METHOD 9253

CHLORIDE (TITRIMETRIC, SILVER NITRATE)

1.0 SCOPE AND APPLICATION

1.1 This method is intended primarily for oxygen bomb combustates or other waters where the chloride content is 5 mg/L or more and where interferences such as color or high concentrations of heavy metal ions render Method 9252 impracticable.

2.0 SUMMARY OF METHOD

2.1 Water adjusted to pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.

3.0 INTERFERENCES

3.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds that precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

3.2 Residual sodium carbonate from the bomb combustion may react with silver nitrate to produce the precipitate, silver carbonate. This competitive reaction may interfere with the visual detection of the end point. To remove carbonate from the test solution, add small quantities of sulfuric acid followed by agitation.

4.0 APPARATUS AND MATERIALS

4.1 Standard laboratory titrimetric equipment, including 1 mL or 5 mL microburet with 0.01 mL gradations, and 25 mL buret.

4.2 Analytical balance: capable of weighing to 0.0001 g.

4.3 Class A volumetric flask: 1 L.

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 Hydrogen peroxide (30%), H_2O_2.

5.4 Phenolphthalein indicator solution (10 g/L).

5.5 Potassium chromate indicator solution. Dissolve 50 g of potassium chromate (K_2CrO_4) in 100 mL of reagent water and add silver nitrate ($AgNO_3$) until a slightly red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 hours after the addition of $AgNO_3$. Then filter the solution to remove the precipitate and dilute to 1 L with reagent water.

5.6 Silver nitrate solution, standard (0.025N). Crush approximately 5 g of silver nitrate ($AgNO_3$) crystals and dry to constant weight at 40°C. Dissolve 4.2473 $\pm$ 0.0002 g of the crushed, dried crystals in reagent water and dilute to 1 L with reagent water. Standardize against the standard NaCl solution, using the procedure given in Section 7.0.

5.7 Sodium chloride solution, standard (0.025N). 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.

5.8 Sodium hydroxide solution (0.25N). Dissolve approximately 10 g of NaOH in reagent water and dilute to 1 L with reagent water.

5.9 Sulfuric acid (1:19), H_2SO_4. Carefully add 1 volume of concentrated sulfuric acid to 19 volumes of reagent water, while mixing.

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 Pour 50 mL or less of the sample, containing between 0.25 mg and 20 mg of chloride ion, into a white porcelain container. Dilute to approximately 50 mL with reagent water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3) using H_2SO_4 (Sec. 5.9) or NaOH solution (Sec. 5.8).

7.2 Add approximately 1.0 mL of K_2CrO_4 indicator solution and mix. Add standard $AgNO_3$ solution dropwise from a 25 mL buret until the orange color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles. Be consistent with endpoint recognition.

7.3 Repeat the procedure described in Secs. 7.1 and 7.2 using exactly one-half as much original sample, diluted to 50 mL with halide-free water.

7.4 If sulfite ion is present, add 0.5 mL of H_2O_2 to the samples described in Secs. 7.2 and 7.3 and mix for 1 minute. Adjust the pH, then proceed as described in Secs. 7.2 and 7.3.

7.5 Calculation

7.5.1 Calculate the chloride ion concentration in the original sample, in milligrams per liter, as follows:

$$\text{Chloride (mg/L)} = [(V_1 - V_2) \times N \times 71{,}000] / S$$

where:

V_1 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Sec. 7.1.

V_2 = Milliliters of standard $AgNO_3$ solution added in titrating the sample prepared in Sec. 7.3.

N = Normality of standard $AgNO_3$ solution.

S = Milliliters of original sample in the 50 mL test sample prepared in Sec. 7.1.

71,000 = 2 x 35,500 mg Cl^-/equivalent, since $V_1 \sim 2V_2$.

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 These data are based on 32 data points obtained by five laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. Three data points were judged to be outliers and were not included in these results.

9.1.1 Precision. The precision of the method as determined by the statistical examination of inter-laboratory 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 1):

$$Repeatability = 0.36\,x*$$

*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:

$$Reproducibility = 0.71\,x*$$

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

9.1.2 Bias. The bias of this method varies with concentration, as shown in Table 2:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Average value (µg/g)	Repeatability (µg/g)	Reproducibility (µg/g)
500	180	355
1,000	360	710
1,500	540	1,065
2,000	720	1,420
2,500	900	1,775
3,000	1,080	2,130

TABLE 2.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND SILVER NITRATE TITRATION

Amount expected (µg/g)	Amount found (µg/g)	Bias, (µg/g)	Percent bias
320	645	325	+102
480	665	185	+39
920	855	-65	-7
1,498	1,515	17	+1
1,527	1,369	-158	-10
3,029	2,570	-460	-15
3,045	2,683	-362	-12

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