



Standard Test Methods for Water-Soluble Halide Ion in Halogenated Organic Solvents and Their Admixtures¹

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This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 *Test Methods 1, 2, and 3*—These test methods cover the determination of water-extractable halide ion in halogenated organic solvents and their admixtures. Fluoride ion is not measured due to the solubility of silver fluoride.

1.2 *Test Method 4*—This test method covers the determination of chloride ion in halogenated organic solvents and their admixtures.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 6.

2. Summary of Test Method

2.1 *Summary of Test Methods 1, 2, 3*—Halide ion present in halogenated organic solvents is extracted with water and precipitated as the silver halide salt with silver nitrate. Quantity of the halide present is determined by comparing the turbidity of the sample to known standards. The distilled water, as well as all glassware used, must be halide-free.

2.2 *Summary of Test Method 4*—This test method is based on the determination of ionizable chloride by titration with mercuric acetate solution using *s*-diphenylcarbazone as the indicator.

3. Significance and Use

3.1 These test methods are used to establish manufacturing and purchasing specifications. These test methods will provide

a means of determining the condition of the solvent in use. A high water soluble chloride level may indicate the start of solvent decomposition.

4. Apparatus

4.1 *Separatory Funnel*, 500-mL,

4.2 *Nessler Tubes*, 50-mL,

4.3 *Erlenmeyer Flask*, 125-mL, and

4.4 *Colorimeter or Turbidimeter*, Method 2.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all test. 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 specification are available.² 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean halide-free distilled water.

5.3 *Chloride Standard (1 mL \cong 0.0001 g Cl^-)*, *Test Methods 1, 2, and 3*—Prepare by adding 0.165 g of sodium chloride (NaCl) to 1 L of halide-free distilled water.

5.4 *Chloride Standard (1 mL = 0.000001 g Cl^-)*, *Test Method 4*—Dissolve 0.0660 g of sodium chloride in water and dilute to 1000 mL. Pipet 25 mL of this solution into a 1000-mL volumetric flask, dilute to volume, and mix.

5.5 *Nitric Acid (sg gr 1.42)*, concentrated nitric acid (HNO_3).

5.6 *Silver Nitrate Solution 0.1 N*—Prepare a 0.1 N solution of silver nitrate ($AgNO_3$).

¹ These test methods are under the jurisdiction of ASTM Committee D26 on Halogenated Organic Solvents and Fire Extinguishing Agents and are the direct responsibility of Subcommittee D26.04 on Test Methods.

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² *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

5.6.1 Prepare the silver nitrate solution by adding 16.99 g of silver nitrate to a 1-L volumetric flask and fill to the line with halide-free distilled water. After shaking to dissolve the AgNO_3 , store in an amber bottle.

5.7 *Mercuric Acetate Solution*, Test Method 4.

5.7.1 *Stock Mercuric Acetate Solution*—Dissolve 1.6 g of mercuric acetate in 500 mL of water containing 3.5 mL of nitric acid. Dilute to 1000 mL and mix.

5.7.2 *Standard Mercuric Acetate Solution*—Dilute 40 mL of stock mercuric acetate solution to 1000 mL and adjust the pH to 1.6 with nitric acid. Standardize in accordance with 7.5.5.

5.7.3 *s-Diphenylcarbazone Solution (Test Method 4)*—Dissolve 0.5 g of *s*-diphenylcarbazone in 100 mL of methanol.

6. Hazards

6.1 *Solvent Hazards*—Contact with the skin should be avoided to prevent removal of natural oils. There are varying degrees of danger to inhalation, ingestion, and contact. The user should refer to the most recent health regulations concerning the individual solvent.

6.2 Concentrated nitric acid is very hazardous in contact with the skin or eyes. The vapors are very toxic and corrosive.

6.3 (**Warning**—Wear safety glasses and rubber gloves when handling the silver nitrate or its solution.)

6.4 Mercuric acetate is toxic.

6.5 The hazards of *s*-diphenylcarbazone are not known.

7. Procedure

7.1 *Test Method 1:*

7.1.1 Transfer 100 mL of sample to a separatory funnel and add an equal volume of halide-free distilled water. Shake vigorously for 2 min to extract the water-soluble halides (see Note 1).

7.1.2 Allow the liquids to separate and discard the solvent layer. Transfer 50 mL of the water extract into a 50-mL Nessler tube and add ten drops of concentrated nitric acid. Prepare standard chloride ion solutions in 50-mL Nessler tubes by adding a volume of standard chloride solution, in millilitres, equal to the density of the solvent being tested divided by two for each part per million (ppm) of equivalent chloride ion desired (see Note 2). Dilute each standard with halide-free distilled water to 50 mL and add ten drops of concentrated nitric acid. Finally, add 1 mL of 0.1 *N* silver nitrate solution to each sample and standard and shake the Nessler tubes thoroughly for 30 s. Compare the sample with standards to determine chloride level (see Note 3).

NOTE 1—This extraction time should be consistent. Slow hydrolyzing organics such as phosgene and trichloroacetyl chloride require approximately 2 min to react completely. Excessive time, however, can permit the halogenated solvent itself to hydrolyze.

NOTE 2—For example, if trichloroethylene were being tested, 1.46/2 or 0.73 mL of standard chloride solution would be needed for each part per million (ppm) of chloride ion desired. For 2 ppm, $0.73 \times 2 = 1.5$ mL would be added. Since the water-soluble halides are usually less than 1 ppm, it will seldom be necessary to prepare more than one or two standards.

NOTE 3—The standards and samples should be prepared simultaneously. To minimize effects of entrained air and changing character of silver

chloride turbidity, let the samples set for 15 min in the dark. This waiting period is especially important when low chlorides (less than 1 ppm) are being determined. Dark storage prevents change in the silver nitrate concentration.

7.2 *Test Method 1A*—The accuracy of Test Method 1 can be improved for samples with chloride levels less than 2 ppm by increasing the solvent-water ratio from 1:1 to 4:1.

7.3 *Test Method 2*—Read the turbidity of standards prepared as described in Test Methods 1 and 1A using a colorimeter or a turbidimeter. Set up a graph to determine chloride levels in samples.

7.4 *Test Method 3*—Extract the sample as described in Test Method 1. Analyze the water extract with an ion chromatograph that has been calibrated with standards in the appropriate ranges. This test method gives superior data over turbidity methods.

7.5 *Test Method 4:*

7.5.1 Wash all glassware with chloride-free water until 10 mL of the washings show no trace of turbidity when 1 mL of silver nitrate solution is added.

7.5.2 Transfer 100 mL of the sample into a 250-mL separatory funnel, add 25 mL of chloride-free water to the sample and shake for 1 min. Transfer the sample to a second 250-mL separatory funnel and drain the water into a 125-mL Erlenmeyer flask. Repeat the extraction once with another 25 mL of water. Combine the water extracts in the Erlenmeyer flask.

7.5.3 Warm the water extract to 60°C to drive off any remaining sample. Cool to room temperature.

7.5.4 Add five drops of *s*-diphenylcarbazone solution and titrate with standard mercuric acetate solution to the pale purple end point.

7.5.5 Pipet 10.00 mL of standard sodium chloride solution into a 250-mL Erlenmeyer flask. Add 20 mL of chloride-free water and five drops of *s*-diphenylcarbazone solution. Titrate with standard mercuric acetate solution to the faint purple end point. Then:

$$\frac{\text{mL NaCl} \times 1.00}{\text{mL mercuric acetate}} = F = \mu\text{g Cl/mL} \quad (1)$$

where:

F = factor for the mercuric acetate solution.

7.5.6 *Calculation*—Calculate parts per million chloride as follows:

$$\text{Chloride, ppm} = (A \times F)/(S \times G) \quad (2)$$

where:

A = mercuric acetate solution required for the titration, mL,

F = factor for the solution (see 7.5.5),

S = sample, mL, and

G = specific gravity of the sample.

8. Report

8.1 Report the following information:

8.1.1 *Test Methods 1, 2, and 3*—Compare the turbidity of the sample with the standards and report halides as none detected, trace, or actual ppm water soluble halides. Note that Test Method 3 is specific to individual halides such as chloride or bromide. Comparisons of sample and standards can be made

3 min after preparation for qualitative or semiquantitative data. Since the turbidity of these mixtures changes on standing, the samples should set in the dark for 15 min before comparison. This gives the best quantitative data.

8.1.2 *Test Method 4*—Report ppm chloride.

9. Precision and Bias

9.1 *Test Methods 1, 2, and 3*:

9.1.1 The precision limits of Test Method 1 have been determined as ± 1 ppm at levels below 5 ppm water-soluble halide ion (see **Note 4**). Using Test Method 1A and Test Method 2 in combination yield precision limits of ± 0.3 ppm. Test Method 3, using an ion chromatograph, gives precision limits of ± 0.1 ppm.

NOTE 4—Precision of data statements have not been documented by formal precision test. These values are believed to be accurate based on repeatability of a number of standards.

9.2 *Test Method 4*:

9.2.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of triplicates obtained by the same analyst on two different days) has been estimated to be 0.005 weight ppm at 4 df. Two such values should be considered suspect (95 % confidence level) if they differ by more than 0.02 weight ppm.

9.2.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of triplicates in four different laboratories) has been estimated to be 0.06 weight ppm at 3 df. Two such values should be considered suspect (95 % confidence level) if they vary by more than 0.3 weight ppm.

10. Keywords

10.1 chloride; halide; halide ion; halogenated; ion; ion chromatograph; solvent; turbidity

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