



Designation: D 1820 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Hydrolyzable Chlorine Compounds in Chlorinated Aromatic Hydrocarbons (Askarels)¹

This standard is issued under the fixed designation D 1820; 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 The values stated in metric units are to be regarded as the standard.

1.3 *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.*

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 This test method is a quantitative potentiometric titration using silver nitrate in an essentially nonaqueous medium to determine chloride ions 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 Many askarels contain polychlorinated biphenyls (PCBs). Manufacture and sale of PCBs have been prohibited by Federal regulation in the United States since 1978. The conditions for continued use, handling, and disposal of PCBs are also regulated. Users of this and other methods of 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 materials 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 from 0.1 to a few parts per million. Therefore, the test must be made in an area where the atmosphere is free from contaminating influences, and it is essential to make a simultaneous 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 *Magnetic Stirrer*, with speed control.

6.2 *Magnetic Stirring Bar*, one-piece molded, TFEfluorocarbon covered.

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

6.4 *Electrode, Silver*.³

NOTE 1—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.

6.5 *Electrode, Standard Glass*.³

6.6 *Potentiometer*,⁴ suitable for use with the glass electrode.

6.7 *Water Bath*, individual glass, 150 mm in diameter and 75 mm high to hold 600 mL of water conveniently.

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

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 Tests.

Current edition approved June 15, 1995. Published August 1995. Originally published as D 1820 – 60. Last previous edition D 1820 – 89a.

² *Annual Book of ASTM Standards*, Vol 10.01.

³ Beckman Catalog No. 39261 silver billet electrode and Catalog No. 40498 glass electrode have been found satisfactory for this purpose.

⁴ Beckman GS or Zeromatic and Leeds & Northrup pH meter have been found satisfactory for this purpose.

shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ 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 7.5 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 Toluene, Chloride-Free—Determine its freedom from chlorides by potentiometric titration.

7.5 Methanol, Chloride-Free—Reflux 5 L of methanol with 0.5 g of silver nitrate (AgNO_3) for $\frac{1}{2}$ 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.

7.6 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 . 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. Check the solution at least monthly to assure a consistent reagent.

NOTE 2—The AgNO_3 solution can also be prepared conveniently by dilution of an ampul of concentrated AgNO_3 solution.⁶

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

7.8 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.

7.9 Sodium Chloride—A sodium chloride crystal, such as that used in infrared spectrometer cells is a good source of sodium chloride.

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 arise from other sources of halogen such as from the laboratory

atmosphere or through contact by 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 25 g into a tared 200-mL beaker to the nearest 0.1 g on a suitable balance.

8.2 Place the magnetic stirring bar into the beaker without touching the bar with the hands.

8.3 Pipet 25 mL of NaOH methanol solution into the beaker and cover it with a watch glass.

8.4 Add about 600 mL of warm water ($40 \pm 1^\circ\text{C}$) to the water bath. Place the water bath on the magnetic stirrer. Immerse the test specimen beaker to a depth of $1\frac{1}{4}$ in. in the water bath and clamp it securely to a firm support. Do not heat the water bath. Allow the 40°C temperature of the water to drift toward equilibrium with room temperature. Stir the sample as fast as possible without splashing for $1 \text{ h} \pm 5 \text{ min}$.

8.5 At the end of 1 h add 0.5 mL of $\text{H}_2\text{SO}_4(1 + 1)$ to the sample from a pipet. Remove from the water bath and dilute to 150 to 175 mL with acetone.

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

NOTE 4—Normal test specimens of askarel require extremely small amounts of AgNO_3 solution. Therefore, when titrating use 0.01-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 0.01-mL increments of AgNO_3 solution give a potential change of less than 1 mV/0.01 mL of solution, add larger amounts such as 0.05 mL until such a change is observed. Then reduce the additions again to 0.01 mL to complete the titration. The end point is the point where the greatest potential change per 0.01-mL increment of AgNO_3 solution is obtained.

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

8.8 For askarels having a viscosity greater than 100 cSt at 37.8°C , follow exactly the procedure outlined in 8.1–8.7 except that after 8.2 add immediately 5 mL of toluene to the askarel test specimen and stirring bar. Stir and heat the sample until it dissolves in the toluene. Then cool to room temperature and proceed as in 8.3. When toluene has been used, include the same amount of toluene in the reagent blank determination.

9. Calculation

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

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

where:

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

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

N = normality of the AgNO_3 solution, and

C = test specimen used, g.

10. Precision and Bias

10.1 Precision:

⁵ *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.

⁶ Such ampuls of concentrated AgNO_3 solution are supplied by Anachemica Chemical Ltd., Champlain, NY.