Chloride, titrimetric, mercurimetric

Parameter and Code:

Chloride, dissolved, I-1184-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine chloride in water containing at least 0.1 mg/L of chloride. Samples containing lower concentrations need to be concentrated by evaporation.

2. Summary of method

2.1 Mercuric and chloride ions form a highly stable, soluble complex.

$$Hg^{+2} + 2Cl^{-1} \rightleftarrows HgCl_2$$

Thus, the chloride in a sample may be titrated with a standard solution of a soluble mercuric salt such as mercuric nitrate. The equivalence point is detected by adding a small amount of diphenylcarbazone to the sample. A slight excess of mercuric ions, above that required to complex all of the chloride, reacts with this indicator to form a blue-violet complex (Dubsky and Trtilek, 1933, 1934; Clarke, 1950).

2.2 The optimum pH range for the titration is between 3.0 and 3.6. If the titration is made in a solution whose pH is less than 3.0, the results will be high, and if in a solution of pH greater than 3.6, the results will be low (Clarke, 1950; Thomas, 1954). The proper pH for the titration is easily obtained by adding bromophenol blue indicator and carefully adding dilute nitric acid or sodium hydroxide to adjust the sample to the desired pH.

2.3 Two standard mercuric nitrate solutions are required. A dilute solution should be used to titrate samples containing less than 200 mg/L chloride; a more concentrated mercuric nitrate solution should be used to titrate samples containing more than 200 mg/L.

3. Interferences

The method is not subject to interference from any of the anions and cations normally found in natural waters; as much as 1,000 mg/L of nitrate, sulfate, phosphate, magnesium, and calcium and 1×10^6 μg/L of aluminum do not interfere. One thousand μg/L of zinc, lead, nickel, ferrous, and chromous ions affect the colors of the solution, but not the accuracy of the titration. Nickel ion at a concentration of 1×10^5 μg/L is purple in neutral solution, green in acid solution, but gray at the chloride end point. Copper ion is tolerable up to 50,000 μg/L. Chromate and ferric ions, if present at concentrations exceeding 10,000 μg/L, must be reduced to their lower valence state prior to titration. The addition of dilute fresh hydroquinone solution insures reduction of these ions. Sulfite ion interferes at concentrations above 10 mg/L; the addition of a small amount of 30-percent hydrogen peroxide eliminates sulfite interference. Bromide and iodide are titrated with the chloride.

4. Apparatus

4.1 *Buret*, 5-, 10-, or 25-mL capacity.

4.2 *Fluorescent lamp*, white.

4.3 *Stirrer*, magnetic.

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 *Hydrogen peroxide*, 30-percent.

5.3 *Hydroquinone solution*, 1 g/100 mL: Dissolve 1.0 g purified hydroquinone in demineralized water and dilute to 100 mL.

5.4 *Mercuric nitrate standard solution I*, 1.00 mL ≎ 1.00 mg Cl^{-1}: Dissolve 4.832 g

$Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.5 *Mercuric nitrate standard solution II*, 1.00 mL ≎ 0.500 mg Cl^{-1}: Dissolve 2.416 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.6 *Mixed indicator solution*: Dissolve 0.5 g crystalline diphenylcarbazone (Eastman Kodak No. 4459) and 0.05 g bromophenol blue (Eastman Kodak No. 752) in 75 mL ethanol (methyl alcohol or specially denatured alcohol No. 3A are also suitable), and dilute to 100 mL with the alcohol. Store in a brown bottle; discard after 6 months.

5.7 *Nitric acid*, 0.05*M*: Dilute 3.0 mL concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.8 *Sodium hydroxide solution*, 0.05*M*: Dissolve 2.0 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 20 mg Cl^{-1} (50.0 mL max) into a 125-mL Erlenmeyer flask, and adjust the volume to approx 50 mL. If the sample contains less than 0.1 mg/L of Cl^{-1}, evaporate an appropriate volume to 50 mL.

6.2 Place the flask on a magnetic stirrer and add 10 drops mixed indicator solution.

6.3 If a blue, blue-violet, or red color develops, add 0.05*M* HNO_3 by drops until the color changes to yellow. Add 1.0 mL excess acid. If a yellow or orange color forms when the mixed indicator is added, add 0.05*M* NaOH solution by drops until the color changes to blue violet; then add 0.05*M* HNO_3 by drops until the color changes to yellow; then add 1 mL excess.

6.4 Titrate the solution with mercuric nitrate standard solution I or II until a blue-violet color persists throughout the solution.

6.5 Determine a blank correction by similarly titrating 50 mL demineralized water.

6.6 Alternatively, the end point of the titration may be determined spectrophotometrically, with attendant improvement in precision. Refer to specific manufacturer's manual for details. Reagents are identical to those specified for the visual determination using the mercurimetric method.

7. Calculations

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

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 36 samples within the range of 0.29 to 243 mg/L may be expressed as follows:

$$S_T = 0.045X + 0.581$$

where

S_T = overall precision, milligrams per liter,

and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8862.

9.2 Precision for seven of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.29	59
11	1.92	40
17	9.25	18
20	26.4	7
16	58.0	5
15	120	4
18	243	5

References

Clarke, F. E., 1950, Determination of chloride in water: Analytical Chemistry, v. 22, p. 553-5, 1458.

Dubsky, J. V., and Trtilek, J., 1933, Microvolumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry): Mikrochemie, v. 12, p. 315.

______1934, Mercurimetric determination of iodide using diphenylcarbazone as indicator: Mikrochemie, v. 15, p. 95.

Thomas, J. F., 1954, Mercurimetric determination of chlorides: American Water Works Association Journal, v. 46, p. 257-62.