Standard Operating Procedure for Chloride and Silica in Lake Water (Lachat Method)

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1.0 Scope and Application

1.1 This method covers the determination of chloride and silica in lake water.

1.2 The approximate working range is 0.03-30.0 mg-Cl/L and 0.01-2.00 mg-Si/L. The method detection limits are 0.030 mg-Cl/L and 0.010 mg-Si/L.

2.0 Summary

2.1 Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms the highly colored ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. Ferric thiocyanante absorbs strongly at 480 nm. The calibration curve is non-linear.

2.2 Soluble silica species react with molybdate under acidic conditions to form a yellow silicamolybdate complex. This complex is subsequently reduced with 1-amino-2-napthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex which has an absorbance maximum at 820 nm.

3.0 Sample Handling and Preservation

3.1 Samples are collected in clean plastic containers

3.2 Samples should be stored at 4°C.

4.0 Interferences

4.1 Chloride

4.1.1 Substances which reduce iron(III) to iron(II) and mercury(III) to mercury(II). (e.g. sulfite, thiosulfate).

4.1.2 Halides which also form strong complexes with mercuric ion (e.g. Br^-, I^-) give a positive result.

4.2 Silica

4.2.1 The interference due to phosphate is reduced by the addition of oxalic acid. An 8" reaction coil after the oxalic acid may be substituted for the 4" coil if found to be necessary.

4.2.2 Tannin and large amounts of iron or sulfides are interferences.

4.2.3 Silica contamination may be avoided by storing samples, standards, and reagents in plastic.

5.0 Apparatus

5.1 13 X 100 mm plastic test tubes.

5.2 Lachat QuikChem AE

5.2.1 XYZ Sampler

5.2.2 Chloride manifold (Lachat Method # 10-117-07-1-C)

5.2.3 Silica manifold (Lachat Method # 10-114-27-1-B)

5.2.4 Printer

6.0 Reagents and Standards

6.1 All reagents should be stored in the appropriate bottles and labeled with the following information:

Identity:	(Oxalic Acid)
Date:	(mm/dd/yy)
Initials of Preparer:	(M.S.)

All standards shall be stored in appropriate bottles and labeled as above with the following also included:

Concentration:	(1000 mg-Cl/L)

6.2 Use deionized water for all solutions.

6.3 Chloride

6.3.1 Stock Mercuric Thiocyanate Solution: In a 1 L volumetric flask, dissolve 4.17 g mercuric thiocyanate ($Hg(SCN)_2$ in approximately 500 mL methanol. Dilute to the mark with methanol and invert three times to mix.

Caution: Mercury is a very toxic metal! Wear gloves!

6.3.2 Stock Ferric Nitrate Reagent, 0.5 M: In a 1 L volumetric flask dissolve 202 g ferric nitrate $Fe(NO_3)_3 \bullet 9H_20$ in approximately 800 mL water. Add 25 mL concentrated nitric acid and dilute to the mark. Invert three times to mix.

6.3.3 Combined Color Reagent: In a 500 mL volumetric flask, mix 75 mL stock mercuric thiocyanate with 75 mL stock ferric nitrate reagent and dilute to the mark with water. Invert three times to mix. Vacuum filter through a 0.45 micrometer membrane filter.

6.4 Silica

6.4.1 Molybdate Reagent: In a 500 mL volumetric flask dissolve 20.0 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] in approximately 400 mL of water. When all solid material has dissolved, add 8.0 mL of concentrated sulfuric acid. Dilute to 500 mL and invert three times to mix. Store in plastic and refrigerate. Degas with helium. Prepare this reagent monthly. Discard if precipitate or blue color is observed.

6.4.2 Oxalic Acid: In a 500 mL volumetric flask, dissolve 50.0 g of oxalic acid [$HO_2CCO_2H•2H_2O$] in approximately 450 mL of water. Dilute to the mark and stir to dissolve. Store in plastic. Do not refrigerate. Degas with helium.

6.4.3 ANSA Reducing Agent: In a 100 mL volumetric flask dissolve 2.0 g of sodium sulfite (Na_2SO_3) in approximately 80 mL of water. Add 0.25 g of 1-amino-2-napthol-4-sulfonic acid. Dissolve and dilute to the mark. Prepare a second solution by dissolving 15 g of sodium bisulfite ($NaHSO_3$) in 300 mL water. In a dark plastic container mix the two solutions. Add 4 mL glycerol. Degas with helium. Store refrigerated and discard when it becomes dark.

6.5 Preparation of Standards

6.5.1 10,000 mg-Cl/L Stock Calibration Solution: In a 500 mL volumetric flask dissolve 8.240 g of Sodium Chloride (NaCl) (dried at 105°C for two hours). Dilute to the mark with water.

6.5.2 1,000 mg-Si/L Stock Calibration Solution: Purchased commercially.

6.5.3 Intermediate Chloride Calibration Standard (1,000 mg-Cl/L): To a 500 mL volumetric flask, add 50 mL 10,000 mg/L Chloride Solution (6.5.1). Dilute to the mark.

6.5.4 Intermediate Silica Calibration Standard (200 mg-Si/L): To a 500 mL volumetric flask, add 100 mL of 1,000 mg/L Silica Solution (6.5.2). Dilute to the mark.

6.5.5 Combined Working Calibration Standards: Prepare standards over the range of analysis. For the working range 0-30 mg-Cl/L and 0-2.00 mg-Si/L, the following standards may be used:

mL Intermediate Standard (6.5.3) Diluted to 1 L	mL Intermediate Standard (6.5.4) Diluted to 1 L	Concentration mg-Cl/L	Concentration mg-Si/L
0.0	---	0.00	---
1.5	---	1.50	---
3.0	---	3.00	---
5.0	0.0	5.00	0.00
10.0	0.5	10.00	0.10
15.0	1.0	15.00	0.20
20.0	2.5	20.00	0.50
25.0	5.0	25.00	1.00
30.0	10.0	30.00	2.00

Note: Use volumetric flasks.

6.5.6 Chloride High Check Control Standard Stock (1,730 mg-Cl/L): In a 1 L volumetric flask dissolve 3.6382 g of Potassium Chloride (KCl) and dilute to the mark.

6.5.7 Chloride Low Check Control Standard Stock (560 mg-Cl/L): In a 1 L volumetric flask dissolve 1.1777 g of Potassium Chloride (KCL) and dilute to the mark.

6.5.8 Silica Control Standard Stock (467 mg-Si/L): In a 1 L volumetric flask dissolve 3.13 g of Sodium Fluorosilicate (Na_2SiF_6) and dilute to the mark.

6.5.9 Silica Intermediate High Check Control Standard (46.7 mg-Si/L): To a 500 mL volumetric flask add 50 mL of Silica Contral Standard Stock (6.5.8) and dilute to the mark.

6.5.10 Silica Intermediate Low Check Control Standard (9.3 mg-Si/L): To a 500 mL volumetric flask add 10 mL of Silica Control Standard Stock (6.5.8) and dilute to the mark.

6.5.11 Combined Working High Control Standard (CH): In a 200 mL volumetric flask, add 2 mL of Chloride High Check Control Standard Stock (6.5.6) and 2 mL of Silica Intermediate High Check Control Standard (6.5.9) and dilute to the mark. The concentrations of the High Control Standard are 17.3 mg-Cl/L and 0.467 mg-Si/L.

6.5.12 Combined Working Low Control Standard (CL): In a 200 mL volumetric flask combine 2 mL of Chloride Low Check Control Standard Stock (6.5.7) and 2 mL of Silica Intermediate Low Check Control Standard (6.5.10) and dilute to the mark. The concentrations of the Low Control Standard are 5.6 mg-Cl/L and 0.093 mg-Si/L.

7.0 Procedure

Follow the Lachat Procedural SOP (Typical Daily Operation Section).

8.0 Calculations

The computer yields results directly in mg-Cl/L and mg-Si/L.

9.0 Quality Control

9.1 The minimum acceptable correlation coefficient for both parameters (r) = 0.995.

9.2 The following items are required with the minimum frequency indicated. Any audit out-of-control requires corrective action.

Audit	Type	Frequency	Limits
Chloride:			
CH	Method	Beg, End, 1/40	17.3 ± 1.2
CL	Method	Beg, End, 1/40	5.6 ± 0.6
Reagent Blank (RB)	Method	Beg, End, 1/40	0.0 ± 0.2
Silica:			
CH	Method	Beg, End, 1/40	0.467 ± 0.053
CL	Method	Beg, End, 1/40	0.093 ± 0.018
Reagent Blank (RB)	Method	Beg, End, 1/40	0.000 ± 0.021

10.0 Waste Disposal

10.1 The effluent from the chloride channel contains mercuric thiocyanante, which is toxic. This waste should be collected and discarded in the orange labeled (corrosive) waste container.

10.2 The effluent from the silica channel is an acidic waste and should be disposed of in the yellow labeled (acidic) waste container.

11.0 Preventative Maintenance

Required maintenance is described in the Lachat Procedural SOP.

12.0 Troubleshooting

The most common problem is air bubbles in the lines due to insufficient purging of reagents with helium.

13.0 References

13.1 Lachat Instruments, Method Number 10-117-07-1-B, Chloride in waters, Revision Date June 1993.

13.2 Lachat Instruments, Method Number 10-114-27-1-B, Silica as silicon dioxide (SiO_2), Revision Date February 1989.

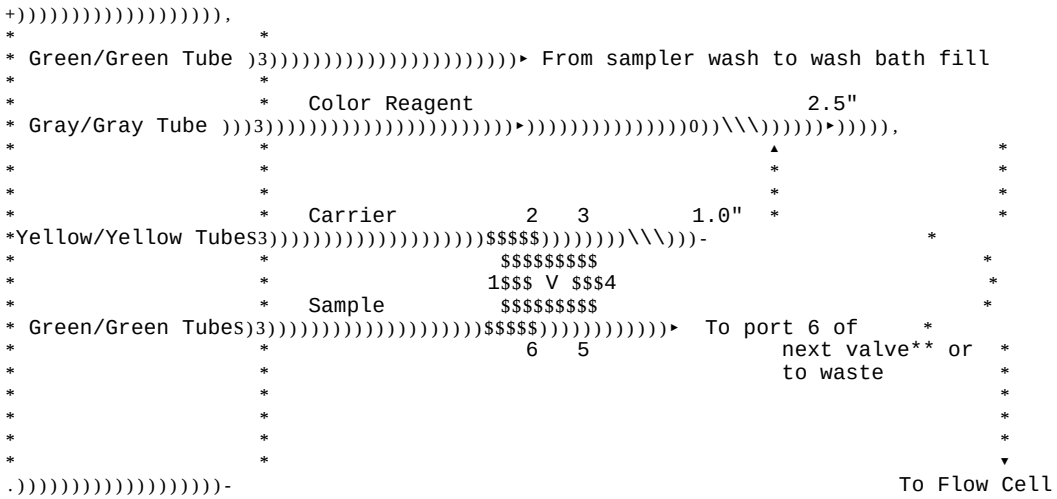
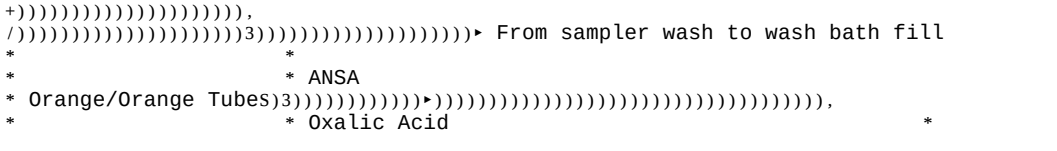


Figure 1. Chloride Analytical Manifold (Lake Water Analysis)

Comments

1. Filter used is 480 nm.
2. Sample loop length is 100 cm.
3. All manifold tubing is 0.8 mm (0.032") ID. This relates to a flow of 5.2 µL/cm.
4. The Carrier is helium degassed DI Water.

** This will occur if more than one parameter is being run simultaneously.



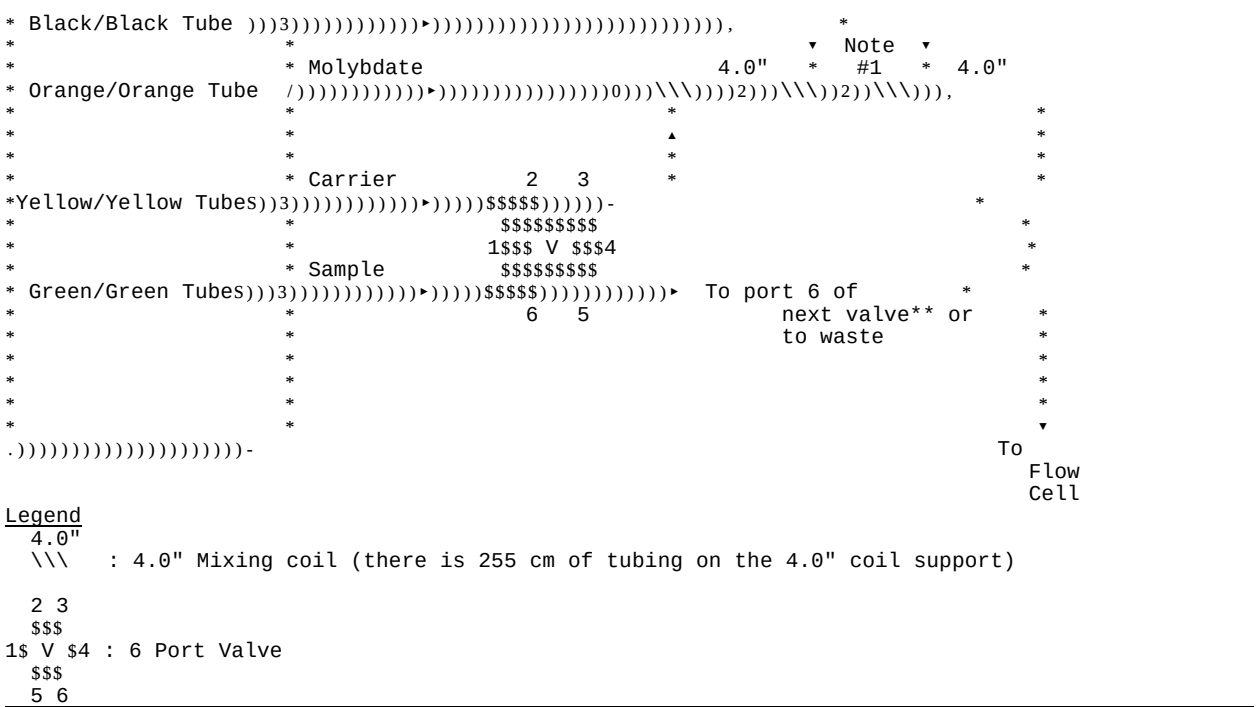


Figure 2. Silica Analytical Manifold (Lake Water Analysis)

Comments

1. Filter used is 820 nm.
2. Sample loop length is 150 cm.
3. All manifold tubing is 0.8 mm (0.032") ID. This relates to a flow of 5.2 µL/cm.
4. The Carrier is helium degassed DI Water.

** This will occur if more than one parameter is being run simultaneously.

Note 1: The manifold will come with a 4.0" coil here. This can be replaced with an 8" coil if found to be necessary. See Interferences Section.

NUTRIENTS SECTION QUALITY CONTROL SHEET

ANALYTE: SILICA **PROGRAM:** LIMNOLOGY **DATA SET:**_____

DATE	SAMPLE		CHECK STANDARD AUDIT		BLANK AUDIT
	FROM	TO	CH	CL	REAGENT BLANK (LB)
			(0.414 to 0.520)	(0.075 to 0.111)	(-0.021 to 0.021)

COMMENTS:_____

_____

ANALYST:_____DATE:____/____/____ TEAM LEADER:_____DATE:____/____/____

NUTRIENTS SECTION QUALITY CONTROL SHEET

ANALYTE: CHLORIDE **PROGRAM:** LIMNOLOGY **DATA SET:**_____

DATE	SAMPLE		CHECK STANDARD AUDIT		BLANK AUDIT
	FROM	TO	CH	CL	REAGENT BLANK (LB)
			(16.1 to 18.5)	(5.0 to 6.2)	(-0.2 to 0.2)

COMMENTS:_____

_____

ANALYST:_____DATE:____/____/____ TEAM LEADER:_____DATE:____/____/____