4500-SiO_2

SILICA

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4500-SiO_2 A. INTRODUCTION

1. Occurrence and Significance

Silicon does not occur free in nature, but rather as free silica (SiO_2) in coarsely crystalline (quartz, rock crystal, amethyst, etc.) and microcrystalline (e.g., flint, chert, jasper) varieties of quartz, the major component of sand and sandstone. Silicon is found in combination with other elements in silicates, represented by feldspar, hornblende, mica, asbestos, and other clay minerals. Silicates also occur in rocks, such as granite, basalt, and shale. Silicon therefore is usually reported as silica (SiO_2) when rocks, sediments, soils, and water are analyzed. The average abundance of silica in different rock types is 7% to 80%, in typical soils 50% to 80%, and in surface and groundwater 14 mg/L.

The common aqueous forms of silica are H_4SiO_4 and $H_3SiO_4^-$. In the presence of magnesium, it can form scale deposits in boilers and in steam turbines. It is considered a nonessential trace element for most plants, but essential for most animals. Chronic exposure to silica dust can be toxic. There is no U.S. EPA drinking water standard MCL for silica.

A more complete discussion of the occurrence and chemistry of silica in natural waters is available.[1]

2. Selection of Method

Perform analyses by the electrothermal atomic absorption method (Section 3113 B) or one of the colorimetric methods (4500-SiO_2 C, D, E, or F), depending on the fraction to be measured. The inductively coupled plasma mass spectrometric method (Section 3125) or the inductively coupled plasma method (Section 3120) also may be applied successfully in most cases (with lower detection limits), even though silica is not specifically listed as an analyte in the method.

Methods 3120 and 3125 determine total silica. 4500-SiO_2 C, D, E, and F determine molybdate-reactive silica. As noted in 4500-SiO_2 C.4, it is possible to convert other forms of silica to the molybdate-reactive form for determination by these methods. Method 3111 D determines more than one form of silica. It determines all dissolved silica and some colloidally dispersed silica. The determination of silica present in micrometer and submicrometer particles depends on the size distribution, composition, and structure of the particles; thus 3111 D does not determine total silica.

Method 4500-SiO_2 C is recommended for relatively pure waters containing from 0.4 to 25 mg/L SiO_2. As with most colorimetric methods, the range can be extended, if necessary, by diluting, by concentrating, or by varying the light path. Interferences due to tannin, color, and turbidity are more severe with this method than with 4500-SiO_2 D. Moreover, the yellow color produced by 4500-SiO_2 C has a limited stability and attention to timing is necessary. When applicable, however, it offers greater speed and simplicity than 4500-SiO_2 D because one reagent fewer is used; one timing step is eliminated; and many natural waters can be analyzed without dilution, which is not often the case with 4500-SiO_2 D. Method 4500-SiO_2 D is recommended for the low range, from 0.04 to 2 mg/L SiO_2. This range also can be extended if necessary. Such extension may be desirable if interference is expected from tannin, color, or turbidity. A combination of factors renders 4500-SiO_2 D, E, and F less susceptible than 4500-SiO_2 C to those interferences; also, the blue color in 4500-SiO_2 D, E, and F is more stable than the yellow color in 4500-SiO_2 C. However, many samples will require dilution because of the high sensitivity of the method. Permanent artificial color standards are not available for the blue color developed in 4500-SiO_2 D.

The yellow color produced by 4500-SiO_2 C and the blue color produced by 4500-SiO_2 D, E, and F are affected by high concentrations of salts. With seawater the yellow color intensity is decreased by 20% to 35% and the blue color intensity is increased by 10% to 15%. When waters of high ionic strength are analyzed by these methods, use silica standards of approximately the same ionic strengths.[2]

Method 4500-SiO_2 E or F may be used where large numbers of samples are analyzed regularly. Method 3111 D is recommended for broad-range use. Although Method 3111 D is usable from 1 to 300 mg/L SiO_2, optimal results are obtained from about 20 to 300 mg/L. The range can be extended upward by dilution if necessary. This method is rapid and does not require any timing step.

The inductively coupled plasma method (Section 3120) also may be used in analyses for silica.

3. Sampling and Storage

Collect samples in bottles of polyethylene, other plastic, or hard rubber, especially if there will be a delay between collection and analysis. Borosilicate glass is less desirable, particularly with waters of pH above 8 or with seawater, in which cases a significant amount of silica in the glass can dissolve. Freezing to preserve samples for analysis of other constituents can lower soluble silica values by as much as 20% to 40% in waters that have a pH below 6. Do not acidify samples for preservation because silica precipitates in acidic solutions.

References

1. Hem JD. Study and interpretation of the chemical characteristics of natural water, 3rd ed. U.S. Geological Survey Water Supply Paper No. 2254; 1985.
2. Fanning KA, Pilson MEQ. On the spectrophotometric determination of dissolved silica in natural waters. Anal Chem. 1973;45:136–140.

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4500-SiO_2 B. (Reserved)

4500-SiO_2 C. Molybdosilicate Method

1. General Discussion

a. Principle: Ammonium molybdate at pH approximately 1.2 reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid, but not the molybdosilicic acid. Even if phosphate is known to be absent, the addition of oxalic acid is highly desirable and is a mandatory step in both this method and 4500-SiO_2 D. The intensity of the yellow color is proportional to the concentration of molybdate-reactive silica. In at least one of its forms, silica does not react with molybdate even though it is capable of passing through filter paper and is not noticeably turbid. It is not known to what extent such unreactive silica occurs in waters. Terms such as colloidal, crystalloidal, and ionic have been used to distinguish among various forms of silica but such terminology cannot be substantiated. Molybdate-unreactive silica can be converted to the reactive form by heating or fusing with alkali. Molybdate-reactive or unreactive does not imply reactivity, or lack of it, toward *other* reagents or processes.

b. Interference: Because both apparatus and reagents may contribute silica, avoid using glassware as much as possible and use reagents low in silica. Also, make a blank determination to correct for silica so introduced. In both this method and 4500-SiO_2 D, tannin, large amounts of iron, color, turbidity, sulfide, and phosphate interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases interference from tannin. If necessary, use photometric compensation to cancel interference from color or turbidity.

c. Minimum detectable concentration: Approximately 1 mg/L SiO_2 can be detected in 50-mL Nessler tubes.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Platinum dishes, 100-mL.

Table 4500-SiO_2:1. Selection of Light Path Length for Various Silica Concentrations

	4500-SiO_2 C	4500-SiO_2 D	
		Silica in 55 mL Final Volume (μg)	
Light Path (cm)	Silica in 55 mL Final Volume (μg)	650 nm Wavelength	815 nm Wavelength
1	200–1300	40–300	20–100
2	100–700	20–150	10–50
5	40–250	7–50	4–20
10	20–130	4–30	2–10

b. Colorimetric equipment: One of the following is required:

1) Spectrophotometer, for use at 410 nm, providing a light path of 1 cm or longer. See Table 4500-SiO_2:1 for light path selection.

2) Filter photometer, providing a light path of 1 cm or longer and equipped with a violet filter having maximum transmittance near 410 nm.

3) Nessler tubes, matched, 50-mL, tall form.

3. Reagents

For best results, set aside and use batches of chemicals low in silica. Use reagent water in making reagents and dilutions. Store all reagents in plastic containers to guard against high blanks.

a. Sodium bicarbonate ($NaHCO_3$), powder.

b. Sulfuric acid (H_2SO_4), 1 N.

c. Hydrochloric acid (HCl), 1 + 1.

d. Ammonium molybdate reagent: Dissolve 10 g $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in water, with stirring and gentle warming, and dilute to 100 mL. Filter if necessary. Adjust to pH 7 to 8 with silica-free NH_4OH or NaOH and store in a polyethylene bottle to stabilize. (If the pH is not adjusted, a precipitate gradually forms. If the solution is stored in glass, silica may leach out and cause high blanks.) If necessary, prepare silica-free NH_4OH by passing gaseous NH_3 into reagent water contained in a plastic bottle.

e. Oxalic acid solution: Dissolve 7.5 g $H_2C_2O_4\cdot2H_2O$ in water and dilute to 100 mL.

f. Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, $Na_2SiO_3\cdot9H_2O$, in water and dilute to 1000 mL. For work of highest accuracy, analyze 100.0-mL portions by the gravimetric method.[1] Store in a tightly stoppered plastic bottle.

g. Standard silica solution: Dilute 10.00 mL stock solution to 1000 mL with water; 1.00 mL = 10.0 μg SiO_2. Calculate the exact concentration from the concentration of stock silica solution. Store in a tightly stoppered plastic bottle.

h. Permanent color solutions:

1) Potassium chromate solution—Dissolve 630 mg K_2CrO_4 in water and dilute to 1 L.

2) Borax solution—Dissolve 10 g sodium borate decahydrate, $Na_2B_4O_7\cdot10H_2O$, in water and dilute to 1 L.

4. Procedure

a. Color development: To 50.0 mL sample add in rapid succession 1.0 mL 1 + 1 HCl and 2.0 mL ammonium molybdate reagent. Mix by inverting at least 6 times and let stand for 5 to 10 min. Add 2.0 mL oxalic acid solution and mix thoroughly. Read the color after 2 min but before 15 min, measuring the time from the addition of oxalic acid. Because the yellow color obeys the Beer–Lambert law, measure photometrically or visually.

b. To detect the presence of molybdate-unreactive silica, digest sample with $NaHCO_3$ before color development. This digestion is not necessarily sufficient to convert all molybdate-unreactive silica to the molybdate-reactive form. Complex silicates and higher silica polymers may require extended fusion with alkali at high temperatures or digestion under pressure for complete conversion. Omit the digestion if all the silica is known to react with molybdate.

If turbid, prepare a clear sample by filtration. Place 50.0 mL, or a smaller portion diluted to 50 mL, in a 100-mL platinum dish. Add 200 mg silica-free $NaHCO_3$ and digest on a steam bath for 1 h. Cool and add slowly, with stirring, 2.4 mL 1 N H_2SO_4. Do not interrupt the analysis but proceed *at once* with the remaining steps. Transfer quantitatively to a 50-mL Nessler tube and dilute to the mark with water. (Tall-form 50-mL Nessler tubes are convenient for mixing even if the solution subsequently is transferred to an absorption cell for photometric measurement.)

c. Preparation of standards: If $NaHCO_3$ pretreatment is used, add to the standards (approximately 45 mL total volume) 200 mg $NaHCO_3$ and 2.4 mL 1 N H_2SO_4, to compensate both for the slight amount of silica introduced by the reagents and for the effect of the salt on color intensity. Dilute to 50.0 mL.

d. Correction for color or turbidity: Prepare a special blank for every sample that needs such correction. Carry 2 identical portions of each such sample through the procedure, including $NaHCO_3$ treatment if this is used. To one portion, add all reagents as directed in paragraph *a* above. To the other portion, add HCl and oxalic acid but no molybdate. Adjust the photometer to zero absorbance with the blank that lacks molybdate before reading the absorbance of the molybdate-treated sample.

e. Photometric measurement: Prepare a calibration curve from a series of approximately 6 standards to cover the optimum ranges cited in Table 4500-SiO_2:1. Follow direction of paragraph *a* above on suitable portions of standard silica solution diluted to 50.0 mL in Nessler tubes. Set the photometer at zero absorbance with water and read all standards, including a reagent blank, against water. Plot micrograms of silica in the final (55 mL) developed solution against the photometer readings. Run a reagent blank and at least one standard with each group of samples to confirm that the calibration curve previously established has not shifted.

f. Visual comparison: Make a set of permanent artificial color standards, using K_2CrO_4 and borax solutions. Mix liquid volumes specified in Table 4500-SiO_2:2 and place them in well-stoppered, appropriately labeled 50-mL Nessler tubes. Verify the correctness of these permanent artificial standards by comparing them visually against standards prepared by analyzing portions of the standard silica solution. Use permanent artificial color standards only for visual comparison.

Table 4500-SiO_2:2. Preparation of Permanent Color Standards for Visual Determination of Silica

Values in Silica (μg)	Potassium Chromate Solution (mL)	Borax Solution (mL)	Water (mL)
0	0.0	25	30
100	1.0	25	29
200	2.0	25	28
400	4.0	25	26
500	5.0	25	25
750	7.5	25	22
1000	10.0	25	20

5. Calculation

$$\text{mg/L SiO}_2 = \frac{\mu\text{g SiO}_2\,(\text{in 55 mL final volume})}{\text{mL sample}}$$

Report whether $NaHCO_3$ digestion was used.

6. Precision and Bias

A synthetic sample containing 5.0 mg/L SiO_2, 10 mg/L Cl^-, 0.20 mg/L NH_3-N, 1.0 mg/L NO_3^--N, 1.5 mg/L organic N, and 10.0 mg/L PO_4^{3-} in distilled water was analyzed in 19 laboratories by the molybdosilicate method with a relative standard deviation of 14.3% and a relative error of 7.8%.

Another synthetic sample containing 15.0 mg/L SiO_2, 200 mg/L Cl^-, 0.800 mg/L NH_3-N, 1.0 mg/L NO_3^--N, 0.800 mg/L organic N, and 5.0 mg/LPO_4^{3-} in distilled water was analyzed in 19 laboratories by the molybdosilicate method, with a relative standard deviation of 8.4% and a relative error of 4.2%.

A third synthetic sample containing 30.0 mg/L SiO_2, 400 mg/L Cl^-, 1.50 mg/L NH-N, 1.0 mg/L NO_3^--N, 0.200 mg/L organic N, and 0.500 mg/L PO_4^{3-}, in distilled water was analyzed in 20 laboratories by the molybdosilicate method, with a relative standard deviation of 7.7% and a relative error of 9.8%.

All results were obtained after sample digestion with $NaHCO_3$.

Reference

1. American Public Health Association, American Water Works Association, Water Environment Federation. In: Eaton AD, Clesceri LS, Greenberg AE, eds. Standard Methods for the Examination of Water and Wastewater. 19th ed. Washington DC: APHA Press; 1995.

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4500-SiO_2 D. Heteropoly Blue Method

1. General Discussion

a. Principle: The principles outlined under 4500-SiO_2 C.1*a*, also apply to this method. The yellow molybdosilicic acid is reduced by means of amino naphthol sulfonic acid to heteropoly blue. The blue color is more intense than the yellow color of 4500-SiO_2 C and provides increased sensitivity.

b. Interference: See 4500-SiO_2 C.1*b*.

c. Minimum detectable concentration: Approximately 20 µg/L SiO_2 can be detected in 50-mL Nessler tubes and 50 µg/L SiO_2 spectrophotometrically with a 1-cm light path at 815 nm.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Platinum dishes, 100-mL.

b. Colorimetric equipment: One of the following is required:

1) Spectrophotometer—for use at approximately 815 nm. The color system also obeys the Beer–Lambert law at 650 nm, with appreciably reduced sensitivity. Use light path of 1 cm or longer. See Table 4500-SiO_2:1 for light path selection.

2) Filter photometer—provided with a red filter exhibiting maximum transmittance in the wavelength range of 600 to 815 nm. Sensitivity improves with increasing wavelength. Use light path of 1 cm or longer.

3) Nessler tubes—matched, 50-mL, tall form.

3. Reagents

For best results, set aside and use batches of chemicals low in silica. Store all reagents in plastic containers to guard against high blanks. Use reagent water that does not contain detectable silica after storage in glass.

All of the reagents listed in 4500-SiO_2 C.3 are required, and in addition:

Reducing agent: Dissolve 500 mg 1-amino-2-naphthol-4-sulfonic acid and 1 g Na_2SO_3 in 50 mL reagent water, with gentle warming if necessary; add this to a solution of 30 g $NaHSO_3$ in 150 mL reagent water. Filter into a plastic bottle. Discard when the solution becomes dark. Prolong reagent life by storing in a refrigerator and away from light. Do not use amino naphthol sulfonic acid that is incompletely soluble or that produces reagents that are dark even when freshly prepared.

4. Procedure

a. Color development: Proceed as in 4500-SiO_2 C.4*a* up to and including the words, "Add 2.0 mL oxalic acid solution and mix thoroughly." Measuring time from the moment of adding oxalic acid, wait at least 2 min but not more than 15 min, add 2.0 mL reducing agent, and mix thoroughly. After 5 min, measure blue color photometrically or visually. If $NaHCO_3$ pretreatment is used, follow 4500-SiO_2 C.4*b*.

b. Photometric measurement: Prepare a calibration curve from a series of approximately six standards to cover the optimum range indicated in Table 4500-SiO_2:1. Carry out the steps described above on suitable portions of standard silica solution diluted to 50.0 mL in Nessler tubes; pretreat the standards if a $NaHCO_3$ digestion is used (see 4500-SiO_2 C.4*b*). Adjust the photometer to zero absorbance with reagent water and read all standards, including a reagent blank, against reagent water. To correct for color or turbidity in a sample, see 4500-SiO_2 C.4*d*. To the special blank add HCl and oxalic acid, but no molybdate or reducing agent. Plot micrograms of silica in the final 55 mL developed solution against absorbance. Run a reagent blank and at least one standard with each group of samples to check the calibration curve.

c. Visual comparison: Prepare a series of not less than 12 standards, covering the range 0 to 120 µg SiO_2, by placing the calculated volumes of standard silica solution in 50-mL Nessler tubes, diluting to the mark with reagent water, and developing the color as described in paragraph *a* above.

5. Calculation

$$\text{mg/L SiO}_2 = \frac{\mu\text{g SiO}_2\,\text{(in 55 mL final volume)}}{\text{mL sample}}$$

Report whether $NaHCO_3$ digestion was used.

6. Precision and Bias

A synthetic sample containing 5.0 mg/L SiO_2, 10 mg/L Cl^-, 0.200 mg/L NH_3-N, 1.0 mg/L NO_3^--N, 1.5 mg/L organic N, and 10.0 mg/L PO_4^{3-} in distilled water was analyzed in 11 laboratories by the heteropoly blue method, with a relative standard deviation of 27.2% and a relative error of 3.0%.

A second synthetic sample containing 15 mg/L SiO_2, 200 mg/L Cl^-, 0.800 mg/L NH_3-N, 1.0 mg/L NO_3^--N, 0.800 mg/L organic N, and 5.0 mg/L PO_4^{3-} in distilled water was analyzed in 11 laboratories by the heteropoly blue method, with a relative standard deviation of 18.0% and a relative error of 2.9%.

A third synthetic sample containing 30.0 mg/L SiO_2, 400 mg/L Cl^-, 1.50 mg/L NH_3-N, 1.0 mg/L NO_3^--N, 0.200 mg/L organic N, and 0.500 mg/L PO_4^{3-} in distilled water was analyzed in 10 laboratories by the heteropoly blue method with a relative standard deviation of 4.9% and a relative error of 5.1%.

All results were obtained after sample digestion with $NaHCO_3$.