ESS Method 140.4: Chloride - Automated Flow Injection Analysis

Environmental Sciences Section
Inorganic Chemistry Unit
Wisconsin State Lab of Hygiene
465 Henry Mall
Madison, WI 53706

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Chloride - Automated Flow Injection Analysis

1.0 Scope and Application

1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 Samples with concentrations in the range of 1.0-100 mg Cl/L can be analyzed directly. However, the range may be extended through the use of a digital diluter. Approximately 100 samples per hour can be analyzed.

2.0 Summary of Method

2.1 The automated procedure for the determination of chloride is based on the liberation of the thiocyanate ion (SCN) from mercuric thiocyanate, through sequestration of mercury by the chloride ion, to form un-ionized, but soluble mercuric chloride. The liberated SCN then reacts with the ferric ion to form highly colored ferric thiocyanate. This is measured colorimetrically. However, since the chemistry does not follow Beer's law, a straight line calibration curve is not obtained, necessitating a greater number of standards.

2.2 The reaction may be written as follows:

$$Hg(SCN)_2 + 2\ Cl^- \rightarrow HgCl_2 + 2(SCN)^- (SCN)^- + Fe^3 \rightarrow (Fe[SCN]) + 2$$

3.0 Sample Handling and Preservation

There are no special requirements, however, the maximum holding time is 28 days.

4.0 Interferences: Interferents belong to two classes:

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

4.2 Other halides which also form strong complexes with mercuric ion (e.g., Br^-, I^-).

If any question of interferences arise, calibration curves should be prepared in water and in the suspected interfering matrix. If the two curves differ significantly, then there is interference and the standards must be prepared in the interfering matrix instead of in water.

5.0 Apparatus: Lachat QuikChem Automated Flow Injection Analyzer which includes:

5.1 XYZ Automatic Sampler

5.2 Proportioning Pump

5.3 Injection Module with a 20 cm 0.8 mm i.d. sample loop.

5.4 Colorimeter

5.4.1 Flow cell, 10 mm, 80 µL

5.4.2 Interference filter wavelength, 480 nm

5.5 Reaction Module 10-117-07-1-B

5.6 Automated Digital Diluter

5.7 IBM Personal System 12 computer

5.8 QuikChem AE System Unit

5.9 Recorder or Quik-Calc II Software System

6.0 Reagents

6.1 Milli-Q: All reagents must be made with Milli-Q water. Millipore Corp., Bedford, MA

6.2 Chloride Color Reagent (Technicon No. T01-0352).

7.0 Standards

7.1 Stock Standard 1000 mg Cl^-/L

7.1.1 Chloride stock solution A, 1000 mg Cl/L: Dissolve 1.6482 g of sodium chloride (NaCl) (dried at 105°C for 1 h) in Milli-Q water and dilute to 1 L.

7.1.2 High level working standards, 20-100 mg Cl/L: Prepare the high level working standards by diluting the following volumes of chloride stock solution A (7.1.1) to 500 mL with Milli-Q water:

Conc. mg Cl/L	mL Stock Standard (7.1.1) 500 mL
100.0	50.0
80.0	40.0
60.0	30.0
40.0	20.0
20.0	10.0

7.2 Stock Standard 100 mg Cl/L

7.2.1 Chloride stock solution B, 100 mg Cl/L: Dilute 50 mL of chloride stock solution A (7.1.1) to 500 mL with Milli-Q water.

7.2.2 Low level working standards 1.0-10 mg Cl/L: Prepare the low level working standards by diluting the following volumes of chloride stock solution B (7.2.1) to 500 mL with Milli-Q water:

Conc. mg Cl/L	mL Stock Standard (1.2) 500 mL
10.0	50.0
5.0	25.0
2.0	10.0
1.0	5.0

8.0 Injection Timing

Pump speed:	35
Cycle period:	30 s
Load period:	15 s
Inject period:	15 s
Inject to start of peak period:	8 s
Inject to end of peak period:	30 s

9.0 System Operation:

9.1 Start-up

9.1.1 Turn on and check diagnostics.

9.1.2 Attach reagent lines.

9.2 Procedure

Follow directions in General Operating Procedures.

10.0 Notes

10.1 Collect the effluent from the chloride channel in a separate waste container of known volume.

10.2 When the container is filled, place it in a hood and add 20 mL of 13% thioacetamide (6.8) for each liter of chloride waste.

10.3 Mix thoroughly and allow the solution (which has a very strong skunk smell) to stand in a hood 24 hours. The container should be capped. Mercuric sulfide precipitate is formed during this time.

10.4 After 24 hours, filter (in a hood) the solution through a Buchner funnel. The clear filtrate can be discarded in a sink in a hood. The residue containing the mercuric sulfide can be stored indefinitely in a glass container and eventually disposed of as a hazardous waste.

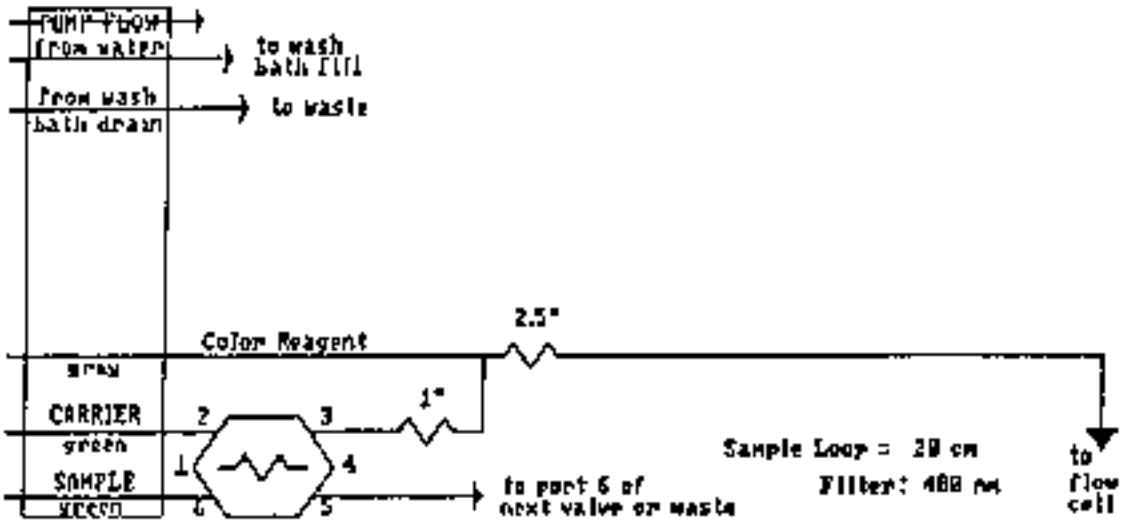
11.0 Precision and Accuracy

Precision and accuracy data are available in the Inorganic Chemistry Unit Quality Assurance Manual.

12.0 References

12.1 U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 325.2, (1979).

12.2 Lachat Instruments, Method 10-117-07-1-B, 1991.



Carrier is Milli-Q Water.

1" is 70.0 cm of tubing on a 1" coil support.
2.5" is 168 cm of tubing on a 2.5 " coil support.

All manifold tubing is 0.8 mm (0.032") i.d. This is 5.2 uL/cm.

Sample Loop:	20 cm
Cycle Period:	30 sec
Number of Standards:	9
Segmented between each Standard	
Check Standard:	40.0 mg/L

Figure 1. Manifold Diagram