Standard Operating Procedure for the Analysis of Silica in Fresh Waters CCAL 32A.2

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Revised April 2014

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1.0 Scope and Application

1.1 This method details the determination of silicate in fresh waters by automated colorimetric analysis. The practical range of determination for this method is 0.00 to 20.00 mg SiO_2/L. Method detection limit for this analysis is 0.10 mg/L as silica.

2.0 Summary of Method

2.1 An automated analysis method is used for the colorimetric determination of silica in fresh water. Silica reacts with molybdate in an acidic environment to form yellow beta-molybdosilicic acid. The acid is reduced with ascorbic acid to form a heteropoly molybdous-blue complex that absorbs at 660 nm (See Reference 16.4). Concentration of silica is determined by comparison of absorbance signal with calibration results obtained from prepared standards of varying concentrations.

3.0 Definitions

3.1 DI water: Water that has been through a deionization system to produce water similar to ASTM Type I reagent with 16.7 Mohms resistivity (ASTM) (Reference 16.3).

3.2 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence, based on a one-sided 99% confidence interval (*t*-value at a significance level of 0.01 and *n-1* degrees of freedom) from at least seven repeated measurements of a low concentration standard measured within an analysis run.

MDL = *ts*

Where,

t = Student's t value at a significance level of 0.01 and $n\text{-}1$ degrees of freedom
s = standard deviation of at least seven repeated measurements of a low level standard

4.0   Interferences

4.1   Oxalic acid is added to the sample stream before addition of ascorbic acid to eliminate interference from phosphates.

4.2   Tannin and large amounts of iron, color, turbidity and sulfide interfere.

4.3   Freezing samples may reduce silica concentration (Reference 16.1)

4.4   Samples, standards and reagents should be stored in polyethylene containers.

4.5   Turbidity and color that persists in the sample after filtration may absorb at the 660 nm. Reanalyze samples without the color reagent as turbidity/color blanks. Any response from the turbidity/color blanks must then be subtracted from the initial analysis response.

5.0   Safety

5.1   The toxicity or carcinogenicity of each reagent has not been precisely determined; however, each chemical should be regarded as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Cautions are included for known extremely hazardous materials.

5.2   The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

    5.2.1   Sulfuric acid
    5.2.2   Oxalic acid

6.0   Equipment and Supplies
Note: *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1   Balance measuring to at least 0.1 mg

6.2   Volumetric flasks and pipettes as required

6.3   Technicon Auto-Analyzer II

      6.3.1   Multichannel proportioning pump
      6.3.2   Colorimetric detector
      6.3.3   Data system
      6.3.4   Alpkem manifold and method 105-71W/B

6.4   Safety glasses

6.5   Nitrile gloves

6.6   Lab coat or apron

6.7   Laboratory exhaust fume hood

6.8   High density polyethylene (HDPE) bottles

7.0   Reagents and Standards

7.1   Preparation of Reagents

Solutions 7.1.2 through 7.1.3 need to be filtered through prewashed GF/F filters after preparation

      7.1.1   *0.1 N Sulfuric Acid:*
            Carefully add 2.8 mL concentrated sulfuric acid to 800 mL DI
            water. Cool and dilute to 1 L.
      7.1.2   *Ammonium Molybdate:*
            Dissolve 10 g of ammonium molybdate in 1 L of 0.1 N sulfuric
            acid. Store in amber polyethylene container. Solution should be
            prepared daily.
      7.1.3   *Oxalic Acid:*
            Dissolve 50 g of oxalic acid in 900 mL of DI water. When
            dissolution complete, dilute to 1 L. Store in amber polyethylene
            container. Reagent is stable.
      7.1.4   *15 % Sodium Laurel Sulfate:*
            Dissolve 4.41 g sodium laurel sulfate in 25 mL DI water.

7.1.5   *Ascorbic Acid:*
Dissolve 17.6 g of U.S.P. quality ascorbic acid in 500 mL of DI water containing 50 mL acetone and dilute to 1 L with DI water. Add 20 mL of 15 % sodium laurel sulfate.

7.2   Preparation of Standards

7.2.1   *Calibration Standards*
Standards are prepared by dilution of a single element standard purchased from a vendor that provides traceability to NIST standards. The stock standard is used to prepare working standards in the table below.

	mg SiO2-Si/L
1	1.00
2	2.34
3	7.02
4	11.69

7.2.2   *Second Source Check Standard:*
Standards are prepared by dilution of a standard purchased from a vendor that provides traceability to NIST standards; this reagent is from a source other than that of the calibration standards. A mixed stock standard is prepared by dilution of the purchased reagent to an intermediate concentration. Check standard concentrations are the same as calibration standard 3.

8.0   Sample Handling and Storage

8.1   Unfiltered samples are filtered upon receipt through glass fiber filters into clean HDPE bottles and stored at 4°C in the dark. Samples are analyzed within 28 days to ensure sample integrity. If samples must be held prior to analysis, they are stored refrigerated at 4°C.

9.0   Quality Control

9.1   Preparation of standards is recorded on worksheets and documented by weight of standard added to a given flask before dilution to volume with DI water. All records of certification are kept on file at CCAL Laboratory.

9.2   Blank: DI water run after the calibration and before and after each check standard.

9.3   Quality Control Check Standard: Calibration standards run in rotation every ten samples to monitor stability and validate the calibration.

9.4   Method Detection Limit (MDL): Established for each analyte. Based on a one-sided 99% confidence interval (t-value) from at least seven repeated measurements of a low concentration standard. The t-distribution value is multiplied by the standard deviation of the population (n-1) to obtain the MDL.

9.5   Analytical Duplicate: Separate analysis from the same sample aliquot. Run a minimum of once every ten samples.

10.0   Calibration and Standardization

10.1   Balances: calibrated yearly by external vendor.

10.2   Pipette delivery checked by weight to within 2% of theoretical weight of aliquot volume.

10.3   Calibration curve with $r^2 \geq 0.998$. (See 17.3 for calibration data set-up.)

10.4   Calibration verification with check standards, monitored throughout the run. If measurement exceeds +/- 10% of the theoretical value, the analysis should be terminated and the instrument recalibrated. The calibration must be verified before continuing analysis.

11.0   Procedure

11.1   Calibration and Analysis Procedure

11.1.1 Prepare reagents and standards as outlined in Section 7.
11.1.2 Set up manifolds as shown in Section 17.1.
11.1.3 Samples are injected into the reaction path at a fixed time interval, determined by the cam timing set in the auto-sampler. Setup or confirm data system parameters as detailed in Section 17.3.
11.1.4 Pump DI water through all reagent and sample lines. Check for leaks and stable bubble pattern (smooth flow). Pump reagents through all lines until the system equilibrates (minimum of one hour).
11.1.5 Record sample id's in the data template.

11.1.6 Calibrate the instrument with standards. Calibration regression equations must have $r^2 \geq 0.998$.

11.2 System Notes

11.2.1 If the baseline is excessively noisy, clean the manifold using the following procedure:
- Place all reagent and carrier lines in rinse water and pump to clear reagents.
- Place all lines in 1.2N HCl solution for several minutes.
- Place lines in DI water and pump until thoroughly rinsed.

11.2.2 If baseline has a large number of air spikes, check pump tubes for excessive wear and replace as necessary.

11.2.3 Poor sensitivity or insufficient color development may be the result of old ammonium molybdate solution. Prepare fresh and flush system thoroughly.

11.2.4 Turbidity and color that persists in the sample after filtration may absorb at the 660 nm. Reanalyze samples without the color reagent as turbidity/color blanks. Any response from the turbidity/color blanks must then be subtracted from the initial analysis response.

12.0 Data Analysis and Calculations

12.1 The data system prepares a calibration curve by plotting response of injected standards versus known standard concentration. The resulting regression equation is used to calculate the sample concentration.

12.2 All results and sample information are filed in the analysis data system by analysis run. Details specific to the instrumental analysis are noted in the Instrument Run Log created and maintained for the AAII. Analytical results are entered into electronic format and entries are verified by a second person.

12.3 Historically, CCAL has reported results as mg Si/L. To convert from SiO_2 to Si, divide results by 2.137; conversely, to covert from Si to SiO_2, multiply by 2.137.

13.0 Method Performance

13.1 This method was validated through inter-laboratory studies. The CCAL Water Analysis Laboratory participates in the USGS Standard Reference

Water QA program and the National Water Research Institute's (NWRI) Environment Canada Proficiency Testing (PT) Program.

14.0 Pollution Prevention

14.1 The chemicals used in this method pose little threat to the environment when properly managed.

14.2 All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.

14.3 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required.

15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC, 20036.

16.0 References

16.1 Standard Methods For The Examination of Water and Wastewater, Method 4500-SiO_2, Automated Method for Molybdate-Reactive Silica. American Public Health Association. 21st Edition, 2005.

16.2 Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination

of the method detection limit. Revision 1.11. Revised July 1, 1990.
Office of the Federal Register, National Archives and Records.

16.3   ASTM. American Society for Testing and Materials. Standard
Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual
Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991.

16.4   Technicon AutoAnalyzer II; Industrial Method No. 105-71W/B; rev Jan
1976. Technicon Industrial Systems; Tarrytown, N.Y. 10591

17.0   Tables, Diagrams, Flowcharts, and Validation Data

17.1   Silica Reaction Manifold
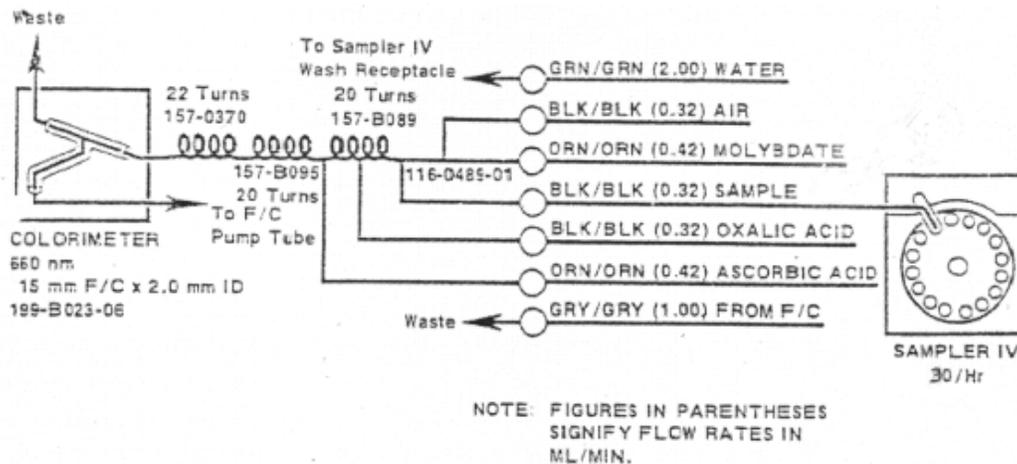
17.2   Silica Manifold Specifications

Carrier is molybdate reagent

Interference filter is 660 nm

Pump tubing is Tygon

Manifold tubing is 0.030 mm i.d.

Mixing coils are 20 turn with mid injection fitting, 20 turn with front
injection, and 22 turn.

15 mm x 2 mm flow cell

17.3   Data System Parameters

Cycle throughput: 30 samples/hr

Cycle Period: 120 s

Analyte Data:
Concentration Units   mg SiO_2/L

Calibration Data:

Level	1	2	3	4
Concentration mg/L	1.00	2.34	7.02	11.69

Calibration Fit Type: linear regression

Sampler Timing:
Minimum Probe in Wash Period: 30 s
Probe in Sample Period: 90 s

18.0   Document Revision History

Original Document: March 2006
Version: 32A.0
Title: Standard Operating Procedure for the Analysis of Silica in Fresh Waters

Edit Date: February 2010
New Version: 32A.1
Section 7.2: change preparation of standards from raw materials, to serial dilution of purchased standards. Change standard concentrations. Add Second Source Check Standard.
Section 13.1: add Environment Canada Proficiency Testing Program participation
Section 17.2: change standard concentrations and order of standards.

Edit Date: April 2014
New Version: 32A.2
Section 1: change working range of method for appropriate significant figures.
Section 7.1: change preparation frequency for ammonium molybdate. Change surfactant addition for preparation of ascorbic acid.
Section 7.2: Add table for standards.
Section 8.0: change holding time for analysis.
Section 17: clarify section headings.
General editing.