Chloride, titrimetric, Mohr

Parameter and Code:

Chloride, dissolved, I-1183-85 (mg/L as Cl): 00940

1. Application

1.1 This procedure is recommended for water containing concentrations of chloride between 10 and 2000 mg/L, although it can be used satisfactorily for measuring chloride concentrations up to 5,000 mg/L.

1.2 Two titrant solutions of different concentrations are recommended. The more dilute titrant is used when the chloride concentration is less than 200 mg/L. However, the end point is not as sharp as when a more concentrated titrant is used, and the latter is recommended when the chloride concentration of the sample exceeds 200 mg/L. In high-chloride waters, the voluminous precipitate tends to mask the end point, and the maximum amount of chloride that can be titrated satisfactorily is about 50 mg. Excessive sample dilution decreases both the precision and accuracy of the determination. Sample aliquots of less than 10 mL are not recommended.

2. Summary of method

2.1 In the well-known Mohr method for determination of chloride, the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. When potassium chromate is used as an indicator, a slight excess of silver precipitates as red-silver chromate. The following reactions occur:

$$Ag^{+1} + Cl^{-1} \rightarrow AgCl$$

$$2Ag^{+1} + CrO_4^{-2} \rightarrow Ag_2CrO_4$$

The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and, therefore, the chromate ion reacts with hydrogen ions.

$$CrO_4^{-2} + H^{+1} \rightleftharpoons HCrO_4^{-1}$$

The solution should not be too alkaline because of the limited solubility of silver hydroxide (Collins, 1928). Calcium carbonate can be used to adjust the pH of acidic waters without danger of making the solution too alkaline. Detection of the end point is facilitated by illuminating the titration with yellow light or by viewing the titration through yellow goggles or a filter.

2.2 Additional information on the principle of the determination is given by Kolthoff and others (1969).

3. Interferences

Iodide and bromide titrate stoichiometrically as chloride. Phosphate, sulfide, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, and then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

4. Apparatus

4.1 *Buret*, 25-mL capacity.

4.2 *Yellow light* (or filter).

5. Reagents

5.1 *Chloride standard solution*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium chromate indicator solution,* 5 g/100 mL: Dissolve 5 g K_2CrO_4 in 100 mL demineralized water. Add silver standard solution II until a small amount of red Ag_2CrO_4 precipitates. Allow to stand overnight and filter to remove the Ag_2CrO_4.

5.3 *Silver standard solution I,* 1.00 mL ≎ 5.00 mg Cl^{-1}. Pulverize approx 30 g $AgNO_3$ crystals in a clean mortar and dry at 105 to 120°C. Discoloration of the crystals indicates decomposition caused by excessive drying temperature or impurities. Dissolve 23.96 g dried $AgNO_3$ in demineralized water and dilute to 950 mL. Standardize by titrating 25.00 mL chloride standard solution diluted to 50 mL. Store in a light-proof bottle.

5.4 *Silver standard solution II,* 1.00 mL ≎ 0.50 mg Cl^{-1}: Dilute 100 mL silver standard solution I with demineralized water to 1,000 mL. Check the titer of the reagent by titrating 10.00 mL chloride standard solution. Store in light-proof bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.00 mL max) into a porcelain evaporating dish, and adjust the volume to approx 50 mL.

6.2 Add 10 drops K_2CrO_4 indicator solution.

6.3 With constant stirring, titrate with silver standard solution I or II until the pink-red Ag_2CrO_4 persists for 10 to 15 sec.

6.4 Determine a blank correction by similarly titrating 50 mL demineralized water. The normal blank correction with silver standard solution II is 0.05 or 0.10 mL. No blank correction is required with the more concentrated titrant.

7. Calculations

$$Cl^{-1}\ (\text{mg/L}) = \frac{1{,}000}{\text{mL sample}} \times (\text{mL titrant} - \text{mL blank}) \times (\text{mg } Cl^{-1} \text{ per mL titrant})$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 37 samples within the range of 0.22 to 244 mg/L may be expressed as follows:

$$S_T = 0.036X + 0.532$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8550.

9.2 Precision for seven of the 37 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
12	0.22	100
7	.29	72
10	8.59	13
21	46.0	4
13	95.8	3
12	123	6
16	244	5

References

Collins, W. D., 1928, Notes on practical water analysis: U.S. Geological Survey Water-Supply Paper 596-H, p. 235-266.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed.]: New York, MacMillan, 1199 p.