

# STANDARD OPERATING PROCEDURE For SM 4500-Cl-B

## The Determination of Chloride

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SOP #: SM 4500-Cl-B

REVISION #: 0

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# MassDEP

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## LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	September 2000	None	
1.0	September 2000	Replaced old DEP Logo with state seal + MassDEP (December 2006)	Title page & header



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## **1.0 SCOPE AND APPLICATION**

- 1.1 The argentometric method is suitable for use in relatively clear waters when 0.15 to 10 mg  $\text{Cl}^-$  are present in the portion titrated. This corresponds to 3 and 200 mg/L.
- 1.2 The potentiometric method is suitable for colored or turbid samples in which color indicated end points might be difficult to observe. The potentiometric method can be used without a pre-treatment step for samples containing ferric ions, chromic, phosphate, ferrous, and other heavy metal ions.
- 1.3 Samples must be neutral or slightly alkaline.

## **2.0 SUMMARY OF METHOD**

- 2.1 Chloride is one of the major inorganic anions in water and wastewater. In potable water, salty taste produced by chloride concentration is variable and dependent on the chemical composition of water. Some waters containing 250 mg

$\text{Cl}^-/\text{L}$  may have a detectable salty taste if the cation is sodium. However the 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 NaCl is a common article of diet and passes unchanged through the digestive system. A high chloride concentration may harm metallic pipes and structures, as well as growing plants.

- 2.2 In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

## **3.0 DEFINITIONS**

- 3.1 Precipitation Titration - a titration in which particular specie reacts with the titrant, forms a solid, and drops out of solution. The reaction is quantitative.

## **4.0 INTERFERENCES**

- 4.1 Substances in amounts normally found in potable waters will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, sulfite, and thiosulfate 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 end point.



## **5.0 SAFETY**

- 5.1 Potassium Chromate  $K_2CrO_4$  indicator solution is toxic and a suspected carcinogen. Avoid breathing powder and wear mask when preparing solutions.

## **6.0 EQUIPMENT AND SUPPLIES**

- 6.1 Buret - 25 mL graduated in tenths of a mL.  
6.2 Porcelain dishes and stirring rods.

## **7.0 REAGENTS AND STANDARDS**

- 7.1 Potassium chromate indicator soln - dissolve 50 g  $K_2CrO_4$  in a little reagent water. Add  $AgNO_3$  solution until a definite red precipitate is formed. Let stand 12 hours filter and dilute to 1.0 L with reagent water.
- 7.2 Standard silver nitrate titrant (0.0141N) - Dissolve 2.395g  $AgNO_3$  in reagent water and dilute to 1.0 L. Standardize against NaCl. 1.00mL = 500 Tg  $Cl^-$ . Store in a brown bottle.
- 7.3 Standard sodium chloride (0.0141N) - dissolve 842.0 mg NaCl (dried at 140°C C) in reagent and dilute to 1000-mL 1-mL = 500 Tg  $Cl^-$ .
- 7.4 Aluminum hydroxide suspension - dissolve 125 g aluminum potassium sulfate  $[AlK(SO_4)_2 \cdot 12H_2O]$  in 1 L reagent water. Warm to 60° C and add 55 mL conc. ammonium hydroxide ( $NH_4OH$ ) slowly with stirring. Let stand about 1 hour, 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.
- 7.5 Hydrogen peroxide,  $H_2O_2$ , 30%.

## **8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE**

- 8.1 The maximum sample portion required is 100-mL. No special preservative is necessary if the sample is to be stored. Sample may be stored for up to 28 days.

## **9.0 QUALITY CONTROL**

- 9.1 The  $AgNO_3$  must be standardized against NaCl when it is prepared.
- 9.2 A duplicate and LFB and a LFM are analyzed with every batch.
- 9.3 A QCS standard is analyzed with every batch.



## 10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Follow same procedure as sample titration. 5-mL of AgNO<sub>3</sub> is equivalent to 5mL of NaCl.

## 11.0 PROCEDURE

- 11.1 Collect 50 mL of sample or a suitable portion diluted to 50mL in a Nessler tube. If the sample is highly colored, add 3mL Al (OH)<sub>3</sub> suspension, mix, let settle, and filter. If sulfide, sulfite, or thiosulfate is present, add 1mL H<sub>2</sub>O<sub>2</sub> and stir for 1 minute.
- 11.2 Directly titrate samples in the pH range 7 to 10. Adjust sample pH to 7 to 10 with H<sub>2</sub>SO<sub>4</sub> or NaOH if it is not in this range. Add 1mL K<sub>2</sub>CrO<sub>4</sub> indicator solution. Titrate in a porcelain dish with standard AgNO<sub>3</sub> titrant to a pinkish yellow end point. Titrate reagent water blank. A blank of 0.3-mL is usual.

## 12.0 DATA ANALYSIS AND CALCULATION

- 12.1 Calculation for 0.0141N AgNO<sub>3</sub>:

$$mg\ Cl^{-} / L = \frac{(A - B) \times (0.5)}{mL\ sample} \times \frac{1000mL}{L}$$

A = mL titration for sample;

B = mL titration for blank

## 13.0 METHOD PERFORMANCE

- 13.1 The smallest volume of titrant that can be measured with the buret (0.1-mL) dictates a minimum detection level of 1-mg Cl<sup>-</sup>/L.
- 13.2 Precision and Bias - SM states that a synthetic sample was analyzed in 41 labs and a relative standard deviation of 4.2% and a relative error of 1.7% was obtained.
- 13.3 Duplicate Precision: The average RPD = 3.78 with a Sd = 2.05
- 13.4 Accuracy and Precision: The percent recovery = 98% with a standard deviation of 0.67.



## 14.0 POLLUTION PREVENTION

- 14.1 The quantity of chemicals purchased should be based on expected usage during its shelf life.
- 14.2 Actual reagent preparation volumes should reflect anticipated usage during its shelf life.

## 15.0 WASTE MANAGEMENT

- 15.1 The U.S. Environmental Protection Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations.

## 16.0 REFERENCES

- 16.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995, American Public Health Association.

## 17.0 TABLES AND VALIDATION DATA

**TABLE 1. Quality Control Elements and Acceptance Limits for the Analysis of Chloride in Reagent Water by Standard Method 4500-CI-B**

QC Elements	Frequency	Acceptance Criteria	Corrective Action





**TABLE 2. Quality Control Tests and Acceptance Limits for the Analysis of Chloride in Reagent Water by Standard Method 4500-Cl<sup>-</sup>B**

Accuracy			Precision		
QC Test	Acceptance Limits (% Recovery)	Frequency	QC Test	Acceptance Limits (RPD <sup>a</sup> )	Frequency
LFB <sup>b</sup>					
LFM <sup>c</sup>					
QCS <sup>d</sup>					

**Table 3. Validation Data**

Sample #	Value	Reported Value	True Value	Acceptance
WP #40		73.0	74.9	68.1 - 83.2
WP #39		10.0	10.8	8.3 - 12.7
WP #38		155	163	150 - 176

**TABLE 4 Precision of Chloride in Reagent Water by Standard Method 4500-Cl<sup>-</sup>B**

Date	Based on Sample Numbers	No. of Samples (n)	Precision (RPD) <sup>b</sup>					
			Mean	SD <sup>a</sup>	Warning Limits (± 2 SD)		Control Limits (± 3 SD)	
					Upper (UWL)	Lower (LWL)	Upper (UCL)	Lower (LCL)
<sup>a</sup> SD = Standard deviation								
<sup>b</sup> RPD = Relative percent difference								



**TABLE 5. Method Detection Limit (MDL) for Chloride Analysis in Reagent Water by Standard Method 4500-Cl<sup>-</sup>B**

Date of Study	No. of Samples Spiked (n)	Spiked Concentration (mg/L)	Accuracy (Mean % Recovery <sup>a</sup> )	Precision (SD <sup>b</sup> in mg/L)	MDL (mg/L)
<p><sup>a</sup> Recovery of spiked concentration</p> <p><sup>b</sup> SD = standard deviation of mean concentration measured</p> <p><sup>c</sup> Method Detection Level (MDL) is 0.02 mg/L F. WES' Reporting Detection Level (RDL) is 0.10 mg/L F.</p>					