METHOD #: 325.3 Approved for NPDES (Editorial Rev. 1978, 1982)

TITLE: Chloride (Titrimetric, Mercuric Nitrate)

ANALYTE: CAS # Cl- Chloride 16887006

INSTRUMENTATION: Titration

STORET No. 00940

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 mL is used.
1.3 Automated titration may be used.

2.0 Summary of Method

2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 Comments

3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5 to 1 mL of H_2O_2.

4.0 Apparatus

4.1 Standard laboratory titrimetric equipment including a 1 mL or 5 mL microburet with 0.01 mL graduations.

5.0 Reagents

5.1 Standard sodium chloride, 0.025 N:Dissolve l.4613 g ± 0.0002 g sodium chloride (dried al 600°C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark 1 mL = 886.5 μg Cl.
5.2 Nitric acid, HNO_3 solution (3 + 997)
5.3 Sodium hydroxide solution, NaOH, (10 g/L)
5.4 Hydrogen peroxide (30%). H_2O_2
5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 mL volumetric and dilute to the mark.
5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 mL of

distilled water acidified with 5.0 mL conc. HNO_3 in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.14 1 N and check. Store in a dark bottle. A 1.00 mL aliquot is equivalent to 5.00 mg of chloride.

5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 mL of distilled water acidified with 0.5 mL conc.HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL of distilled water acidified with 0.25 mL of conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water,Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 mL aliquot is equivalent to 500 ug of chloride.

5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 mL 95% ethanol in a 100 mL volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.

5.10 Xylene cyanole FF solution: Dissolve 0.005 g of xylene cyanole FF dye in 95% ethanol or isopropanol in a 100 mL volumetric and dilute to the mark with 95% ethanol or isopropanol.

6.0 Procedure

6.1 Use 50 mL of sample or an aliquot of sample diluted to 50 mL with distilled water, so that the concentration of chloride does not exceed 20 mg aliquot. If the sample or aliquot contains more than 2.5 mg of chloride, use 0.025 N mercuric nitrate titrant (5.7) in step 6.6. If the sample or aliquot contains than 2.5 mg of chloride, use 0.0141N mercuric nitrate (5.8) in step 6.6. Determine an indicator blank on 50 mL chloride-free water using step 6.6. If the sample contains less than 0.1 mg/L of chloride concentrate an appropriate volume to 50 mL.

6.2 Add 5 drops of mixed indicator reagent (5.9), shake or swirl solution.

6.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow.

6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.

6.5 Add 1 mL excess HNO_3 solution (5.2).

6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Xylene cyanol FF solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

6.7 Additional steps to eliminate particular interferences:

6.7.1 If chromate is present and iron is not present the end point may be difficult to detect.

6.7.2 If chromate is present at > 100 mg/L and iron is not present, add 2 mL

of fresh hydroquinone solution (5.5).

6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (5.5).

6.7.4 If sulfite ion is present, add 0.5 mL of H_2O_2 solution (5.4) to 50 mL sample and mix for 1 minute.

7.0 Calculation

$$\text{mg chloride/l} = \frac{(A - B)N \times 35{,}450}{\text{mL of sample}}$$

where:

A = mL titrant for sample
B = mL titrant for blank
N = normality mercuric nitrate titrant

mg NaCl/L = mg chloride/L x 1.65

8.0 Precision and Accuracy

8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-1.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/L, the standard deviation was ±1.0.

8.3 A synthetic unknown sample containing 241 mg/L chloride, 108 mg/L Ca, 82 mg/L Mg, 3.1 mg/L K, 19.9 mg/L Na, 1.1 mg/L nitrate N, 0.25 mg/L nitrite N, 259 mg/L sulfate 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%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D512-67, Method A, p270 (1976).