Designation: D5194 – 24

Standard Test Method for Trace Chloride in Liquid Aromatic Hydrocarbons[1]

This standard is issued under the fixed designation D5194; 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 total chloride (organic and inorganic) in liquid aromatic hydrocarbons and cyclohexane.

1.2 The test method is applicable to samples with chloride concentrations of 1 mg⁄kg to 25 mg/kg.

1.3 Bromides and iodides, if present, will be calculated as chlorides.

1.4 Materials, such as styrene, that are polymerized by sodium biphenyl reagent cannot be analyzed by this test method.

1.5 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see Section 7.

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals

D1193 Specification for Reagent Water

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D3505 Test Method for Density or Relative Density of Pure Liquid Chemicals (Withdrawn 2023)[3]

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 *Other Documents:*[4]

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200

3. Summary of Test Method

3.1 A known amount of hydrocarbon sample is transferred into a separatory funnel containing toluene. Sodium biphenyl reagent is added to convert organic halogens into inorganic halides. The excess reagent is decomposed with water and the phases are separated. The aqueous phase is acidified, washed, and concentrated. Acetone is added and the solution is titrated with silver nitrate solution.

4. Significance and Use

4.1 Organic and inorganic chlorine compounds can have a deleterious effect on equipment and reactions in processes involving aromatic hydrocarbons.

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

*A Summary of Changes section appears at the end of this standard

4.2 Maximum chloride levels are often specified for process streams and for aromatic hydrocarbon products.

5. Apparatus

5.1 *Titrator,* potentiometric, recording, + 2000 mV range, 1 mV resolution with dispenser having a volume readout of 0.00 mL to 9.99 mL or 0.00 mL to 99.99 mL and 0.01 % resolution.

5.2 *Electrode,* glass, reference.

5.3 *Electrode,* silver, billet type.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types II or III of Specification D1193.

6.3 *Acetone,* 99.9 % purity.

6.4 *Congo Red Paper.*

6.5 *Detergent,* residue free.

6.6 *Isobutanol,* 99.9 % minimum purity.

6.7 *Isooctane.*

6.8 *Nitric Acid,* concentrated.

6.9 *Nitric Acid,* 5-M. Dilute 160 mL concentrated nitric acid to 500 mL with water.

6.10 *Potassium Chloride,* primary standard.

6.11 *Potassium Chloride Solution,* saturated.

6.12 *Scouring Powder,* cleanser.

6.13 *Silver Nitrate,* 99.99 % minimum purity.

6.14 *Silver Nitrate Solution,* 0.01 N, standardized to 0.1 %.

NOTE 1—This solution may be obtained as follows:
(*1*) Purchase from a laboratory supply company, (*2*) Weigh to four places, 1.680 g to 1.720 g silver nitrate, transfer quantitatively into a 1000 mL volumetric flask, make to mark with water, and mix well.

$$\text{Normality of solution} = \frac{\text{Weight } AgNO_3}{169.9}$$

or (*3*) Dissolve 8.5 g silver nitrate in 500 mL water to give a 0.1 N solution. Weigh 0.09 g to 0.10 g of dried (105 °C) potassium chloride to the nearest 0.1 mg into a 250 mL electrolytic beaker, add 100 mL of water and a stirring bar. While stirring, titrate with the silver nitrate solution.

$$\text{Normality of } AgNO_3 \text{ solution} = \frac{\text{Weight KCl}}{0.0746 \times \text{mL } AgNO_3}$$

Pipet 50.00 mL of the solution into a 500 mL volumetric flask, dilute to mark with water, and mix well. Divide the calculated normality of the 0.1 N solution by 10 to give the normality of final $AgNO_3$ solution.

6.15 *Sodium Biphenyl Reagent*—The reagent is normally packed in individual vials that contain 0.2 g to 0.4 g of active sodium each.

6.16 *Toluene,* 99.9 % minimum purity.

7. Hazards

7.1 A material, such as styrene, which is polymerized by sodium biphenyl can cause a violent reaction and should never be used as the sample.

7.2 Consult current OSHA regulations and suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

8. Sampling

8.1 Refer to Practice D3437 for proper sampling and handling of liquid hydrocarbons analyzed by this test method.

9. Electrode Preparation

9.1 Clean the surface of the silver electrode with mild detergent and scouring powder, and rinse with water.

9.2 Immerse the electrode in the saturated potassium chloride solution until the electrode tip turns light gray.

9.3 Rinse well with water and attach to the titrimeter.

9.4 Repeat the electrode preparation when the silver chloride film begins to peel from the surface, or if the film becomes discolored.

10. Procedure for Total Chloride

10.1 Extreme care must be used to prevent contamination and all glassware should be exclusively reserved for this analysis. Just prior to use, the glassware should be rinsed with water followed by acetone and then air dried.

10.2 Place 50 mL of toluene into a 250 mL separatory funnel and pipet in the amount of the liquid sample that corresponds to the estimated chloride content as prescribed in Table 1.

NOTE 2—It is generally more convenient to measure the liquid samples by volume and then convert to mass using density or relative density. Table 2 lists the relative densities of several pure hydrocarbons. Densities of unknowns may be determined by using Test Methods D891, D3505 or D4052.

NOTE 3—Alternately, place the sample into a 125 mL bottle and weigh. From the contents of this bottle add the appropriate amount of the sample to the toluene in the separatory funnel. Reweigh the bottle, and determine the weight of the analytical specimen.

TABLE 1 Specimen Size

Estimated chloride, mg/kg	Specimen volume, mL
0 to 5	100
5 to 25	50

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.