitable plastic container and add, in quick succession, 1 mL of HCl (1 + 1) and 2 mL of the ammonium molybdate solution. Mix well.

12.2 After exactly 5 min, add 1.5 mL of oxalic acid solution and again mix well.

12.3 After 1 min, add 2 mL of amino-naphthol-sulfonic acid solution. Mix well and allow to stand for 10 min.

12.4 Prepare a reagent blank by treating a 50.0-mL aliquot of water as directed in 12.1-12.3.

12.5 Measure the absorbance of the sample at 815 nm against the reagent blank (or at 640 nm for higher concentrations).

### 13. Calculation

123.1 Silica concentration in micrograms SiO<sub>2</sub> per litre may be read directly from the calibration curve at 815 nm prepared in 101.3. For measurements made at 640 nm, silica concentration may be read directly in milligrams SiO<sub>2</sub> per litre from the calibration curve prepared in 101.3.

### 134. Precision and Bias <sup>6</sup>

134.1 The collaborative test of this test method was performed using reagent water by six laboratories, two operators each. Each operator made six determinations at each level, for a total of 72 determinations at each level.

134.2 *Precision*—The overall and single-operator precision of this test method for measurements at 815 nm in reagent water are shown in Table 1.

134.3 *Bias*—Recoveries of known amounts of silica from reagent water are shown in Table 2.

14.4 Under the allowances made in Section 1.5 of D 2777-86, these precision and bias data may not meet the current requirements of interlaboratory studies of Committee D-19 test methods.

### 15. Keywords

145.1 colorimetric; silica; water

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR: D19 – 147.

**APPENDIX****(Nonmandatory Information)****X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS****X1.1 Test Method A (Gravimetric—Total Silica)**

X1.1.1 This test method was discontinued in 1988. This test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 The gravimetric procedures covered by Test Method A are applicable to the determination of total silica present in water and waste water. The lower limit of this method is 5 mg of silica. Since the method includes an evaporation step, the applicable concentration range depends upon the volume of sample used in the determination.

X1.1.3 Silicon compounds dissolved or suspended in the water are concentrated and precipitated as partially dehydrated silica by evaporation with hydrochloric acid (HCl). Dehydration is completed by ignition, and the silica is volatilized as silicon tetrafluoride. The residue is weighed before and after volatilization as silicon tetrafluoride to obtain the weight of silica in the original sample. Complex silicate residues that do not yield to this treatment are dissolved by alkali fusion and dehydrated with HCl.

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.

*ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.*

*This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).*