



Standard Test Method for Hydrolyzable Chlorine Compounds in Chlorinated Aromatic Hydrocarbons (Askarels) by Refluxing¹

This standard is issued under the fixed designation D 2441; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of hydrolyzable chlorine compounds in chlorinated aromatic hydrocarbons (askarels).

1.2 *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.* For a specific hazard statement, see Section 8.

1.3 The values stated in SI units are to be regarded as the standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water^{2,3}

D 1820 Test Method for Hydrolyzable Chlorine Compounds in Chlorinated Aromatic Hydrocarbons (Askarels)⁴

3. Summary of Test Method

3.1 This test method uses a quantitative potentiometric titration using silver nitrate in an essentially nonaqueous medium to determine chloride ions. These are obtained after methanolic sodium hydroxide hydrolysis of unstable chlorine compounds in chlorinated aromatic hydrocarbons of the askarel dielectric class.

4. Significance and Use

4.1 The measured chloride ion, reported as parts per million in the askarel test specimen, is indicative of the relative stability of the askarel under prescribed conditions of test.

4.2 Refluxing with methanolic sodium hydroxide offers the detection of certain chlorine addition compounds that could be present as impurities and do not respond fully to hydrolysis at the lower temperature used in Test Method D 1820.

4.3 Many askarels contain polychlorinated biphenyls (PCBs). Manufacture and sale of PCBs has been prohibited by Federal regulation in the United States since 1978. The conditions for continued use and the handling and disposal of PCBs are also regulated. Users of this and other methods for measuring the properties of askarels containing PCBs are responsible for following applicable Federal, state, and local regulations.

5. Interferences

5.1 The presence of compounds containing hydrolyzable halogen other than chlorine, that is, bromine and iodine, will give positive results, as will also any other foreign substance capable of forming an insoluble compound with silver nitrate. Such material would not normally be present in an askarel.

5.2 The amount of chloride ions measured when the test is applied to normally stable askarels is very small, ranging near 1 ppm. Therefore, the test must be made in an area where the atmosphere is free of contaminating influences and it is essential to make a blank determination. The value obtained on the blank will indicate the degree to which the test environment, reagents, and glassware are satisfactory for this type of testing.

6. Apparatus

6.1 *Flask*, borosilicate glass, 500-mL, with 24/40 standard-taper joint.

6.2 *Reflux Condenser*, with mated 24/40 standard-taper joint.

6.3 *Combination Magnetic Stirrer⁵ and Hot Plate.*

6.4 *Magnetic Stirring Bar.⁶*

6.5 *Microburet*, 1.0-mL capacity, graduated in 0.01-mL divisions.

6.6 *Electrodes*, silver and glass.⁷

¹ This test method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.06 on Chemical Test.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 10.01.

⁴ *Annual Book of ASTM Standards*, Vol 10.03.

⁵ A Tempco, Aloe Scientific Co., St. Louis 3, MO, Catalog No. V-75655 or equivalent is satisfactory.

⁶ A TFE-fluorocarbon-covered, 1-in. long magnetic stirring bar from Fisher Scientific Co., Catalog No. 9-311-9 or equivalent is satisfactory.

⁷ Beckman Catalog No. 39261 silver billet electrode and Catalog No. 40498 glass electrode have been found satisfactory for this purpose. Although the silver billet-glass electrode system is preferred, a silver electrode with a mercurous sulfate reference electrode may be used. However, a silver-silver chloride electrode system should not be used.

6.7 *Potentiometer*,⁸ suitable for use with the glass electrode.

7. Reagents and Materials

7.1 *Purity of Reagents*—Use reagent grade chemicals 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.⁹ 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.

7.2 *Purity of Water*—Use reagent grade water conforming to Specification D 1193, unless otherwise specified. In addition, the water shall be chloride-free, as detected by this test.

7.3 *Acetone, Chloride-free*—Prepare chloride-free acetone by distillation from silver nitrate, as described in 7.4 for methanol. Determine its freedom from chlorides by potentiometric titration. A chloride content equivalent to less than 0.01 mL of 0.0025 *N* silver nitrate solution per 100 mL should be derived.

7.4 *Methanol, Chloride-free*—Reflux 5 L of methanol with 0.5 g of silver nitrate (AgNO_3) for ½ h. (Alternatively, prepare chloride-free methanol by distillation over sodium hydroxide (NaOH).) Distill the methanol from the silver nitrate, discarding the first 100 mL to flush the apparatus. Continue the distillation until about 90 % of the methanol has been distilled from the flask. Discard the remaining 10 %. Check the methanol by titration to assure its purity. The chloride ion concentration should be equivalent to less than 0.02 mL of 0.0025 *N* silver nitrate solution per 100 mL of methanol.

7.5 *Silver Nitrate, Standard Solution (0.0025 N)*—Weigh accurately 0.4247 g of silver nitrate (AgNO_3). Transfer it to a 1-L volumetric flask. Add water to dissolve the AgNO_3 (Note 1). Add 3.0 mL of concentrated nitric acid (HNO_3 , sp gr 1.42) and then add water to the 1-L mark of the volumetric flask. Standardize this solution against a pure chloride standard (Note 2). Check the solution at least monthly to assure a consistent reagent.

NOTE 1—The AgNO_3 solution can also be prepared conveniently by dilution of an ampul¹⁰ of concentrated AgNO_3 solution.

NOTE 2—A sodium chloride crystal such as used in infrared spectrometer cells is a good source of sodium chloride.

7.6 *Sodium Hydroxide, Methanol Solution (4 g/L)*—Dissolve 4.0 g of NaOH in 1 L of chloride-free methanol.

7.7 *Sulfuric Acid (1 + 1)*—With constant stirring pour 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) into 1 volume of water.

⁸ Beckman GS or Zeromatic and Leeds and Northrup pH meters have been found satisfactory for this purpose.

⁹ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

¹⁰ Such ampuls of concentrated AgNO_3 solution are supplied by Anachemica Chemical Ltd., Champlain, NY.

8. Procedure

NOTE 3—**Caution:** Because of the very small amount of chloride determined in normal askarels, be sure that during the test contamination does not occur from other sources of halogen such as from the laboratory atmosphere or through contact with the human skin. The test should not be made in a laboratory where strong halogen solutions are handled, stored, or evaporated. All glassware, apparatus, and the area in which the test is run must be analytically clean.

8.1 To analyze low-viscosity (readily pourable) askarels, weigh 100 g into a tared 500-mL flask to the nearest 0.1 g on a suitable balance.

8.2 Using clean dry tongs, place the magnetic stirring bar in the flask.

8.3 Add by graduate cylinder, 100 mL of 0.1 *N* methanolic NaOH solution.

8.4 Attach the reflux condenser and reflux vigorously for 1 h. Measure the reflux time from the start of boiling.

8.5 Turn off the heat and place a container of cold water under the flask to cool the sample.

8.6 Rinse down the condenser with acetone and quantitatively transfer the solution into a 400-mL beaker, using a total of 100 mL of acetone.

8.7 Add 3 mL of $\text{H}_2\text{SO}_4(1 + 1)$ to the sample from a pipet.

8.8 Place the sample beaker on the magnetic stirrer. Stir the sample, insert the silver-glass electrode system, and titrate with 0.0025 *N* AgNO_3 solution, using the microburet.

8.8.1 Normal test specimens of askarel require extremely small amounts of AgNO_3 solution. Therefore, when titrating use 0.05-mL additions of the AgNO_3 solution and allow sufficient time for equilibrium to be established before recording the emf change. If three or four additions of 0.05-mL increments of AgNO_3 solution give a potential change of less than 1 mV/0.05 mL of solution, add larger amounts such as 0.10 mL until such a change is observed. Then reduce the additions again to 0.05 mL to complete the titration. The end point is the point where the greatest potential change per 0.05 mL increment of AgNO_3 solution is obtained.

8.9 Make a blank determination exactly as above, omitting the askarel test specimen.

9. Calculation

9.1 Calculate the amount of reactive (hydrolyzable) chlorine as follows:

$$\text{Reactive chlorine, ppm} = [(A - B)/C] \times 35.46 \times 10^3$$

where:

A = millilitres of AgNO_3 solution required for titration of the test specimen,

B = millilitres of AgNO_3 solution required for titration of the blank,

N = normality of the AgNO_3 solution, and

C = grams of test specimen used.

10. Report

10.1 Report the hydrolyzable chloride content (average of two duplicate determinations) to the nearest integral part per million. If the average of the two determinations is less than 1 ppm, report the hydrolyzable chloride content as 1 ppm.