

Standard Operating Procedure for the
Analysis of Silicon in Fresh Waters
CCAL 32B.1

Cooperative Chemical Analytical Laboratory
College of Forestry
Oregon State University
3015 Western Blvd
Corvallis, Oregon

Prepared by Kathryn Motter
And Laura Hartley
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Standard Operating Procedure for the Analysis of Silicon In Fresh Waters CCAL 32A.2

1.0 Scope and Application

- 1.1 This method details the determination of silicon in fresh waters by automated segmented flow, colorimetric analysis. The practical range of determination for this method is 0.00 to 10.00 mg Si/L. Method detection limit for this analysis is 0.05 mg/L as silicon.

2.0 Summary of Method

- 2.1 An automated analysis method is used for the colorimetric determination of silicon in fresh water. Silica reacts with molybdate in an acidic environment to form yellow beta-molybdosilicic acid. The acid is reduced by aminonaphtholsulfonic acid to form a heteropoly molybdous-blue complex that absorbs at 660 nm (See Reference 16.4). Concentration of silicon 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.

$$\text{MDL} = ts$$

Where,

t = Student's t value at a significance level of 0.01 and $n-1$ 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 reducing agent to eliminate interference from phosphates, and reduce tannin interferences.
- 4.2 Large amounts of tannin, iron, color, turbidity and sulfide interfere.
- 4.3 Freezing samples may reduce silicon concentration (Reference 16.1)
- 4.4 Samples, standards and reagents should be stored in polyethylene containers. Avoid using glassware.
- 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
 - 5.2.3 Sodium Bisulfite

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 Polyethylene volumetric flasks and pipettes as required
- 6.3 Astoria Pacific Astoria Analyzer
 - 6.3.1 302 Micropump (peristaltic)
 - 6.3.2 307 Digital Detector
 - 6.3.3 Data system; FasPac Software
 - 6.3.4 411 XYZ Sampler
 - 6.3.5 303A Cartridge Base
- 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 7.1.5 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 1.00 g of ammonium molybdate in 100 mL of 0.1 N sulfuric acid. Filter. 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. Filter. Store in amber polyethylene container. Reagent is stable.

7.1.4 *Stock Reducing Agent:*
Dissolve 60.0 g sodium bisulfate and 2.00 g sodium sulfite in 400 mL DI water. Add 1.00 g 1-amino-2-naphthol-4-sulfonic acid (ANSA) and mix well. Dilute to 500 mL. Filter. Store in amber polyethylene bottle. Stable for 4 months.

7.1.5 *Working Reducing Agent:*
Dilute 20 mL of stock reducing agent to 200 mL with DI water. Filter. Add 0.20 mL Dowfax. Make fresh daily.

7.1.6 *Startup/Shutdown Solution:*
Add 2 – 3 mL of Dowfax to 1-L DI water.

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 SiO ₂ -Si/L
1	1.00
2	2.50
3	5.00
4	10.00

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 or a different lot number from the same vendor. 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 1% 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. Setup or confirm data system parameters as detailed in Section 17.3.
- 11.1.4 Pump startup solution through all reagent until stable flow. Check for leaks and stable bubble pattern (smooth flow). Pump reagents through all lines until the system equilibrates.
- 11.1.5 Record sample ids 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 DI water and pump to clear reagents.
 - Place all lines in 20% Contrad NF solution for 20 minutes.
 - Place lines in DI water and pump until thoroughly rinsed.
 - Pump startup solution through reagent lines until stable bubble pattern.
- 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 If bubbles “stick” in debubbler, soak debubbler in 20 – 30% Contrad NF solution for 2 – 3 hours. Rinse thoroughly with DI water.
- 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 Astoria Analyzer. 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 Si to SiO₂, 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: Guide to Minimizing Waste in Laboratories*, available from the American Chemical Society at www.acs.org.

15.0 Waste Management

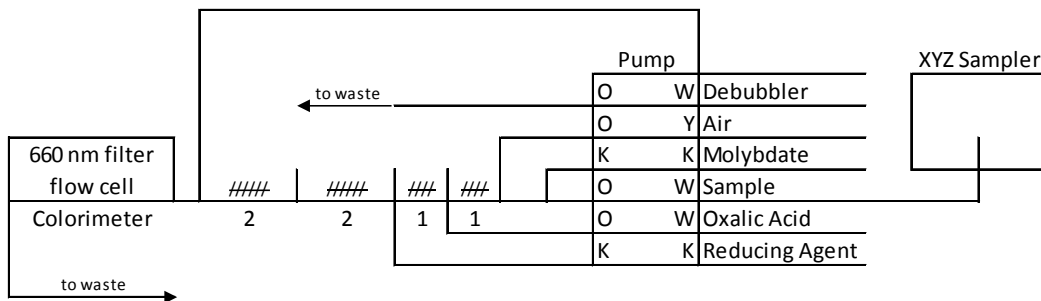
- 15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required.
- 15.2 For further information on waste management, consult *Less is Better: Guide to Minimizing Waste in Laboratories*, available from the American Chemical Society at www.acs.org, and *Environmental Management Guide For Small Laboratories* (233B00001) from the US Environmental Protection Agency at <https://nepis.epa.gov>.

16.0 References

- 16.1 Standard Methods For The Examination of Water and Wastewater, Method 4500-SiO₂ E, Automated Method for Molybdate-Reactive Silica. American Public Health Association. 22nd Edition, 2012.
- 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 Astoria 2 Analyzer: Operation Manual. Astoria-Pacific Inc., Clackamas, OR 97015-0830.
- 16.5 FASPac 2: Flow Analyzer Software Package, Version 2.3. Astoria-Pacific Inc., Clackamas, OR 97015-0830.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Silicon Reaction Manifold (CCAL modified)



Mixing Coil 1: 135 cm 0.034" id PE tubing on 7 cm coil support

Mixing Coil 2: 255 cm 0.034" id PE tubing on 12 cm coil support

17.2 Silicon Manifold Specifications (CCAL modified)

Carrier is molybdate reagent

Interference filter is 660 nm

Pump tubing is PVC

Manifold tubing is 0.034" id PE tubing

10 mm x 15 mm flow cell

17.3 Data System Parameters

Cycle throughput: 51 samples/hr

Cycle Period: 70 s

Analyte Data:

Concentration Units: mg Si/L

Calibration Data:

Level	1	2	3	4
Concentration mg/L	1.00	2.50	5.00	10.00

Calibration Fit Type: 2nd Order

Sampler Timing:

Minimum Probe in Wash Period: 45 s

Probe in Sample Period: 25 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.

Edit Date: April 2018

New Version: 32B.1

Change in instrumentation from Technicon AAI to Astoria Analyzer, 4/19/2017

Change in chemistry from Technicon 105-71W/B to 4500-SiO₂ E, 4/19/2017

Change to FASpac software, 8/10/2015

Changes throughout document to reflect instrument/chemistry changes

Title change from Silica to Silicon; changed throughout document

Title Page: new author, address change

Section 1: change in calibration range