



Standard Test Method for Low-Level Total Silica in High-Purity Water by Flameless Atomic Absorption Spectroscopy¹

This standard is issued under the fixed designation D 4517; 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 determination of total silica in water.

1.2 This test method is applicable in the range from 25 to 250 $\mu\text{g/L}$ of silica as SiO_2 . Higher concentrations may be determined by decreasing the aliquot volume (see Note 6). Concentration range should not be extended by dilution.

1.3 This test method determines total silica, and does not distinguish between soluble and insoluble forms.

1.4 This test method was tested on reagent water only. It is the user's responsibility to assure the validity of the test method for waters of other matrices.

1.5 *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 859 Test Method for Silica in Water²
- D 1066 Practice for Sampling Steam²
- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
- D 4453 Practice for Handling of Ultra-Pure Water Samples²

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling of Water and Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water. Current edition approved Aug. 30, 1985. Published October 1985.

² *Annual Book of ASTM Standards*, Vol 11.01.

4. Summary of Test Method

4.1 Total silica is determined using an atomic absorption spectrophotometer in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred, and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, the absorption signal during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919. Pretreatment of the graphite tube may be used to enhance the sensitivity and repeatability, or both, of the test.³

4.2 Total silica is determined using a freshly ultrasonically treated and shaken aliquot of sample.

4.3 This test method determines low-level total silica in high purity water. Refer to Test Method D 859, Method B, for determination of molybdate-reactive silica.

5. Significance and Use

5.1 Control of silica in boiler feedwater and boiler water is necessary to minimize the formation of scale-forming silicates which decrease heat transfer in the boiler. Volatilization and carryover of silica with the steam may cause hard, glassy siliceous deposits to form on turbine blades which reduce turbine efficiency.

5.2 Colloidal silica which is not removed by boiler water pretreatment processes may be solubilized in the boiler and thus contribute to the dissolved silica concentration in the boiler. Both dissolved and total silica are of interest.

6. Interferences

6.1 For a complete discussion of general interferences with furnace procedures, the analyst is referred to Practice D 3919.

6.2 Relatively pure water such as demineralizer effluent, condensate, or high-pressure boiler feedwater are of sufficient purity to minimize potential interferences such as sodium, orthophosphate, or sulfate.

³ Rawa, Judith A. and Earl L. Henn, "Determination of Trace Silica in Industrial Process Waters by Flameless Atomic Absorption Spectrometry," *Analytical Chemistry*, Vol 51, March 1979.

6.3 Graphite tube pretreatment with the calcium/lanthanum reagent has been found to improve the silica response with some graphite tube materials or designs. Since response problems may include memory effects as well as poor sensitivity, the following procedure must be used to determine whether pretreatment is needed.

6.3.1 Following instrument set-up and blank determination as described in 10.1-10.3, inject 10 to 12 replicates of a standard containing 100 to 150 µg/L of SiO₂. Treat the tube in accordance with 6.4, and repeat. Note whether the response of the two sets is constant, indicating no memory effect, or whether the first set shows increasing response. Note also whether the response of the second set is greater than that of the first. If either sensitivity or repeatability is improved, tube pretreatment is recommended.

6.4 Pretreatment may be accomplished as follows:

6.4.1 Inject into the furnace the diluted calcium/lanthanum reagent using the maximum aliquot recommended by the manufacturer of the tube, and start the atomization program. Repeat three times, or more if necessary. Run blank atomization cycles until the furnace blank is constant.

6.4.2 Proceed to calibrate the furnace and analyze samples in accordance with Sections 10 and 11. The absorbance enhancement may deteriorate after numerous injections, in which case retreatment will be required. Refer to Practice D 3919.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*, for use at 251.6 nm.

NOTE 1—A wavelength other than 251.6 nm may be used if it has been determined to be equally suitable.

NOTE 2—The manufacturer's instructions should be followed for all instrument parameters.

7.2 *Silicon Light Source*, silicon hollow cathode lamp.

7.3 *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Atomization temperature must be reached as rapidly as possible for maximum sensitivity.

NOTE 3—Special furnace accessories are commercially available to provide a means of accelerating atomization temperature.

7.4 *Graphite Tubes*, compatible with furnace device. Standard graphite tubes are preferred, particularly when tube pretreatment is practiced. Pyrolytic graphite tubes may be used if it has been determined by the analyst that the precision, bias, and sensitivity of the determination are not compromised.

7.5 *Pipets*:

7.5.1 Microlitre, with disposable, polypropylene tips. Sizes may range from 1 to 1000 µL, as required.

7.5.2 Millilitre, 50.0 mL.

7.6 *Strip Chart Recorder*—A recorder is strongly recommended so that there will be a permanent record of analysis and any instrument problems can be easily recognized (such as drift, incomplete atomization, changes in sensitivity, etc.). A fast recorder response (0.2 s or less for full scale deflection) is recommended to ensure accuracy. Electronic peak measuring devices may be used if their response time is sufficiently fast.

7.7 *Ultrasonic Cleaner*, operable at >20 KHz.

7.8 *Flasks*, volumetric, 100 and 1000-mL polyethylene.

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.⁴ 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*—All references to reagent water in this method shall be understood to conform to Specification D 1193, for reagent water Type II. In addition, the reagent water shall be made silica-free and determined as such in accordance with this method. The collecting apparatus and storage containers for the reagent water must be made of suitable materials that will not contaminate the reagent water with silica (see Section 9).

NOTE 4—Silica-free water may be prepared by distillation, demineralization, and passage through a 0.22 µm filter. Total removal of colloidal silica may be done by treating the above water with hydrofluoric acid, letting it stand for 24 h, and then processing it through strong base ion-exchange resin in the hydroxide form.

8.3 *Calcium/Lanthanum Reagent*—Wet 2.90 g of lanthanum oxide (La₂O₃ 99.99 % pure) with about 50 mL of water in a 100 mL volumetric flask. Carefully add 5.5 mL of concentrated nitric acid (HNO₃ sp gr 1.42) and swirl to dissolve. Add 0.100 g of calcium oxide (CaO) and swirl to dissolve. Dilute to volume with water. This solution contains 100 mg/L CaO and 2500 mg/L La. Dilute 1:100 for injection. The diluted reagent is needed only for pretreatment of the graphite tube as described in 6.4.

8.4 *Silica Stock Solution* (1 mL = 1 mg SiO₂)—Dissolve 4.7 g of sodium metasilicate (Na₂SiO₃·9H₂O) and dilute to 1 L with water. Determine the silica concentration of this solution in accordance with Test Method D 859, Method A.

8.5 *Silica Working Solution* (1 mL = 0.05 mg SiO₂)—Dilute 50.0 mL of the silica stock solution (see 8.4) to 1 L with water in a volumetric flask. The concentration of this diluted standard is calculated after confirming the concentration of the stock solution.

8.6 *Argon*, standard, welder's grade, commercially available.

9. Sampling

9.1 Collect the sample in accordance with the applicable ASTM standards: Practice D 1066, Specification D 1192, and Practices D 3370.

9.2 Since silica is such a ubiquitous material, meticulous sample collection, handling, and injection into the furnace are necessary to avoid contamination.

⁴ *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.

9.2.1 Collect samples only in plastic or TFE-fluorocarbon containers. Polystyrene, polypropylene, linear polyethylene, and TFE-fluorocarbon have been found to be generally suitable, but tests should be conducted on sample containers before use to determine their suitability.

9.2.2 Sample containers must be ultrasonically cleaned before use. Fill the sample containers with water and immerse in an operating ultrasonic cleaner for at least 1 min. Remove, shake vigorously, and drain. Additional cycles of cleaning may be found necessary.

9.2.3 Before actual sample collection, rinse sample container with the sample it is to contain three times with vigorous shaking, then fill. Do not allow any object to touch the inside of the bottle or cap.

10. Calibration

10.1 Prepare standards for test calibration containing about 0, 50, 100, 150, and 250 µg/L of SiO₂ by diluting 0, 100, 200, 300, and 500 µL of the silica working solution (see 8.4) to 100 mL with water in separate volumetric flasks.

NOTE 5—The exact concentration of the prepared silica standards is determined from the result obtained by the gravimetric standardization of the stock solution in 8.4.

10.2 Zero the instrument without making an injection or initiating an atomization program.

10.3 Set the atomization program (drying, charring, atomizing) according to the manufacturer’s instructions.

NOTE 6—While sample size and furnace programming vary among instruments, the following analytical conditions have generally been found to be suitable. It is up to the analyst to optimize analytical conditions for the instrument used.

Aliquot—An aliquot size of 10 to 100 µL, depending on tube size and concentration of sample. The same aliquot size must be used for all standard, sample, and blank injections.

Function	Temperature, °C	Time, s
Dry	100	1 s/µL
Char	1000	30
Atomize	2800	7

10.4 Determine the furnace blank by initiating the atomization program without making an injection. Repeat until the furnace blank reproduces within 10 %.

NOTE 7—Determination of the furnace blank is a mechanism for evaluating the acceptability of the graphite tube for silica determination.

10.5 Inject a measured aliquot of the 100 µg/L of SiO₂ standard solution (see 10.1) into the furnace, and initiate the present atomization program. Repeat this analysis until the response reproduces within 10 %.

10.6 Determine the acceptability of the water by injecting a measured aliquot of the “0” standard solution into the furnace and initiating the preset atomization program. Repeat this analysis until the response reproduces within 10 %.

10.7 Inject a measured aliquot of each of the remaining standard solutions as described in 10.5.

10.8 Prepare a calibration curve by plotting absorbance or peak height versus concentration as micrograms per litre of SiO₂ on linear paper if direct readout in terms of concentration is not possible with the instrument.

11. Procedure

11.1 Rinse the microlitre pipet with water and inject an aliquot of water to test pipet and furnace cleanliness before sample analysis. After samples containing a high concentration of silica are analyzed, additional atomization cycles may be needed to reduce the furnace blank to prior level.

11.2 Ultrasonicate for at least 1 min and then vigorously shake sample. Immediately withdraw an aliquot (refer to 10.3 and Note 6) with the microlitre pipet. Do not touch pipet tip to any object.

11.3 Analyze sample as described in 10.2-10.4.

NOTE 8—If the total silica concentration of the sample is below the detection limit with the normal maximum injection volume for the instrument used, multiple injections may be used as follows. Inject an aliquot, start program. Stop at completion of drying step. Repeat as required. Allow program to run to completion when enough sample has been injected. Both precision and bias will decrease when this technique is used.

12. Calculation

12.1 Sample concentration is read directly from calibration curve prepared in 10.8. If multiple injections are used as discussed in Note 8, divide the result by the number of injections.

13. Precision and Bias ⁵

13.1 The single-operator and overall precision of this test method within its designated range for ten operators in six different laboratories at 251.6 nm may be expressed as follows:

$$S_o = 0.061X + 2.0$$

$$S_t = 0.13X + 3.8$$

where:

S_o = pooled single-operator precision, µg/L,

S_t = overall precision, µg/L, and

X = total silica concentration, µ g/L.

13.2 Recoveries of known amounts of total silica in a series of prepared standards for ten operators in six different laboratories at 251.6 nm are as follows:

µg/L Added	µg/L Found	Bias	% Bias	Statistically Significant
35	28	-7	-20.7	no
75	73	-2	-2.7	no
150	146	-4	-2	no
250	250	0	0	...


13.3 These data reflect optimum graphite tube treatment and conditions as determined in 6.3.1. If this test method is not run under such conditions, these data may not apply.

13.4 These data apply only to reagent water.

14. Keywords

14.1 atomic spectroscopy; boiler water; graphite furnace; high-purity water; silica

⁵ Supporting data for this test method have been filed at ASTM Headquarters. Request RR:D19-1121.

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