**Designation: D5194 − 13**

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

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D1193 Specification for Reagent Water

D1555M Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons and Cyclohexane [Metric]

D3437 Practice for Sampling and Handling Liquid Cyclic Products

D3505 Test Method for Density or Relative Density of Pure Liquid Chemicals

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:*[3]

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.

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 to 9.99 mL or 0.00 to 99.99 mL and 0.01 % resolution.

5.2 *Electrode,* glass, reference.

5.3 *Electrode,* silver, billet type.

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons 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] 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**

## 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.[4] 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 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 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 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' Material 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.

10.3 Add the contents of one vial of sodium biphenyl reagent, stopper the separatory funnel, and gently swirl to mix thoroughly, venting the funnel from time to time. If the resulting solution or suspension is not blue-green, add more sodium biphenyl reagent (one vial at a time) until the blue green color persists.

NOTE 4—The sodium biphenyl reagent has a limited shelf life, given as six months by the manufacturer. This can be extended, in most cases, to approximately one year by keeping the reagent under refrigeration. If this is done, the reagent should be kept at room temperature for several days just prior to use to dissolve any sodium biphenyl that may have precipitated upon cooling.

**TABLE 1 Specimen Size**

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

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[4] *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.

**TABLE 2 Densities of Hydrocarbons**

| Component | Density *in vacuo* at 20°C g/cc |
|---|---|
| Benzene | 0.87908 |
| Cyclohexane | 0.77849 |
| Ethylbenzene | 0.86685 |
| Isopropylbenzene (cumene) | 0.86160 |
| Styrene | 0.90586 |
| Toluene | 0.86686 |
| *m*-Xylene | 0.86408 |
| *o*-Xylene | 0.87968 |
| *p*-Xylene | 0.86076 |

10.4 Allow the mixture to stand for approximately 10 min. Slowly add 20 mL water and swirl gently with the funnel unstoppered until the blue-green color changes to white. Stopper the funnel again and rock it gently for 1 min, venting the pressure frequently through the stopcock.

10.5 Add 10 mL 5 *N* nitric acid, and then 5 mL isobutanol. Shake gently, releasing the pressure frequently through the stopcock.

10.6 Drain the aqueous phase into another 250-mL separatory funnel containing 50 mL isooctane and shake well. Drain the aqueous phase into a 250-mL electrolytic beaker.

10.7 Make a second extraction of the specimen solution with 20 mL water acidified with 6 drops of 5-*M* nitric acid and drain the aqueous phase into the separatory funnel containing the isooctane. After shaking, allow the phases to separate and drain the aqueous phase into the beaker containing the first water extract.

10.8 Test the aqueous solution with Congo red paper, and if it does not test acidic, add 5-*N* nitric acid dropwise with stirring until the test paper turns dark blue.

10.9 Evaporate the solution to about 30 mL on a hot plate.

10.9.1 **Warning:** Loss of chloride may result if the solution is boiled or evaporated below 25 mL.

10.10 Allow the solution to cool, and add 100 mL of acetone. Titrate the solution potentiometrically with standard 0.01 *N* silver nitrate solution and determine the volume of titrant used to reach the end point.

10.11 Determine a blank for each group of samples, using all the reagents including as many vials of sodium biphenyl as were used in the analysis of a sample. Follow all the operations of the analysis, except omit the specimen itself.

## 11. Procedure for Inorganic Chloride

11.1 Follow the procedure in Section 10 but without adding the sodium biphenyl reagent to either the sample or the blank.

## 12. Procedure for Organic Chloride

12.1 Follow the procedures given in Sections 10 and 11 to determine the total and inorganic chlorides. Subtract the inorganic from the total chloride to give the organic chloride.

## 13. Calculation

13.1 Calculate either the total or inorganic chloride as follows:

$$\text{Chloride, mg/kg} = \frac{35{,}500\,(A - B)}{VD} N \tag{1}$$

where:

$A$ = volume of titrant for aqueous phase, mL,
$B$ = volume of titrant for blank, mL,
$N$ = normality of silver nitrate solution,
$V$ = volume of sample, mL, and
$D$ = density or relative density of sample.

13.2 Calculate organic chloride as follows:

$$\text{Organic chloride, mg/kg} = T - I \tag{2}$$

where:

$T$ = total chloride, mg/kg and
$I$ = inorganic chloride, mg/kg.

13.3 Report chloride to the nearest 0.1 mg/kg.

## 14. Precision and Bias

14.1 *Precision:*

14.1.1 The data for determining the precision of this test method are based on the analyses of toluene, ethylbenzene, and *p*-xylene that had been spiked with organic chloride compounds to the 1, 5, and 25 mg/kg chloride levels each.

14.1.2 The following criteria should be used to judge the acceptability (95 % probability) of results obtained by this test method. The criteria were derived from a round robin between three laboratories. Each sample was run on two different days in each laboratory.

14.1.2.1 *Intermediate Precision (formerly called Repeatability)*—Results in the same laboratory should not be considered suspect unless they differ by more than 0.5 mg/kg.

14.1.2.2 *Reproducibility*—Results from each of two laboratories should not be considered suspect unless they differ by more than 0.9 mg/kg.

14.2 *Bias*—The bias of this test method cannot be determined because no referee method is available to determine the true value.

## 15. Quality Guidelines

15.1 Laboratories shall have a quality control system in place.

15.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

15.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed.

15.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

15.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

## 16. Keywords

16.1 aromatic hydrocarbons; chloride; cyclohexane; ethylbenzene; *p*-xylene; toluene

## SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D5194-11a) that may impact the use of this standard. (Approved July 1, 2013.)

*(1)* Updated Section 6.15 to reflect multiple size vials available for reagent.

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