

METHOD #: 370.1 Approved for NPDES (Editorial Revision 1978)

TITLE: Silica, Dissolved (Colorimetric)

ANALYTE: Silica, SiO₂

INSTRUMENTATION: Spectrophotometer

STORET No. Dissolved 00955

1.0 Scope and Application

- 1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.
- 1.2 The working range of the method is approximately 2 to 25 mg silica/L. The upper range can be extended by taking suitable aliquots; the lower range can be extended by the addition of amino-naphthol-sulfonic acid solution, as described in (6.8).

2.0 Summary of Method

- 2.1 A well-mixed sample is filtered through a 0.45 μ membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample. The color complex is then measured spectrophotometrically.
- 2.2 In the low concentration modification the yellow (410 nm) molybdosilicic acid color is reduced by 1-amino-2-naphthol-4-sulfonic acid to a more intense heteropoly blue (815 nm or 650 nm).

3.0 Interferences

- 3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution. See (6.7).
- 3.2 Tannin interference may be eliminated and phosphate interferences may be decreased with oxalic acid.
- 3.3 Large amounts of iron and sulfide interfere.
- 3.4 Contact with glass should be minimized, silica free reagents should be used as much as possible. A blank should be run.

4.0 Apparatus

- 4.1 Platinum dishes, 100 mL.
- 4.2 Colorimetric equipment-one of the following:
 - 4.2.1 Spectrophotometer for use at 410 nm, 650 nm and/or 815 nm with a 1 cm or longer cell.
 - 4.2.2 Filter photometer with a violet filter having maximum transmittance as near 410 nm as possible and a 1 cm or longer cell.
 - 4.2.3 Nessler tubes, matched, 50 mL, tall form.

5.0 Reagents

- 5.1 Use chemicals low in silica and store in plastic containers.
- 5.2 Sodium bicarbonate, NaHCO_3 , powder.
- 5.3 Sulfuric acid, H_2SO_4 , 1 N.
- 5.4 Hydrochloric acid, HCl , 1 + 1.
- 5.5 Ammonium molybdate reagent: Place 10 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in distilled water in a 100 mL volumetric. Dissolve by stirring and gently warming. Dilute to the mark. Filter if necessary. Adjust to pH 7 to 8 with silica free NH_4OH or NaOH . Store in plastic bottle.
- 5.6 Oxalic acid solution: Dissolve 10 g $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ in distilled water in a 100 mL volumetric flask, dilute to the mark. Store in plastic.
- 5.7 Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$, in recently boiled and cooled distilled water. Dilute to approximately 900 mL. Analyze 100.0 mL portions by gravimetry (ref. 1, p. 484). Adjust concentration to 1.000 mg/L SiO_2 . Store in tightly stoppered plastic bottle.
- 5.8 Standard silica solution: Dilute 10.0 mL stock solution to 1 liter with recently boiled and cooled distilled water. This is 10 mg/L SiO_2 (1.00 mL = 10.0 μg SiO_2). Store in a tightly stoppered plastic bottle.
- 5.9 Permanent color solutions
 - 5.9.1 Potassium chromate solution: Dissolve 630 mg K_2CrO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark.
 - 5.9.2 Borax solution: Dissolve 10 g sodium borate decahydrate, $(\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O})$ in distilled water in a 1 liter volumetric flask and dilute to the mark.
 - 5.10 Reducing agent: Dissolve 500 mg of 1-amino-2-naphthol-4-sulfonic acid and 1 g Na_2SO_3 in 50 mL distilled water with gentle warming if necessary. Dissolve 30 g NaHSO_3 in 150 mL distilled water. Mix these two solutions. Filter into a plastic bottle. Refrigerate and avoid exposure to light. Discard when it darkens. If there is incomplete solubility or immediate darkening of the aminonaphthosulfonic acid solution do not use.

6.0 Procedure

- 6.1 Filter sample through a 0.45 μ membrane filter.
- 6.2 Digestion: If molybdate unreactive silica is present and its inclusion in the analysis is desired, include this step, otherwise proceed to 6.3.
 - 6.2.1 Place 50 mL, or a smaller portion diluted to 50 mL, of filtered (6.1) sample in a 100 mL platinum dish.
 - 6.2.2 Add 200 mg silica-free NaHCO_3 (5.2) and digest on a steam bath for 1 hour. Cool.
 - 6.2.3 Add slowly and with stirring 2.4 mL H_2SO_4 (5.3).
 - 6.2.4 Immediately transfer to a 50 mL Nessler tube, dilute to the mark with distilled water and proceed to 6.3 without delay.
- 6.3 Color development
 - 6.3.1 Place 50 mL sample in a Nessler tube.
 - 6.3.2 Add rapidly 1.0 mL of 1 + 1 HCl (5.4) and 2.0 mL ammonium molybdate reagent (5.5).
 - 6.3.3 Mix by inverting at least 6 times.
 - 6.3.4 Let stand 5 to 10 minutes.
 - 6.3.5 Add 1.5 mL oxalic acid solution (5.6) and mix thoroughly.
 - 6.3.6 Read color (spectrophotometrically or visually) after 2 minutes

but before 15 minutes from the addition of oxalic acid.

6.4 Preparation of Standards

6.4.1 If digestion (6.2) was used add 200 mg NaHCO_3 (5.2) and 2.4 mL H_2SO_4 (5.3) to standards to compensate for silica introduced by these reagents and for effect of the salt on the color intensity.

6.5 Photometric measurement

6.5.1 Prepare a calibration curve using approximately six standards to span the range shown below with the selected light path.

Selection of Light Path Length for Various
Silica Concentrations

Light Path cm	Silica in 54.5 mL final volume (μg)
1	200-1300
2	100-700
5	40-250
10	20-130

6.5.2 Carry out the steps in 6.3 using distilled water as the reference. Read a blank.

6.5.3 Plot photometric reading versus μg of silica in the final solution of 54.5 mL. Run a reagent blank and at least one standard with each group of samples.

6.6 Visual Comparison

6.6.1 Prepare a set of permanent artificial color standards according to the table. Use well stoppered, properly labeled 50 mL Nessler tubes.

Silica value mg	Potassium chromate solution (5.9.1) ml	Borax solution (5.9.2) mL	Distilled water mL
0.00	0.0	25	30
0.10	1.0	25	29
0.20	2.0	25	28
0.40	4.0	25	26
0.50	5.0	25	25
0.75	7.5	25	22
1.00	10.0	25	20

- 6.6.2 Verify permanent standards by comparison to color developed by standard silica solutions.
- 6.6.3 These permanent artificial color standards are only for color comparison procedure, not for photometric procedure.
- 6.7 Correction for color or turbidity
 - 6.7.1 A special blank is run using a portion of the sample and carrying out the procedure in 6.1, 6.2 if used, and 6.3 except for the addition of ammonium molybdate (6.3.2).
 - 6.7.2 Zero the photometer with this blank before reading the samples.
- 6.8 Procedure for low concentration ($< 1000 \mu\text{g/L}$)
 - 6.8.1 Perform steps 6.1 and 6.2 if needed.
 - 6.8.2 Place 50 mL sample in a Nessler tube.
 - 6.8.3 In rapid succession add 1.0 mL of 1 + 1 HCl (5.4).
 - 6.8.4 Add 2.0 mL ammonium molybdate reagent (5.5).
 - 6.8.5 Mix by inverting at least six times.
 - 6.8.6 Let stand 5 to 10 minutes.
 - 6.8.7 Add 1.5 mL oxalic acid solution (5.6).
 - 6.8.8 Mix thoroughly.
 - 6.8.9 At least 2, but not more than 15 minutes after oxalic acid addition, add 2.0 mL reducing agent (5.10).
 - 6.8.10 Mix thoroughly.
 - 6.8.11 Wait 5 minutes, read photometrically or visually.
 - 6.8.12 If digestion (6.2) was used see (6.4).
 - 6.8.13 Photometric measurement
 - 6.8.13.1 Prepare a calibration curve using approximately 6 standards and a reagent blank to span the range shown below with the selected light path.

Selection of Light Path Length for Various Silica Concentrations

Light Path cm	Silica in 56.5 mL 650 nm	Final volume, μg 815 nm
1	40-300	20-100
2	20-150	10-50
5	7-50	4-20
10	4-30	2-10

6.8.13.2 Read versus distilled water.

6.8.13.3 Plot photometric reading at 650 nm or at 815 nm versus μg of silica in 56.5 mL.

6.8.13.4 For turbidity correction use 6.1, 6.2 if used and 6.8.2-6.8.11 omitting 6.8.4 and 6.8.9.

6.8.13.5 Run a reagent blank and at least one standard (to check calibration curve drift) with each group of samples.

6.8.14 Visual comparison

6.8.14.1 Prepare not less than 12 standards covering the range of 0 to 120 μg SiO_2 by placing the calculated volumes of standard silica (5.8) in 50 mL Nessler tubes, diluting to the mark and develop the color as in 6.8.2-6.8.11.

7.0 Calculations

7.1 Read μg SiO_2 from calibration curve or by visual comparison

7.2

$$\text{mg/L SiO}_2 = \frac{\mu\text{g/SiO}_2}{\text{mL sample}}$$

7.3 Report whether NaHCO_3 digestion (6.2) was used

8.0 Precision and Accuracy

8.1 A synthetic unknown sample containing 5.0 mg/L SiO_2 , 10 mg/L chloride, 0.200 mg/L ammonia N, 1.0 mg/L nitrate N, 1.5 mg/L organic N, and 10.0mg/L phosphate 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%.

8.2 Another synthetic unknown sample containing 15.0 mg/L SiO_2 , 200 mg/L chloride, 0.800 mg/L ammonia N, 1.0 mg/L nitrate N, 0.800 mg/L organic N, and 5.0 mg/L phosphate 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%.

8.3 A third synthetic unknown sample containing 30.0 mg/L SiO_2 , 400 mg/L chloride, 1.50 mg/L ammonia N, 1.0 mg/L nitrate N, 0.200 mg/L organic N, and 0.500 mg/L phosphate 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 .

- 8.4 Photometric evaluations by the amino-naphthol-sulfonic acid procedure have an estimated precision of ± 0.10 mg/L in the range from 0 to 2 mg/L (ASTM).
- 8.5 Photometric evaluations of the silico-molybdate color in the range from 2 to 50 mg/L have an estimated precision of approximately 4% of the quantity of silica measured (ASTM).

Bibliography

1. Annual Book of ASTM Standards, Part 3 1, "Water", Standard D859-68, p 401(1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 487, Method 426B, (1975).