CEL212 Environmental Engineering  
Second Semester 2012-13  
Laboratory Experiment 4: Chlorides

Reference Material:  
• AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater  

Methods: Mohr Method (4500 B-Cl⁻; Argentometric Method)

Objectives: Determine chloride ion concentration in a water sample.

Background:  
Chloride in the form of chloride (Cl⁻) ion is one of the major inorganic anions in water and wastewater. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system (Average estimate of excretion: 6 g of chlorides/person/day; additional chloride burden due to human consumption on wastewater: 15 mg/L). Along the sea coast chloride may be present in high concentration because of leakage of salt water into the sewage system. It also may be increased by industrial process. In potable water, the salty taste produced by chloride concentration is variable and depends on the chemical composition of water. Some waters containing 250 mg/L Cl⁻ may have a detectable salty taste if sodium cation is present. 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. In addition, a high chloride contents may harm metallic pipes and structures as well as growing plants.

The measured chloride ions can be used to know salinity of different water sources. For brackish water (or sea water or industrial brine solution), it is an important parameter and indicates the extent of desalting of apparatus required. It also interferes with COD determination and thus it requires a correction to be made on the basis of amount present or else a complexing agent, such as HgSO₄ can be added. Further, chloride ions are used as tracer ions in column studies to model fate of different contaminants in soil and liquid media.

Lab Procedure  
Method:  
The Mohr Method uses silver nitrate for titration (normality: 0.0141) \((method applicability: 0.15 \text{ to } 10 \text{ mg/L chloride ions})\). This corresponds to \(1 \text{ mL of } 0.0141 \text{ equals to } 1 \text{ mg chloride in solution}\). The silver nitrate solution is standardized against standard chloride solution, prepared from sodium chloride (NaCl). During the titration, chloride ion is precipitated as white silver chloride (Eq.1):

\[
\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl} \quad \text{(Solubility product constant, } K_{sp}=3\times10^{-10}\)\]  (1)

The indicator (potassium chromate) is added to visualize the endpoint, demonstrating presence of excess silver ions. In the presence of excess silver ions, solubility product of silver chromate
exceeded and it forms a reddish-brown precipitate (Eq.2). This stage is taken as evidence that all chloride ions have been consumed and only excess silver ions have reacted with chromate ions:

\[ 2\text{Ag}^+ + \text{CrO}_4^{2-} \leftrightarrow \text{Ag}_2\text{CrO}_4 \quad (K_{sp} = 5 \times 10^{-12}) \]  

**Apparatus:** Burette, conical flask, pipette, measuring cylinder

**Reagents:** Potassium chromate indicator solution, standard silver nitrate titrant.

**Steps:**

1. Take 25 ml sample in a conical flask. Measure sample pH.
2. Add 1.0 ml indicator solution.
3. Titrate with standard silver nitrate solution to pinkish yellow end point and note down volume of titrant used. Also measure sample pH.
4. Calculate chloride ion concentration using Eq.(3):

   \[
   \text{Chloride Ion Concentration (mg/L)} = \left(\frac{A \times N \times 35.45}{1000} \right) / V_{\text{sample}} \quad (3)
   \]

   Where: \( A = \text{volume of titrant used} \), \( N \) is normality of silver nitrate (here we used \( N/71 \) or 0.0141 \( N \)), and \( V_{\text{sample}} \) is volume of sample used (mL).

**Precautions:**

1. A uniform sample size must be used, preferably 100 mL, so that ionic concentrations needed to indicate the end point will be constant.
2. The pH must be in the range of 7 to 8 as silver ions are precipitated as AgOH at high pH levels and the chromate ions are converted to \( \text{Cr}_2\text{O}_7^{2-} \) at low pH values.
3. A definite amount of indicator must be used to provide a certain concentration of chromate ions, otherwise silver chromate may form too soon or not soon enough.
4. Caution should be made to notice indicator color change as it can varies person-to-person. The usual range is 0.2 to 0.4 mL of titrant.

**Answer these questions also (for Submission with Lab report):**

1. Does the measured chloride ion concentration exceed the receiving body (i.e., river in this case) maximum concentration criteria? Look at the CPCB website for getting allowable concentration information. Comment on it.

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   **Practice Problems (Not for submission)**

1. What is the role of chromate ions in chloride determination?
2. As potassium chromate is an oxidizing agent, what would happen to chloride determination if the sample were consists of organic matter (say 100 mg/L glucose) as well.
3. Why pH range is important in chloride determination?
4. Would the analytical results by the Mohr method for chlorides be higher, lower or the same as the true color value if any excess of indicator were accidentally added to the sample? Why?