METHOD 9252A

CHLORIDE (TITRIMETRIC, MERCURIC NITRATE)

1.0   SCOPE AND APPLICATION

    1.1   This method is applicable to ground water, drinking, surface, and saline waters, and 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   INTERFERENCES

    3.1   Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

    3.2   Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5-1 mL of H_2O_2.

    3.3 Bromide and iodide are also titrated with mercuric nitrate in the same manner as chloride.

    3.4 Ferric and chromate ions interfere when present in excess of 10 mg/L.

4.0   APPARATUS AND MATERIALS

    4.1   Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations.

    4.2   Class A volumetric flasks: 1 L and 100 mL.

    4.3   pH Indicator paper.

    4.4   Analytical balance: capable of weighing to 0.0001 g.

5.0   REAGENTS

5.1   Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2   Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3   Standard sodium chloride solution, 0.025 N: Dissolve 1.4613 g $\pm$ 0.0002 g of sodium chloride (dried at 600°C for 1 hr) in chloride-free water in a 1 liter Class A volumetric flask and dilute to the mark with reagent water.

5.4   Nitric acid (HNO_3) solution: Add 3.0 mL concentrated nitric acid to 997 mL of reagent water ("3 + 997" solution).

5.5   Sodium hydroxide (NaOH) solution (10 g/L): Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.6   Hydrogen peroxide (H_2O_2): 30%.

5.7   Hydroquinone solution (10 g/L): Dissolve 1 g of purified hydroquinone in reagent water in a 100 mL Class A volumetric flask and dilute to the mark.

5.8   Mercuric nitrate titrant (0.141 N): Dissolve 24.2 g $Hg(NO_3)_2 \cdot H_2O$ in 900 mL of reagent water acidified with 5.0 mL concentrated HNO_3 in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Step 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 mL aliquot is equivalent to 5.00 mg of chloride.

5.9   Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $Hg(NO_3)_2 \cdot H_2O$ in 50 mL of reagent water acidified with 0.05 mL of concentrated HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Sec. 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.025 N and check. Store in a dark bottle.

5.10   Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL of reagent water acidified with 0.25 mL of concentrated HNQ (sp. gr. 1.42) in a 1 liter Class A volumetric flask and dilute to the mark with reagent water. Filter, if necessary. Standardize against standard sodium chloride solution (Sec. 5.3) using the procedures outlined in Sec. 7.0. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 mL aliquot is equivalent to 500 µg of chloride.

5.11   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 Class A volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.

5.12   Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in 100 mL Class A volumetric flask and dilute to the mark with 95% ethanol or isopropanol.

6.0   SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1   All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2   There are no special requirements for preservation.

7.0   PROCEDURE

7.1   Place 50 mL of sample in a vessel for titration. If the concentration is greater than 20 mg/L chloride, use 0.141 N mercuric nitrate titrant (Sec. 5.8) in Sec. 7.6, or dilute sample with reagent water. If the concentration is less than 2.5 mg/L of chloride, use 0.0141 N mercuric nitrate titrant (Sec. 5.10) in Sec. 7.6. Using a 1 mL or 5 mL microburet, determine an indicator blank on 50 mL chloride-free water using Sec. 7.6. If the concentration is less than 0.1 mg/L of chloride, concentrate an appropriate volume to 50 mL.

7.2   Add 5 to 10 drops of mixed indicator reagent (Sec. 5.11); shake or swirl solution.

7.3   If a blue-violet or red color appears, add HNO_3 solution (Sec. 5.4) dropwise until the color changes to yellow. Proceed to Sec. 7.5.

7.4   If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (Sec. 5.5) dropwise until the color changes to blue-violet; then add HNO_3 solution (Sec. 5.4) dropwise until the color changes to yellow.

7.5   Add 1 mL excess HNO_3 solution (Sec. 5.4).

7.6   Titrate with 0.025 N mercuric nitrate titrant (Sec. 5.9) until a blue-violet color persists throughout the solution. If volume of titrant exceeds 10 mL or is less than 1 mL, use the 0.141 N or 0.0141 N mercuric nitrate solutions, respectively. If necessary, take a small sample aliquot. Alphazurine indicator solution (Sec. 5.12) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.

> Note: The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting the accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acidic, and gray at the chloride end point. When applying this method to samples that contain colored ions or that require modified indicator, it is recommended that the operator become familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

7.6.1   If chromate is present at <100 mg/L and iron is not present, add 5-10 drops of alphazurine indicator solution (Sec. 5.12) and acidify to a pH of 3 (indicating paper). End point will then be an olive-purple color.

7.6.2   If chromate is present at >100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution (Sec. 5.7).

7.6.3   If ferric ion is present use a volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 mL fresh hydroquinone solution (Sec. 5.7).

7.6.4   If sulfite ion is present, add 0.5 mL of H_2O_2 solution (Sec. 5.6) to a 50 mL sample and mix for 1 min.

7.7   Calculation:

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

where:

A = mL titrant for sample;

B = mL titrant for blank; and

N = normality of mercuric nitrate titrant.

8.0   QUALITY CONTROL

8.1   All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for specific quality control guidelines.

8.2   Analyze a standard reference material to ensure that correct procedures are being followed and that all standard reagents have been prepared properly.

8.3   Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent, to determine if contamination has occurred.

8.4   Run one matrix spike and matrix duplicate every analytical batch or twenty samples, whichever is more frequent. Matrix spikes and duplicates are brought through the whole sample preparation and analytical process.

9.0   METHOD PERFORMANCE

9.1   Water samples--A total of 42 analysts in 18 laboratories analyzed synthetic water samples containing exact increments of chloride, with the results shown in Table 1. In a single laboratory, using surface water samples at an average concentration of 34 mg Cl⁻/L, the standard deviation was ±1.0. 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 nitrate N, 259 mg/L sulfate and 42.5 mg/L total alkalinity (contributed by $NaHCO_3$) in reagent 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%.

9.2   Oil combustates--These data are based on 34 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase oil in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in these results.

9.2.1   Precision and bias.

9.2.1.1   Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

Repeatability - The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 2):

$$Repeatability = 7.61 \sqrt{x}*$$

*where x is the average of two results in µg/g.

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 20.02 \sqrt{x}*$$

*where x is the average value of two results in µg/g.

9.2.1.2   Bias. The bias of this method varies with concentration, as shown in Table 3:

Bias = Amount found - Amount expected

10.0 REFERENCES

1.   Annual Book of ASTM Standards, Part 31, "Water," Standard D512-67, Method A, p. 270 (1976).

2.   Standard Methods for the Examination of Water and Wastewater, 15th ed., (1980).

3.   U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 (1983), Method 325.3.

TABLE 1. ANALYSES OF SYNTHETIC WATER SAMPLES
FOR CHLORIDE BY MERCURIC NITRATE METHOD

Increment as Chloride (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as	
		Bias (%)	Bias (mg/L)
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	-4.7

TABLE 2. REPEATABILITY AND REPRODUCIBILITY
FOR CHLORINE IN USED OILS BY BOMB
OXIDATION AND MERCURIC NITRATE TITRATION

Average value, μg/g	Repeatability, μg/g	Reproducibility, μg/g
500	170	448
1,000	241	633
1,500	295	775
2,000	340	895
2,500	381	1,001
3,000	417	1,097

TABLE 3. RECOVERY AND BIAS DATA FOR CHLORINE IN
USED OILS BY BOMB OXIDATION AND
MERCURIC NITRATE TITRATION

Amount expected, μg/g	Amount found, μg/g	Bias, μg/g	Percent bias
320	460	140	+44
480	578	9	+20
920	968	48	+ 5
1,498	1,664	166	+11
1,527	1,515	- 12	- 1
3,029	2,809	-220	- 7
3,045	2,710	-325	-11

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                        │    START    │
                        ╰──────┬──────╯
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                               ▼
              ┌────────────────────────────────┐
              │  7.1 Place 50 mL               │
              │  sample in titration           │
              │  vessel; determine             │
              │  concentration of              │
              │  mercuric nitrate              │
              │  titrant to use in             │
              │  Step 7.6; determine           │
              │  an indicator blank            │
              └────────────────┬───────────────┘
                               │
                               ▼
              ┌────────────────────────────────┐
              │                                │
              │  7.2 Add indicator             │
              │  to sample; shake              │
              │                                │
              └────────────────┬───────────────┘
                               │
                               ▼
                         ◇─────────◇         No      ◇─────────◇    Yes    ┌──────────────────┐
                        ╱ 7.3 Is    ╲ ─────────────▶ ╱ 7.4 Is    ╲ ───────▶ │ 7.4 Add sodium   │
                        ╲ sample     ╱               ╲ sample     ╱          │ hydroxide until  │
                        ╱ blue-violet╲               ╱ yellow or  ╲          │ sample is        │
                        ╲ or red?    ╱               ╲ orange?    ╱          │ blue-violet; add │
                         ◇────┬────◇                  ◇────┬────◇            │ nitric acid until│
                              │ Yes                        │ No             │ sample is yellow │
                              ▼                            ▼                └──────────────────┘
              ┌──────────────────────┐      ┌──────────────────────┐
              │ 7.3 Add nitric acid  │ ───▶ │ 7.5 Add 1 mL nitric  │
              │ until sample is      │      │ acid                 │
              │ yellow               │      │                      │
              └──────────────────────┘      └──────────┬───────────┘
                                                       │
                                                       ▼
                                            ┌──────────────────────┐
                                            │ 7.6 Titrate with     │
                                            │ mercuric nitrate     │
                                            │ until blue-violet    │
                                            │ color persists       │
                                            └──────────┬───────────┘
                                                       │
                                                       ▼
                                            ┌──────────────────────┐
                                            │ 7.7 Calculate        │
                                            │ concentration of     │
                                            │ chloride in sample   │
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                                                       │
                                                       ▼
                                                 ╭───────────╮
                                                 │   STOP    │
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