Arikaree Environmental Laboratory
Revision 1
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SiO_2 by FIA

TITLE: Lachat QuikChem Method 10-114-27-1-A

ANALYTES: SiO_2(Si)

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1) Applicable Matrices

a) This method is applicable to ground, surface and waste waters.

b) The method is applicable in the range from 0.01 to 10.0 mg/L for Si analysis.

2) Scope and Application

a) Soluble silica species react with molybdate to form a yellow silicamolybdate complex. The complex is reduced with 1-amino-2-napthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex having a maximum absorbance at 820nm

3) Interferences

a) Phosphate causes positive signal interference and is reduced with oxalic acid.

b) Tannins and large amounts of iron or sulfides. Sulfide interference can be mitigated by boiling an acidified sample, and EDTA will eliminate iron interference

4) Equipment and Supplies

a) Analytical balance capable with 0.0001g sensitivity.

b) Top loading balance with 0.01g sensitivity.

c) Pipets capable of precisely dispensing1.0-5.0mL and 0.1-1.0mL

d) Pipet tips appropriate for each pipette.

e) Class A volumetric flasks and pipettes for reagent and standard preparation.

f) Lachat 8500 flow-injected autoanalyzer with SiO_2 manifold, 10.00mm flow cell, and interference filter at 820 nm.

g) Water purifier for preparation of ASTM Type I water (Ultrapure).

h) Various Class A volumetric pipettes for dilution of calibration standards.

5) Reagents and Standards

<u>1,000ppm Si Stock Standard</u>

1.) Use purchased 1,000ppm Si Standard

Ammonium Molybdate Solution

1.) In 500mL volumetric flask, dissolve 20.0g ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Using a graduated cylinder, dilute 8.0mL sulfuric acid. Dilute to the 500mL mark with ultrapure water, replace stopper and invert to mix. Store in a Nalgene and degas with helium. Refrigerate.

Oxalic Acid Solution

1.) In a 500mL volumetric flask, dissolve 50.0g oxalic acid ($HO_2CCO_2H\cdot 2H_2O$). Dilute to the 500mL mark with ultrapure water, replace stopper and invert to mix. Store in a Nalgene and degas with helium.

ANSA Reducing Reagent

1.) In a 500mL volumetric flask dissolve 2.0g sodium sulfite (Na_2SO_3). Stir until dissolved. Then dissolve 0.25g 1-amino-2-napthol-4-sulfonic acid (ANSA). Stir until dissolved. Then dissolve 15g sodium bisulfite ($NaHSO_3$). Use a pipet to dilute 4mL of glycerol. Stir until dissolved. Dilute to 500mL mark with ultrapure water. Replace stopper and invert to mix. Store in brown plastic Nalgene.

50ppm Si Matrix Spike Solution

1.) In a 100mL class A volumetric flask, dilute 5.0mL of 1,000ppm Si Stock Standard. Dilute to the 100mL mark with ultrapure water, replace stopper and invert to mix. Store in a 125mL Nalgene. Refrigerate.

6) Sample Collection, Preservation, Shipment, and Storage

a) Collect and filter samples in clean plastic bottles. Samples shall be filtered through a 0.45µm membrane filter. Keep samples refrigerated between 0-4°C.

7) Quality Control

a) Calibrate before each analytical run. Analyze Instrument Performance Check (IPC)/ from a second source standard after calibration. Calibration r-value is required to be > 0.995, if not re-calibrate.

b) Run an initial calibration verification blank (ICVB) at the beginning of each run and then once every 20 samples. ICVB must be <LOD. If not, re-analyze, if still out of control qualify data. Subsequent blanks (CCVB) must be <LOD, or less than 10% of the measured concentration in the samples from the adjacent set.

c) Analyze a Continuing Calibration Verification Standard (CCVS) with every 20 samples.

d) A duplicate and matrix spike must be analyzed every 20 samples (5%). Prepare a spiked sample by pipetting 0.1mL of 50.0ppm Si matrix spike solution into empty lachat sample tube. Pipet 4.9mL of sample into the same tube. Seal tube with parafilm wax and invert several times to mix. Place in correct location in autosampler rack.

8) Calibration

a) Prepare calibration standards as listed below. Use only class A volumetric pipettes and flasks. Dilute using ultrapure water.

Standard	mg/L Si	mL 1,000ppm Si Standard	Total volume
A	10.0	5.0	500mL
B	5.0	5.0	1,000mL
C	2.0	1.0	500mL
D	1.0	50.0 of Standard A	500mL
E	0.5	50.0 of Standard B	500mL
F	0.2	50.0 of Standard C	500mL
G	0.1	5.0 of Standard A	500mL

9) Procedure for Lachat 8500 operation

a) Install silica Lachat manifold if not installed already.

b) Turn on the Lachat autoanalyzer by moving the switch on the power strip behind the autosampler to the on position. The instrument will go through its normal startup routine (autosampler probe moves, switching valves on the instrument turn, etc.).

c) Place reagent tubing into water and start the peristaltic pump. Clamp each pump tube clamp onto the rollers. Push the tensioner cam lever back one click.

d) Hit the space bar on the computer keyboard to “wake-up” the computer. Double-click on the Omnion icon on the desktop.

e) Hit the space bar on the computer keyboard to “wake-up” the computer. If the computer is on, restart before continuing. After reboot, double click on the Omnion icon.

f) Make sure the concentrations for the IPC/QCS sample are correct by clicking on the sample in the worksheet. If the values are incorrect, change them by highlighting all of the samples in the DQM set (most likely DQM1) and clicking “clear DQM set” from the menu. Change the concentration in the “Run Properties” window in the upper right of the screen. Highlight the DQM samples again and right click. Select define DQM set. Set the frequency to once.

g) Start inputting sample names/numbers into the worksheet. To add more spaces for samples, highlight a row and right click. Select “Insert many” and input how many rows to add. Remember to hit “enter’ after each sample is input. Use the benchsheet to enter the sample identifiers. To enter multiple samples quickly, select multiple rows and right click. Go to “Columns” and select “Auto SampleID.” Enter the part of the sample identifier that will not change in the “Fixed Part of Sample ID” then the number or letter to

start. Click “Accept.” It is helpful if the number of rows highlighted matches the number of samples to be input automatically.

h) Once finished, highlight the entire worksheet and right click. Go to “Columns” and select “Auto-number cups.” Make sure the number of cups in the worksheet matches what is on the benchsheet. If the numbers do not match, check the duplicates and matrix spikes to see if they match. Once you find a matching duplicate and spike set, you will know where the discrepancy is located.

i) Remove the reagent lines from the water and begin placing them in their corresponding reagent bottles. Allow reagents to flow through manifold for ~10 minutes.

j) Click on the “Configuration” menu at the top of the Omnion window. Go to “Autosamplers” and click the button “Intialize Autosampler.” This will put the sampler probe into the wash well to begin drawing water through the sample line.

k) After reagent has been pumping for ~10 min. click the preview button at the top of the Omnion window. This will let you see the baseline before starting the run. The baseline is flat and the signal is where it is expected, click “Stop” next to the “Preview” button and then click “Start.”

l) During the beginning of the run, watch to make sure there is good Gaussian peak shape and the peak expection window is integrating the entire peak correctly.

m) After the calibration standards are integrated, check the calibration curve by clicking on the bottom button on the left side of the channel window. Make sure calibration coefficient is ≥0.995 and %RSD for each standard is under 10%. If either of these limits are exceeded begin by excluding peaks that may skew the curve. If this does not correct the problem, recalibrate.

n) Next, be sure the initial calibration check standards are within 10% of the expected value. It not, reanalyze the standards. If this does not correct the issue, recalibrate.

o) After everything in the beginning is in control, the rest of the run can be monitored for duplicate RPD’s/differences and matrix spike recoveries. If these are out of control, try reanalyzing the samples. Also, a continuing calibration verification blank (CCVB) and continuing calibration verification standard will be analyzed every 20 samples. Make sure these are within 10% of known value.

p) If everything in the run goes to plan, the instrument will stop after all of the samples in the worksheet have been analyzed. The reagent lines can be removed and placed into ultrapure water for ~10min. After the 10min., remove tubes from water and hang them on the hook above the pump and allow air to be pumped through the manifold. Pump air until all water has been evacuated from the manifold lines.

q) Release the pump tubes on the pump and stop the pump. Turn of the Lachat by flipping the switch on the power strip behind the autosampler.

r) Samples in the test tubes can be disposed by dumping the sample into the waste drum. The tubes will be cleaned and used again.

10) Corrective Action for Out-of-Control Data

a) Any CCV blank that exceeds the LOD, the analyst must inspect the concentration of the previous sample. If the blank is greater than 10% of the previous sample, reanalyze the blank immediately following the CCVS. No samples can be run until the blank meets requirements.

b) CCV and LCS standards must fall within 10% of true value (90%-110% Recovery). If not re-mix and re-analyze, if still out of range re-calibrate. Fill out corrective action report.

11) Contingencies for Handling Out-of-Control Data

a) Samples that fail the CCVB or ICVS will have to be qualified back to the last sample that the quality control met the above conditions.

12) Waste Management

a) All waste must be collected (except for waste from probe wash well) and disposed of in the phosphorus and silica waste carboy.

13) References

a) Standard Methods for the Examination of Water and Wastewater, 22nd ed. Clesceri, L.S.; Greenberg, A.

b) Lachat QuikChem Method 10-114-27-1-A. Silica (SiO_2) in Waters. R. McKnight, revision date 30 January, 1991.