SECTION D.13
SILICA, DISSOLVED

CEDR Method Codes: SIF L01

a) Scope and Application

i.) This method describes the determination of dissolved silicate, mainly in the form of silicic acid found in estuarine and/or coastal waters.

ii.) In Chesapeake Bay tidal waters, the applicable range can be as low as 0.001 to 0.004 mg Si/L for samples near the Bay mouth, to as high as 0.03 to 0.30 mg Si/L when very high nitrite samples are encountered.

iii.) The method detection limits (MDL) are determined on a yearly basis, and should be established using the guidelines in Chapter 6, Section C.8.

b) Summary of Method

i.) Tidal samples are field-filtered through 0.7 µm glass fiber filters.

ii.) In this method the silicate in the samples reacts with ammonium molybdate under acidic conditions to form β-molybdosilicic acid. This complex is then reduced by ascorbic acid to form molybdenum blue that is measured at 660 nm. The color is proportional to the silicate concentrations present in the sample. The colorimetric procedure conforms to EPA Method 366.0 (1997).

c) Interferences

i.) Sample turbidity should be removed by filtration prior to analysis.

ii.) Interference from phosphate may be suppressed by adding oxalic acid.

iii.) Hydrogen sulfide may be removed by either boiling prior to analysis, by oxidation with bromine or stripping with nitrogen gas after acidification.

iv.) Large amounts of iron and sulfide interfere with analysis.

v.) The difference in refractive index of seawater and reagent water should be corrected for when analyzing estuarine/coastal samples. Alternatively, match the salinity of the calibration standards to the salinity of the samples.

d) Apparatus and Materials

i.) Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube or recorder or computer based data system.

ii.) Plastic containers and labware should be utilized for the analysis of silica. Any glassware used in the analysis must be low in silica to avoid sample reagent contamination. Washing with 10% HCl and thoroughly rinse with reagent water has been found to be effective. A laboratory's glassware cleaning method will be considered sufficient if all quality control samples are within the expected ranges.

e) Reagents

i.) Stock reagent solutions: The specific recipe for these reagents is generally instrument-dependent and may change due to the concentration of the samples being analyzed. This method lists the chemicals needed for the reaction but not the specific amount.

(1) Ammonium Molybdate Solution: Prepare this reagent by dissolving ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 0.05M H_2SO_4. Store the solution in plastic container for up to three months at 4 ± 2°C.

(2) Ascorbic Acid Solution - Dissolve ascorbic acid ($C_6H_8O_6$) in 200 mL of reagent water and acetone (C_3H_6O) and dilute in a volumetric flask with reagent water. Store in a plastic container. This solution is stable for one week if stored at 4 ± 2 °C. Discard the solution if it turns brown.

(3) Oxalic Acid Solution - Dissolve of oxalic acid ($C_2H_2O_4$) in approximately 800 mL of reagent water and dilute to 1000 mL with reagent water. Store in a plastic container. This solution is stable for approximately 3 months.

ii.) Calibration standards: Laboratories may purchase or prepare stock and working standards. The calibration check standard must be purchased or made from a second source.

(1) Stock Silicate Solution: Sodium hexafluorosilicate ($NaSiF_6$), pre-dried at 105 °C for 2 hours to remove moisture. To prepare the stock solution, dissolve 0.6696 g in 1000 mL reagent water. The solution is stable for one year when stored at 4 ± 2°C.

(2) Prepare a series of standards each analysis day by diluting suitable volumes of stock silicate solutions with reagent water or artificial seawater.

(3) Salinity matching is unnecessary if using a flow injection analyzer or if background correction is built into the instrument. If need to match the salinity of the standards to the samples, select one of the options.

i) When working with samples of known salinity it is recommended that the standard curve concentrations be prepared in artificial sea water diluted to that salinity and that the sampler wash solution also be artificial sea water diluted to that salinity.

ii) When analyzing samples of varying salinities, it is recommended that the standard curve be prepared in reagent water and refractive index corrections be made to the sample concentrations.

(4) Standards should bracket the expected concentration of the samples, and not exceed two orders of magnitude. At least five calibration standards with equal increments in concentration should be used to construct the calibration curve.

iii.) Reagent water: Refer to Chapter 6, Section 4.2.

iv.) Artificial seawater (ASW): Refer to Chapter 6, Section 4.3. This can be used for the matrix at an appropriate salinity for the samples being analyzed.

f) Sample Handling

i.) Samples must be filtered using a 0.7 µm glass fiber filter as soon as possible after collection, preferably on the field, refrigerated and stored in HDPE bottles.

ii.) Samples may be refrigerated at ≤ 6 °C for up to 28 days.

g) Procedure

i.) Prepare calibration standards to establish a curve that brackets the expected concentration of samples. Samples above the highest calibration standard may be diluted to fall within the calibration curve. See Chapter 6, Section C.5 for additional calibration requirements.

ii.) Sample analysis.

a. If samples have not been freshly collected and are frozen, thaw prior to analysis.

b. Allow the instrument to warm up sufficiently to obtain a steady instrument state, ready to collect data. Use a sampling rate which ensures reliable results.

c. Analytical sequence: The samples and associated QC samples are typically run according to the following sequence.

i. Five calibration standards within the linear range of the instrument, not to exceed two orders of magnitude. Set up and run standards in order of decreasing concentration.

1. An additional calibration standard with zero analyte concentration to estimate the y-intercept and

2. The lowest standard must have a concentration ≤ PQL or reporting limit.

ii. Initial calibration verification (ICV) standard, traceable to a national standard;

iii. Reagent/method blank;

iv. Twenty CBP samples;

v. One matrix spike sample and one duplicate sample;

vi. Reagent/Method blank; and,

vii. One mid-range continuing calibration verification standard (CCV), per range.

viii. Repeat steps iv – vii until all samples are analyzed. If the QC samples indicate that the system is out of control, recalibration is necessary.

iii.) If a low concentration sample peak follows a high concentration sample peak, a certain amount of carryover can be expected in continuous flow instruments. If this low-concentration peak is not clearly defined it is recommended that the sample be reanalyzed at the end of the run.

h) Calculations

i.) Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply concentration by the appropriate dilution factor.

ii.) Refractive index correction for estuarine/coastal systems is optional, and shall be performed in accordance with procedures described in Section 6.7.3.2.

iii.) Report results in units of mg Si/L.

i) Quality Control

i.) This method should be used by analysts experienced in the use of colorimetric analyses, matrix interferences and procedures for their correction. Analyst training and/or a demonstration of capability should be documented.

ii.) Method detection limits (MDL): Method detection limits should be established using the procedures in Chapter 6, Section C.8.

iii.) Certified reference material (CRM): The laboratory must analyze a silicate CRM to verify the accuracy of the initial calibration. Alternatively, a material from a second source or lot that is traceable to a national standard may be used.

iv.) Additional quality control parameters are listed in the table below.

Table 6.D.13 Frequency of Routine Calibration, Blank and QC Samples for Silica

Control Sample	**Frequency of Application**	**Acceptance Criteria**	**Corrective Actions**
Instrument Calibration	Each analysis day	Using all standards in curve, r ≥ 0.995. Linear at PQL or RL	Repeat full calibration.
Initial Calibration Verification (ICV)– *2nd source or CRM, Traceable to a national standard*	After calibration standards, prior to sample analysis	90-110% recovery of known concentration	Recalibrate and verify prior to analysis.
Method Blank	Beginning and end of preparation batch (20 samples)	≤ PQL or reporting limit (RL)	Reanalyze another aliquot of blank solution. Investigate possible sources of contamination.
Continuing Calibration Verification (CCV)	Beginning and end of preparation batch	90-110% recovery of known concentration	Investigate problem; rerun all samples following the last in-control CCV or ICV.

Matrix Spike Sample	At least 1 per 20 samples	80 – 120% recovery	Spike another sample aliquot and analyze. If still exceeds control limits, suspect matrix interference and remove interference if possible.
Laboratory Duplicate Sample	At least 1 per 20 samples	20% RPD[1]	Analyze another sample aliquot. Qualify the sample result if still exceeds precision limits.

[1] Laboratories may establish less stringent RPD criteria for duplicate samples near the reporting limit.

j) References

i.) Fishman, M. J. and Friedman, L., "Silica, colorimetric, molybdate blue, automated-segmented flow" in Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey Method ID I-2700-85. 1989.

ii.) Zhang, Jiazhong, "Determination of Dissolved Silicate in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis", in U.S. EPA Methods for Determination of Chemical Substances in Marine and Estuarine Matrices – 2nd Edition (EPA/600/R-97/072). Sep 1997, Method 366.0.