Designation: D859 – 05

An American National Standard

Standard Test Method for Silica in Water [1]

This standard is issued under the fixed designation D859; 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 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 µg/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 µg/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:*[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 Closed Conduits
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
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 Molecular Absorption Spectrometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

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 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

[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 Feb. 1, 2005. Published February 2005. Originally approved in 1945. Last previous edition approved in 2000 as D859 – 00. DOI: 10.1520/D0859-05.

[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.

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 13) is based on data obtained at 815 nm. A direct reading spectrophotometer or filter photometer may be used.

NOTE 2—Photometers and photometric practices shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

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.

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.[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, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. 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. Type II water was specified at the time of round robin testing of this test method.

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 (Na_2SO_3). After dissolving, add the solution to 100 mL of a solution containing 30 g of sodium hydrogen sulfite ($NaHSO_3$). Make up to 200 mL with water 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 ± 5°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 ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$) 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 ($H_2C_2O_4\cdot2H_2O$) in 100 mL of water.

8.7 *Silica Solution, Standard (1 mL = 0.1 mg SiO_2)*— Dissolve 0.473 g of sodium metasilicate ($Na_2SiO_3\cdot9H_2O$) in water and dilute to 1 L. Check the concentration of this solution gravimetrically.[4]

NOTE 5—This solution may require filtration to remove fine particulate

[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 *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.

[4] Refer to former Test Method A (Gravimetric—Total Silica) last published in the 1988 *Annual Book of ASTM Standards* for complete description of procedure.