4500-Cl⁻

CHLORIDE

Methods A and B: Approved by Standard Methods Committee, 2021. Joint Task Group: Ekram Aker (chair), Gözde Nur Kitapçı, Semih Sahan, Sevtap Gökçe.
Methods C-G: Approved by Standard Methods Committee, 1997. Editorial revisions, 2021. Joint Task Group: Scott Stieg (chair), Bradford R. Fisher, Owen B. Mathre, Theresa M. Wright.

4500-Cl⁻ A. INTRODUCTION

1. Occurrence

Chloride, in the form of chloride (Cl^-) ion, is one of the major inorganic anions in water and wastewater. The salty taste produced by chloride concentrations is variable and depends on the chemical composition of water. Some waters containing 250 mg/L Cl^- may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1000 mg/L when the predominant cations are calcium and magnesium.

The chloride concentration is higher in wastewater than in raw water because sodium chloride (NaCl) is a common dietary component and passes unchanged through the digestive system. Along the sea coast, chloride may be present in high concentrations because of leakage of salt water into the sewerage system. Chloride also may be increased by industrial processes.

A high chloride content may harm metallic pipes and structures, as well as growing plants.

2. Selection of Method

Six methods are presented for the determination of chloride. Because the first two are similar in most respects, selection is largely a matter of personal preference. The argentometric method (4500-Cl^- B) is suitable for use in relatively clear waters when 0.15 to 10 mg Cl^- are present in the portion titrated, and native color or turbidity will not interfere with visual detection of the endpoint. A preliminary digestion with hydrogen peroxide removes interferences from sulfide and thiosulfate. The endpoint of the mercuric nitrate method (4500-Cl^- C) is easier to detect than the endpoint of the argentometric method (4500-Cl^- B). Use the potentiometric method (4500-Cl^- D) for colored or turbid samples in which color-indicated endpoints are difficult to observe. The potentiometric method can be used without a pretreatment step for samples containing ferric ions (if not present in an amount greater than the chloride concentration), chromic, phosphate, and ferrous and other heavy-metal ions. The ferricyanide method (4500-Cl^- E) is an automated technique. Flow injection analysis (4500-Cl^- G), an automated colorimetric technique, is useful for analyzing large numbers of samples. Chloride may be determined simultaneously with several other anions by ion chromatography (Section 4110), or by the capillary ion electrophoresis method (Section 4140). Methods 4500-Cl^- C and G in which mercury, a highly toxic reagent, is used require special disposal practices to avoid improper sewage discharges. Follow appropriate regulatory procedures (see Section 1090).

3. Sampling and Storage

Collect representative samples in clean, chemically resistant glass or plastic bottles. The maximum sample portion required is 100 mL. No special preservative is necessary if the sample is to be stored.

4500-Cl⁻ B. ARGENTOMETRIC METHOD

1. General Discussion

a. Principle: In a neutral or slightly alkaline solution, potassium chromate can indicate the endpoint of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

b. Interference: Substances in amounts normally found in potable waters do not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide. Orthophosphate in excess of 25 mg/L interferes by precipitating as silver phosphate. Iron in excess of 10 mg/L interferes by masking the endpoint.

2. Apparatus

a. Erlenmeyer flask, 250-mL.

b. Buret, 50-mL.

3. Reagents

a. Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in 500 mL of reagent water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 h, filter, and dilute to 1 L with reagent water.

b. Standard silver nitrate titrant, 0.0141 M (0.0141 N): Dissolve 2.395 g $AgNO_3$ in reagent water and dilute to 1000 mL. Standardize against NaCl by the procedure described in 4500-Cl^- B.4*b*; 1.00 mL = 500 µg Cl^-. Store in a brown bottle.

c. Standard sodium chloride, 0.0141 M (0.0141 N): Dissolve 824.0 mg NaCl (dried at 140 °C) in reagent water and dilute to 1000 mL; 1.00 mL = 500 µg Cl^-.

d. Special reagents for removal of interference:

1) Aluminum hydroxide suspension—Dissolve 125 g aluminum potassium sulfate or aluminum ammonium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$ or $AlNH_4(SO_4)_2 \cdot 12H_2O$, in 1 L reagent water. Warm to 60 °C and add 55 mL conc ammonium hydroxide (29.0% NH_4OH) slowly while stirring. Let stand about 1 h, transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with reagent water, until free from chloride. When freshly prepared, the suspension occupies a volume of approximately 1 L.

2) Phenolphthalein indicator solution.

3) Sodium hydroxide (NaOH), 1 N.

4) Sulfuric acid (H_2SO_4), 1 N.

5) Hydrogen peroxide (H_2O_2), 30%.

4. Procedure

a. Sample preparation: Use a 100-mL sample or a suitable portion diluted to 100 mL. If the sample is highly colored, add 3 mL $Al(OH)_3$ suspension, mix, let settle, and filter. Proceed to 4*b*.

Alternatively, in refinery samples or similar samples that contain very high concentrations of sulfide, sulfite, or thiosulfate that might interfere with the titration, boil the sample to a volume of approximately 70 mL and add 3 mL H_2O_2. Continue boiling until the sample volume is approximately 50 mL, and cool to room temperature.[1] Proceed to 4*b*.

b. Titration: Adjust the sample pH to 8-10 with H_2SO_4 or NaOH, using a pH electrode with a nonchloride-containing reference electrode. (If only a chloride-type electrode is available, determine amount of acid or alkali needed for adjustment and discard this sample portion. Treat a separate portion with the required acid or alkali and continue the analysis.) Add 1.0 mL K_2CrO_4 indicator solution. Titrate with standard $AgNO_3$ titrant to a pinkish yellow endpoint. Be consistent in endpoint recognition.

Standardize $AgNO_3$ titrant and establish a reagent blank value by the titration method outlined above. A blank of 0.2 to 0.3 mL is usual.

5. Calculation

$$Cl^- \text{ mg/L} = \frac{(A-B)\times N\times 35\,450}{\text{mL sample}}$$

where:

A = mL titration for sample,
B = mL titration for blank, and
N = normality of $AgNO_3$.

$$NaCl \text{ mg/L} = (Cl^- \text{ mg/L})\times 1.65$$

6. Precision and Bias

A synthetic sample containing 241 mg/L Cl^-, 108 mg/L Ca, 82 mg/L Mg; 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L NO_3^--N, 25 mg/L NO_2^--N, 259 mg/L SO_4^{2-}, and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 41 laboratories by the argentometric method, with a relative standard deviation of 4.2% and a relative error of 1.7%.

Reference

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4500-Cl⁻ C. Mercuric Nitrate Method

1. General Discussion

a. Principle: Chloride can be titrated with mercuric nitrate, $Hg(NO_3)_2$, because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the titration endpoint by formation of a purple complex with the excess mercuric ions. Xylene cyanol FF serves as a pH indicator and endpoint enhancer. Increasing the strength of the titrant and modifying the indicator mixtures extend the range of measurable chloride concentrations.

b. Interference: Bromide and iodide are titrated with $Hg(NO_3)_2$ in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in excess of 10 mg/L.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Erlenmeyer flask, 250-mL.

b. Microburet, 5-mL with 0.01-mL graduation intervals.

3. Reagents

a. Standard sodium chloride, 0.0141 M (0.0141 N): See 4500-Cl⁻ B.3*c*.

b. Nitric acid (HNO_3), 0.1 N.

c. Sodium hydroxide (NaOH), 0.1 N.

d. Reagents for chloride concentrations below 100 mg/L:

1) Indicator-acidifier reagent—The HNO_3 concentration of this reagent is an important factor in the success of the determination and can be varied as indicated in paragraph a or b below to suit the alkalinity range of the sample. The reagent contains sufficient HNO_3 to neutralize a total alkalinity of 150 mg/L as $CaCO_3$ to the proper pH in a 100-mL sample. Adjust the amount of HNO_3 [see *d*1)b below] to accommodate samples of alkalinity different from 150 mg/L.

a) Dissolve, in the order named, 250 mg s-diphenylcarbazone, 4.0 mL conc HNO_3, and 30 mg xylene cyanol FF in 100 mL 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow endpoint and high results.

b) Because pH control is critical, adjust the pH of highly alkaline or acid samples to 2.5 ± 0.1 with 0.1 N HNO_3 or NaOH, not with sodium carbonate (Na_2CO_3). Use a pH meter with a nonchloride type of reference electrode for pH adjustment. If only the usual chloride-type reference electrode is available for pH adjustment, determine the amount of acid or alkali required to obtain a pH of 2.5 ± 0.1 and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue analysis. Under these circumstances, omit HNO_3 from indicator reagent.

2) Standard mercuric nitrate titrant, 0.007 05 M (0.0141 N)—Dissolve 2.3 g $Hg(NO_3)_2$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in 100 mL reagent water containing 0.25 mL conc HNO_3. Dilute to just under 1 L. Make a preliminary standardization by following the procedure described in 4500-Cl⁻ C.4*a*. Use replicates containing 5.00 mL standard NaCl solution and 10 mg sodium bicarbonate ($NaHCO_3$) diluted to 100 mL with reagent water. Adjust titrant to 0.0141 N and make a final standardization; 1.00 mL = 500 µg Cl⁻. Store away from light in a dark bottle.

e. Reagent for chloride concentrations greater than 100 mg/L—

1) Mixed indicator reagent—Dissolve 0.50 g diphenylcarbazone powder and 0.05 g bromophenol blue powder in 75 mL 95% ethyl or isopropyl alcohol and dilute to 100 mL with the same alcohol.

2) Strong standard mercuric nitrate titrant, 0.0705 M (0.141 N)—Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 mL reagent water containing 5.0 mL conc HNO_3. Dilute to just under 1 L and standardize by following the procedure described in 4500-Cl⁻ C.4*b*. Use replicates containing 25.00 mL standard NaCl solution and 25 mL reagent water. Adjust titrant to 0.141 N and make a final standardization; 1.00 mL = 5.00 mg Cl⁻.

4. Procedure

a. Titration of chloride concentrations less than 100 mg/L: Use a 100-mL sample or smaller portion so that the chloride content is less than 10 mg.

Add 1.0 mL indicator-acidifier reagent. (The color of the solution should be green-blue at this point. A light green indicates pH less than 2.0; a pure blue indicates pH more than 3.8.) For most potable waters, the pH after this addition will be 2.5 ± 0.1. For highly alkaline or acid waters, adjust pH to about 8 before adding indicator-acidifier reagent.

Titrate with 0.0141 N $Hg(NO_3)_2$ titrant to a definite purple endpoint. The solution turns from green-blue to blue a few drops before the endpoint.

Determine blank by titrating 100 mL reagent water containing 10 mg $NaHCO_3$.

b. Titration of chloride concentrations greater than 100 mg/L: Use a sample portion (5 to 50 mL) requiring less than 5 mL titrant to reach the endpoint. Measure into a 150-mL beaker. Add approximately 0.5 mL mixed indicator reagent and mix well. The color should be purple. Add 0.1 N HNO_3 dropwise until the color just turns yellow. Titrate with strong $Hg(NO_3)_2$ titrant to first permanent dark purple. Titrate a reagent water blank using the same procedure.

5. Calculation

$$Cl^- \text{ mg/L} = \frac{(A-B)\times N\times 35\,450}{\text{mL sample}}$$

where:

A = mL titration for sample,
B = mL titration for blank, and
N = normality of $Hg(NO_3)_2$.

$$\text{NaCl mg/L} = (Cl^- \text{ mg/L}) \times 1.65$$

6. Precision and Bias

A synthetic sample containing 241 mg/L Cl⁻, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L NO_3^--N, 0.25 mg/L NO_2^--N, 259 mg/L SO_4^{2-}, and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

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4500-Cl⁻ D. Potentiometric Method

1. General Discussion

a. Principle: Chloride is determined by potentiometric titration with silver nitrate solution with a glass and silver-silver chloride electrode system. During titration an electronic voltmeter is used to detect the change in potential between the two electrodes. The endpoint of the titration is that instrument reading at which the greatest change in voltage has occurred for a small and constant increment of silver nitrate added.

b. Interference: Iodide and bromide also are titrated as chloride. Ferricyanide causes high results and must be removed. Chromate and dichromate interfere and should be reduced to the chromic state or removed. Ferric iron interferes if present in an amount substantially higher than the amount of chloride. Chromic ion, ferrous ion, and phosphate do not interfere.

Grossly contaminated samples usually require pretreatment. Where contamination is minor, some contaminants can be destroyed simply by adding nitric acid.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Glass and silver-silver chloride electrodes: Prepare in the laboratory or purchase a silver electrode coated with AgCl for use with specified instruments. Instructions on the use and care of electrodes are supplied by the manufacturer.

b. Electronic voltmeter, to measure potential difference between electrodes: A pH meter may be converted to this use by substituting the appropriate electrode.

c. Mechanical stirrer, with plastic-coated or glass impeller.

3. Reagents

a. Standard sodium chloride solution, 0.0141 M (0.0141 N): See 4500-Cl⁻ B.3*c*.

b. Nitric acid (HNO_3), conc.

c. Standard silver nitrate titrant, 0.0141 M (0.0141 N): See 4500-Cl⁻ B.3*b*.

d. Pretreatment reagents:

1) Sulfuric acid (H_2SO_4), 1 + 1.

2) Hydrogen peroxide (H_2O_2), 30%.

3) Sodium hydroxide (NaOH), 1 N.

4. Procedure

a. Standardization: The various instruments that can be used in this determination differ in operating details; follow the manufacturer's instructions. Make necessary mechanical adjustments. Then, after allowing sufficient time for warmup (10 min), balance the internal electrical components to give an instrument setting of 0 mV or, if a pH meter is used, a pH reading of 7.0.

1) Place 10.0 mL standard NaCl solution in a 250-mL beaker, dilute to about 100 mL, and add 2.0 mL conc HNO_3. Immerse the stirrer and electrodes.

2) Set the instrument to desired range of millivolts or pH units. Start the stirrer.

3) Add standard $AgNO_3$ titrant, recording the scale reading after each addition. At the start, large increments of $AgNO_3$ may be added; then, as the endpoint is approached, add smaller and equal increments (0.1 or 0.2 mL) at longer intervals, so the exact endpoint can be determined. Determine the volume of $AgNO_3$ used at the point at which there is the greatest change in instrument reading per unit addition of $AgNO_3$.

4) Plot a differential titration curve if the exact endpoint cannot be determined by inspecting the data. Plot the change in instrument reading for equal increments of $AgNO_3$ against the volume of $AgNO_3$ added, using an average of buret readings before and after each addition. The procedure is illustrated in Figure 4500-Cl⁻:1.

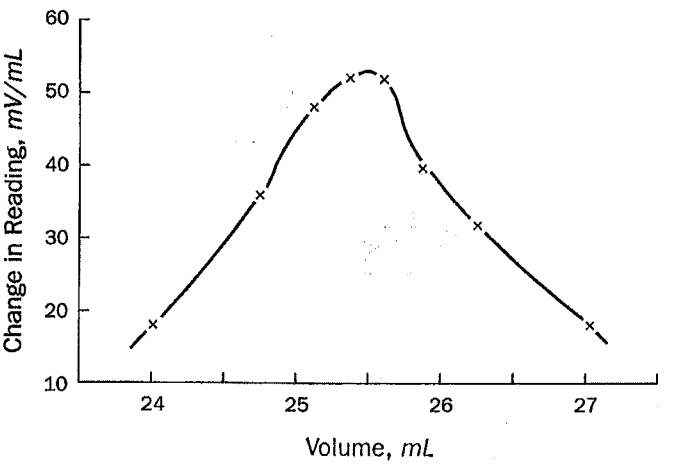
b. Sample analysis:

1) Pipet 100.0 mL sample, or a portion containing not more than 10 mg Cl⁻, into a 250-mL beaker. In the absence of interfering substances, proceed with paragraph *b*3 below.

2) In the presence of organic compounds, sulfite, or other interferences (such as large amounts of ferric iron, cyanide, or sulfide) acidify the sample with H_2SO_4, using litmus paper. Boil for 5 min to remove volatile compounds. Add more H_2SO_4, if necessary, to keep solution acidic. Add 3 mL H_2O_2 and boil for 15 min, adding chloride-free reagent water to keep the volume above 50 mL. Dilute to 100 mL, add NaOH solution dropwise until alkaline to litmus, then 10 drops in excess. Boil for 5 min, filter into a 250-mL beaker, and wash the precipitate and paper several times with hot reagent water.

3) Add conc HNO_3 dropwise until acidic to litmus paper, then 2.0 mL in excess. Cool and dilute to 100 mL if necessary. Immerse the stirrer and electrodes and start the stirrer. Make any necessary adjustments according to the manufacturer's instructions and set the selector switch to an appropriate setting for measuring the difference of potential between electrodes.

4) Complete the determination by titrating according to paragraph *a*4 above. If an endpoint reading has been established from previous determinations for similar samples and conditions, use



Experimental Data Plotted Above

Volume, mL	23.50	24.50	25.00	25.25	25.50	25.75	26.00	26.50	27.50
Change, mV/mL	18	36	48	52	52	40	32	18	

Figure 4500-Cl⁻:1. Example of differential titration curve (endpoint is 25.5 mL).

this predetermined endpoint. For the most accurate work, make a blank titration by carrying chloride-free reagent water through the procedure.

5. Calculation

$$Cl^- \text{ mg/L} = \frac{(A-B) \times N \times 35\,450}{\text{mL sample}}$$

where:

A = mL $AgNO_3$,
B = mL blank, and
N = normality of titrant.

6. Precision and Bias

In the absence of interfering substances, the precision and bias are estimated to be about 0.12 mg for 5 mg Cl^-, or 2.5% of the amount present. When pretreatment is required to remove interfering substances, the precision and bias are reduced to about 0.25 mg for 5 mg Cl^-, or 5% of amount present.

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4500-Cl⁻ E. Automated Ferricyanide Method

1. General Discussion

a. Principle: Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly colored ferric thiocyanate, of which the intensity is proportional to the chloride concentration.

b. Interferences: Remove particulate matter by filtration or centrifugation before analysis. Guard against contamination from reagents, water, glassware, and sample preservation process. No chemical interferences are significant.

c. Application: The method is applicable to potable, surface, and saline waters, and domestic and industrial wastewaters. The concentration range is 1 to 200 mg/L Cl^-; it can be extended by dilution.

d. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

a. Automated analytical equipment: An example of the continuous-flow analytical instrument consists of the interchangeable components shown in Figure 4500-Cl⁻:2.

b. Filters, 480-nm.

3. Reagents

a. Stock mercuric thiocyanate solution: Dissolve 4.17 g $Hg(SCN)_2$ in about 500 mL methanol, dilute to 1000 mL with methanol, mix, and filter through filter paper.

b. Stock ferric nitrate solution: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in about 500 mL reagent water, then carefully add 21 mL conc HNO_3. Dilute to 1000 mL with reagent water and mix. Filter through paper and store in an amber bottle.

c. Color reagent: Add 150 mL stock $Hg(SCN)_2$ solution to mL stock $Fe(NO_3)_3$ solution. Mix and dilute to 1000 mL with reagent water. Add 0.5 mL polyoxyethylene 23 lauryl ether.

d. Stock chloride solution: Dissolve 1.6482 g NaCl, dried at 140 °C, in reagent water and dilute to 1000 mL; 1.00 mL = 1.00 mg Cl^-.

e. Standard chloride solutions: Prepare chloride standards in the desired concentration range, such as 1 to 200 mg/L, using stock chloride solution.

4. Procedure

Set up manifold as shown in Figure 4500-Cl⁻:2 and follow general procedure described by the manufacturer.

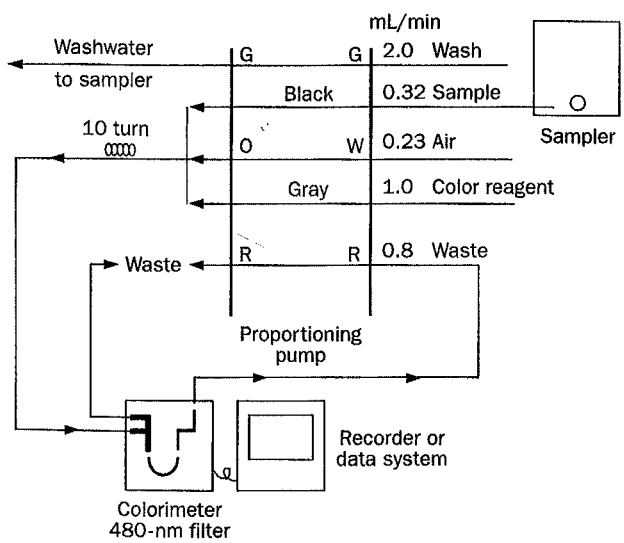

Figure 4500-Cl⁻:2. Flow scheme for automated chloride analysis.

5. Calculation

Prepare standard curves by plotting response of standards processed through the manifold against chloride concentrations in standards. Compute sample chloride concentration by comparing sample response with standard curve.

6. Precision and Bias

With an automated system in a single laboratory 6 samples were analyzed in septuplicate. At a concentration ranging from about 1 to 50 mg/L Cl^- the average standard deviation was 0.39 mg/L. The coefficient of variation was 2.2%. In 2 samples with added chloride, recoveries were 104% and 97%.

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4500-Cl⁻ F. (Reserved)

4500-Cl⁻ G. Mercuric Thiocyanate Flow Injection Analysis

1. General Discussion

a. Principle: A water sample containing chloride is injected into a carrier stream to which mercuric thiocyanate and ferric nitrate are added. The chloride complexes with the Hg(II), displacing the thiocyanate anion, which forms the highly colored ferric thiocyanate complex anion. The resulting peak's absorbance is measured at 480 nm. The peak area is proportional to the concentration of chloride in the original sample.

Also see 4500-Cl^- A and Section 4130, Flow Injection Analysis (FIA).

b. Interferences: Remove large or fibrous particulates by filtering sample through glass wool. Guard against contamination from reagents, water, glassware, and the sample preservation process.

Substances such as sulfite and thiosulfate, which reduce iron(III) to iron(II) and mercury(II) to mercury(I), can interfere. Halides, which also form strong complexes with mercuric ion (e.g., Br^-, I^-), give a positive interference.

c. Quality control (QC): The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

2. Apparatus

Flow injection analysis equipment consisting of:

a. FIA injection valve with sample loop.

b. Multichannel proportioning pump.

c. FIA manifold with flow cell (Figure 4500-Cl^-:3). Relative flow rates only are shown. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as PTFE.

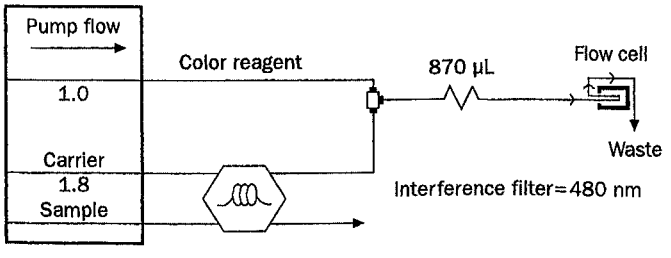

Figure 4500-Cl^-:3. FIA chloride manifold.

d. Absorbance detector, 480 nm, 10-nm bandpass.

e. Valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) to prepare carrier and all solutions.

a. Stock mercuric thiocyanate solution: In a 1-L volumetric flask, dissolve 4.17 g mercuric thiocyanate, $Hg(SCN)_2$, in about 500 mL methanol. Dilute to mark with methanol and mix. **Caution: Mercuric thiocyanate is toxic. Wear gloves.**

b. Stock ferric nitrate reagent, 0.5 M: In a 1-L volumetric flask, dissolve 202 g ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, in approximately 800 mL water. Add 25 mL conc HNO_3 and dilute to the mark. Invert to mix.

c. Color reagent: In a 500-mL volumetric flask, mix 75 mL stock mercuric thiocyanate solution with 75 mL stock ferric nitrate reagent and dilute to the mark with water. Invert to mix. Vacuum filter through a 0.45-µm membrane filter. The color reagent also is available as a commercially prepared solution that is stable for several months.

d. Stock chloride standard, 1000 mg/L Cl^-: In a 105 °C oven, dry 3 g primary standard grade sodium chloride, NaCl, overnight. In a 1-L volumetric flask, dissolve 1.648 g primary standard grade sodium chloride in about 500 mL water. Dilute to the mark and invert to mix.

e. Standard chloride solutions: Prepare chloride standards for the calibration curve in the desired concentration range, using the stock standard (¶ *d* above), and diluting with water.

4. Procedure

Set up a manifold equivalent to that in Figure 4500-Cl^-:3 and follow the method supplied by the manufacturer or laboratory standard operating procedure for this method.

5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus chloride concentration.

Table 4500-Cl⁻:1. Results of Single-Laboratory Studies with Selected Matrices

Matrix	Sample/Blank Designation	Known Addition (mg/L Cl⁻)	Recovery (%)	Relative Standard Deviation (%)
Wastewater treatment plant influent	Reference sample[a]	—	101	—
	Blank[b]	10	104	—
		20	102	—
	Site A[c]	0	—	0.4
		10	92	—
		20	101	—
	Site B[c]	0	—	0.2
		10	97	—
		20	106	—
	Site C[c]	0	—	0.4
		10	102	—
		20	102	—
Wastewater treatment plant effluent	Reference sample[a]	—	101	—
	Blank[b]	10	104	—
		20	102	—
	Site A[c]	0	—	0.3
		10	98	—
		20	101	—
	Site B[c]	0	—	0.2
		10	99	—
		20	103	—
	Site C[c]	0	—	0.4
		10	91	—
		20	97	—
Landfill leachate	Reference sample[a]	—	100	—
	Blank[b]	10	101	—
		20	100	—
	Site A[d]	0	—	0.3
		10	97	—
		20	103	—
	Site B[d]	0	—	0.2
		10	89	—
		20	103	—
	Site C[d]	0	—	0.5
		10	89	—
		20	103	—

[a] U.S. EPA nutrient QC sample, 51.7 mg/L Cl⁻.
[b] Determined in duplicate.
[c] Samples diluted 5-fold. Samples without known additions determined 4 times; samples with known additions determined in duplicate. Typical relative difference between duplicates 0.2%.
[d] Sample from Site A diluted 50-fold, those from B and C 100-fold. Samples without known additions determined 4 times; samples with known additions determined in duplicate; typical relative difference between duplicates 0.5%.

The calibration curve gives a good fit to a second-order polynomial.

6. Precision and Bias

a. Recovery and relative standard deviation: The results of single-laboratory studies with various matrices are given in Table 4500-Cl⁻:1.

b. MDL: A 100-µL sample loop was used in the method described above. Using a published MDL method[1] analysts ran 21 replicates of a 1.0-mg/L Cl⁻ standard. These gave a mean of 1.19 mg/L Cl⁻, a standard deviation of 0.027 mg/L Cl⁻, and an MDL of 0.07 mg/L Cl⁻. This is only an estimate because the ratio of standard to the MDL is above guidelines (see Section 1030 C). A lower MDL may be obtained by increasing the sample loop volume and increasing the ratio of carrier flow rate to reagents flow rate. A higher MDL may be obtained by decreasing the sample loop volume and decreasing this ratio.

Reference

1. U.S. Environmental Protection Agency. 2017. Definition and Procedure for the Determination of Method Detection Limits. Appendix B to 40 CFR 136 rev. 1.11 amended June 30, 1986. 49 CFR 43430.