Standard Test Method for
Low-Level Total Silica in High-Purity Water by Flameless Atomic Absorption Spectroscopy[1]

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 µg/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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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:*[2]

D859 Test Method for Silica in Water
D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[3]
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
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4453 Practice for Handling of High Purity Water Samples
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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 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 D3919. Pretreatment of the graphite tube may be used to enhance the sensitivity and repeatability, or both, of the test.[4]

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 D859, Test 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 that decrease heat transfer in the boiler. Volatilization and

[4] Rawa, J. A., and Henn, E. L., "Determination of Trace Silica in Industrial Process Waters by Flameless Atomic Absorption Spectrometry," *Analytical Chemistry*, Vol 51, March 1979.

carryover of silica with the steam may cause hard, glassy siliceous deposits to form on turbine blades that reduce turbine efficiency.

5.2 Colloidal silica that 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 D3919.

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

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 SiO_2. 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 of 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 D3919.

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 *Data System*—Fast transient signal data are collected and processed using an internal microprocessor or external desktop computer systems. Data can be stored on disks, transmitted to central servers, or printed in hard copy. Data may be evaluated and processed using the instrument's dedicated systems to determine analyte concentrations. Users of this practice may use a strip chart recorder to obtain sample and calibration data, if desired.

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.[5] 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 D1193, 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 (La_2O_3 99.99 % pure) with about 50 mL of water in a 100 mL volumetric flask. Carefully add 5.5 mL of concentrated nitric acid (HNO_3 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.

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[5] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.4 *Silica Stock Solution* (1 mL = 1 mg SiO_2)—Dissolve 4.7 g of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) and dilute to 1 L with water. Determine the silica concentration of this solution in accordance with Test Method D859, Test Method A.

8.5 *Silica Working Solution* (1 mL = 0.05 mg SiO_2)—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 D1066, Guide D1192, Practices D3370, and Practice D4453.

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

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 SiO_2 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 SiO_2 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 SiO_2 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 minute 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[6]

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.

13.5 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 98, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

14. Quality Control

14.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing each element.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze five working standards containing concentrations of silica that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

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.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

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 mid-range concentration of each element. 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. The replicates may be interspersed with samples.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in the table in 13.2. This study should be repeated until the recoveries are within the limits given in the table. 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 *Continuing Calibration Verification (CCV):*

14.4.1 To ensure that the test method is in control, analyze a Continuing Calibration Verification (CCV) containing a known concentration of silica. The CCV is run every 10 samples in an analytical batch, and after the last sample in the analytical batch (even if there are less than 10 samples in an analytical batch). The result obtained for a CCV shall fall within ±10 % 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 A method blank is used to verify that no contaminants were introduced from the reagents or processing, and undergoes all sample preparation processes. Analyze a method blank with each batch.

14.6 *Continuing Calibration Blank (CCB):*

14.6.1 The CCB is usually prepared like the calibration standards without any added analyte. Analyze a CCB with each batch. The concentration of silica found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of silicais found above this level, analysis of samples is halted until the contamination is eliminated, and a CCB 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.

14.7 *Matrix Spike (MS):*

14.7.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of silica and taking it through the analytical method.

14.7.2 The spike concentration plus the background concentration of silica 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.

14.7.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and

V = volume (mL) added with spike.

14.7.4 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 results must be qualified with an indication that they do not fall within the performance criteria of the test method.

Note 9—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.8 *Duplicate:*

14.8.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.8.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

14.8.3 If the result exceeds the precision limit, 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.

14.9 *Independent Reference Material (IRM):*

14.9.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

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