Designation: D7457 – 12

Standard Test Method for Determining Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry[1]

1. Scope

1.1 This test method covers the measurement of chloride in aromatic hydrocarbons, their derivatives, and related chemicals as defined by the method. Aromatics typically do not have any source of chlorides other than organic. The presence of metallic or inorganic chlorides is theoretically possible but not likely and this method does not purport to address recovery of those compounds.

1.2 This test method is applicable to samples with chloride concentrations from 0.24 to 5.0 mg/kg. The test method limit of detection (LOD) is 0.07 mg/kg.

1.3 This test method is preferred over Test Method D5194 for products, such as styrene, that are polymerized by the sodium biphenyl reagent.

1.4 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.

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

1.6 *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 specific hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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
D5194 Test Method for Trace Chloride in Liquid Aromatic Hydrocarbons
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
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200 [3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

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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.

3.1.1 *calibration factor/recovery factor, n*—an indication of the efficiency of the measurement computed by dividing the measured value of a standard by its theoretical value.

3.1.2 *dehydrating tube or drying vessel, n*—a chamber containing concentrated sulfuric acid that scrubs the combustion effluent gases to remove water vapor prior to entering the titration cell.

3.1.3 *endpoint routine/test titration, n*—processes which allow the coulometer to set the endpoint and gain values to be used for sample analysis.

3.1.4 *oxidative pyrolysis, n*—a process in which a sample is evaporated in an inert gas atmosphere and combusted afterwards completely in an oxygen-rich atmosphere at high temperature to break down the components of the sample into elemental oxides.

3.1.5 *reference electrode, n—used in conjunction with sensor electrode to measure the potential of the titration cell.*

3.1.6 *sensor electrode, n*—detects changes in silver ion concentration.

3.1.7 *titration cell, n*—vessel that contains the sensor-reference electrode pair and generator electrode pair along with the cell electrolyte.

3.1.8 *titration parameters, n*—various instrumental conditions that can be changed for different types of analysis and analyzers.

3.1.9 *working electrode pair (generator electrode), n*—an electrode pair consisting of an anode and a cathode.

4. Summary of Test Method

4.1 An aliquot of sample is introduced into a combustion tube maintained at 900 to 1100°C having a flowing stream of oxygen combustion gas and argon inert gas. Oxidative pyrolysis converts the organic and inorganic halides to hydrogen halides that then flow into a titration cell where it reacts with silver ions present in the electrolyte. The silver ion thus consumed is coulometrically replaced and the total electrical work to replace it is a measure of the amount of organic halides in the specimen, which was introduced (see Annex A1).

5. Significance and Use

5.1 This test method is useful for determining organic as well as inorganic chloride compounds that can prove harmful to equipment and reactions in processes involving hydrocarbons. The combination of both the organic and inorganic chloride is commonly termed “total chloride” and since the inorganic chlorides are partially recovered, the result for total chloride will be biased low.

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

5.3 Organic chloride species are potentially damaging to refinery processes. Hydrochloric acid can be produced in hydro treating or reforming reactors and this acid accumulates in condensing regions of the refinery.

6. Interferences

6.1 Both nitrogen and sulfur interfere at concentrations greater than approximately 0.1 %.

6.2 Bromides and iodides, if present, will be calculated as chlorides. However, fluorides are not detected by this test method.

6.3 Both organic and inorganic chloride in the sample will be measured due to conversion of both species to HCL during the oxidative pyrolysis process which is commonly termed as total chloride. The results for total chloride will be biased low since the measurement of total chloride is the sum of both organic and inorganic chloride compounds in the sample and inorganic compounds (if present) are only partially converted. The measurement of only the “organic chloride” in the sample can be measured by water washing the sample prior to analysis to remove the inorganic chloride in the sample. Partial loss of organic halogens which are partially soluble into the water wash, such as chloroacetic acid, may occur. The water washing procedure can not be applied to water soluble samples.

7. Apparatus

7.1 *Pyrolysis Furnace,* which can maintain at 900 to 1100°C and sufficient to pyrolyze the organic matrix and convert all chlorine present in the sample to hydrogen chloride. Furnace systems with the furnace orientated horizontally or vertically can be used.

7.2 *Pyrolysis Tube,* made of quartz and constructed in a way that the sample can be evaporated in an inert gas stream, and be pyrolyzed afterwards in the presence of oxygen. The inlet end of the tube must have a sample inlet port with a septum through which the sample can be injected by syringe. The inlet end must also have side arms for the introduction of oxygen and inert carrier gas. The pyrolysis tube must be of ample volume, so that complete pyrolysis of the sample is ensured.

7.3 *Titration Cell,* containing sensor electrode, reference electrode and working electrode pair. An inlet from the pyrolysis tube and magnetic stirring is also required. (**Warning—**Excessive stirring speed will decouple the stirring bar and cause it to bounce in the titration cell, possibly damaging the electrodes. A slight vortex in the cell is adequate.)

7.4 *Microcoulometer,* with connections for the electrodes, capable of measuring the potential of the sensor electrode, and comparing this potential with a bias potential, and amplifying the difference to the working electrode pair to generate a current. The microcoulometer output voltage signal should be proportional to the generating current.

7.5 *Controlling Unit,* for programming and setting the operating parameters of the instrument and integration of data.

7.6 *Flow Control*—The apparatus must be quipped with flow controllers capable of maintaining a constant supply and flow of oxygen and argon gas.

7.7 *Sample Inlet (Boat Inlet or Direct Injection).*

7.7.1 *Boat Inlet Systems (Horizontal Furnace).*

7.7.1.1 *Automated Boat Drive (Required),* having variable stops, such that the sample boat may be driven into the furnace and stopped at various points as it enters the furnace thereby ensuring the controlled combustion of the sample and preventing the formation of soot or coke, both of which indicate incomplete sample combustion. If direct injection is used with a horizontal system, the automated boat drive is not required.

7.7.1.2 *Boat Inlet Cooler (Required)*—Sample volatility and injection volume require an apparatus capable of cooling the sample boat prior to sample introduction. Thermoelectric coolers (peltier) or re-circulating refrigerated liquid devices have both been found effective. Other approaches can be used as long as the performance criteria of the method are not affected. If direct injection is used with a horizontal system, the boat inlet cooler is not required.

7.7.1.3 *Quartz or Ceramic Sample Boats,* of sufficient size to hold 90 to 250 µL or mg of sample.

7.7.2 *Direct Injection (Both Horizontal or Vertical Furnace).*

7.7.2.1 *Direct Injection (Required)*—A sample introduction system capable of directly injecting sample into the furnace (either vertical or horizontal) at a controlled rate thereby ensuring the controlled combustion of the sample and preventing the formation of soot or coke, both of which indicate incomplete sample combustion.

7.8 *Autosampler (Required),* capable of accurately delivering 90 to 240 µL of sample into the pyrolysis tube or sample boat if a boat inlet with automated boat drive and inlet system is used. An autosampler is required to ensure the accuracy and performance of the method is maintained.

NOTE 1—Multiple rinsing with clean solvent and/or sample between sample injections and/or between sampling from different sample vials is recommended to minimize carryover contamination. An independent solvent flush from a separate vial and different from the solvent wash thereby providing a clean, uncontaminated solvent may also be used. These features may be used as long as they do not degrade the performance and accuracy of the method.

7.9 *Dehydrating Tube or Drying Vessel,* positioned at the outlet of the pyrolysis tube so that effluent gases are bubbled through concentrated sulfuric acid. The water vapor formed in the combustion gases are trapped while all other gases including hydrogen halides are allowed to flow through into the titration cell.

7.10 *Gas-Tight Sampling Syringe,* having a capacity up to 250 µL and capable of accurately delivering 90 to 240 µL of sample. Syringes of differing sizes (100 or 250 µL) are permissible to be used as long as the precision and accuracy of the method are not degraded.

7.11 *Balance,* analytical, with sensitivity to 0.0001 g.

7.12 *Gas Regulators*—Two-stage gas regulators must be used for the reactant and carrier gas.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used 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.[4] Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Type II can be used as long as the precision and accuracy of the method is not degraded.

8.3 *Solvent*—The solvent of choice must be capable of dissolving the chloride sample. The solvent of choice should have a boiling point similar to the sample being analyzed. Suggested possibilities include, but are not limited to isooctane, toluene, *p*-xylene and methanol.

8.4 *Purity of Solvent*—The blank value of the solvent used must be smaller than 0.1 µg/Kg chlorides. Before using, the blank value of the solvent must be checked by carrying out a chlorine determination with the device being used for this analysis.

8.5 *Acetic Acid*—Glacial acetic acid ($CHRR_3COOH$), concentration: 97 %.

8.6 *Cell Electrolyte Solution*—Several electrolyte solutions based on acetic acid solutions. Please follow instrument manufacturer's recommendation.

NOTE 2—Bulk quantities of the electrolyte should be stored in a dark place and dark bottle and is recommended to be prepared fresh at least every two weeks.

8.7 *Inner Electrolyte Solution*—Please follow the instrument manufacturer's recommendation.

8.8 *Outer Electrolyte Solutions*—Please follow the instrument manufacturer's recommendation.

8.9 *Gases.*

8.9.1 *Argon,* 99.996 % minimum purity required as inert and carrier gas.

8.9.2 *Oxygen,* 99.995 % minimum purity is required as the oxidation gas.

8.10 *Sodium Acetate,* anhydrous, ($NaCH_3CO_2$), fine granular.

8.11 *Sodium Sulfate,* (Na_2SO_4), crystalline and anhydrous.

8.12 *Sulfuric Acid,* (95 to 98 %), (H_2SO_4) concentrated.

8.13 *2,4,5-Trichlorophenol or 2,4,6-Trichlorophenol (TCP),* ($C_6H_3OCl_3$) fine granular.

8.14 *100 µg/mL—Chloride Standard Stock Solution*—Weigh either 2,4,5-trichlorophenol or 2,4,6-trichlorophenol in the range of 0.0850 to 0.0950 g (target weight of 0.0929 g) to the

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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.

nearest 0.0001 g and record the actual weight. Transfer to a 500-mL volumetric flask and dilute to the mark with the selected solvent (see 8.3 and 8.4). Calculate the exact concentration using calculation Eq 1:

$$\mu g\ Cl/mL = \frac{(TCP) \times (\%\ CL) \times K1 \times CI}{500\ mL} \qquad (1)$$

where:

TCP = 2,4,5, Trichlorophenol, g,
% CL = 0.5385 g-Cl/g-TCP (% Chloride in TCP),
K1 = 10^6 µg/g (used to convert g to µg), and
CI = % Chemical Impurity; the % purity of TCP used to prepare the Chloride Standard Stock Solution. (for example: If 99 % purity, use a CI factor = 0.99. If no correction for CI is used, use a CI factor = 1.0).

8.15 *10 µg/mL-Chloride Standard Working Solution*—Pipet 50 mL of the chloride standard stock solution (see 8.14) into a 500-mL volumetric flask, and dilute to the mark with solvent.

NOTE 3—Other calibration standard sources and diluents may be used if precision and accuracy are not degraded.

NOTE 4—A correction for chemical impurity can be used if deemed necessary.

NOTE 5—Commercially available standards are available and can be used as long as the precision and bias of the method is not degraded.

9. Hazards

9.1 Consult the current version OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this test method.

9.2 Flammable hydrocarbons are used in this test method. Use materials that are rated for containing these hydrocarbons in all sample containers and sample transfer apparatus. Exercise extra care when using flammable materials near the oxidative furnace.

9.3 Use safety goggles or face shields and rubber gloves when handling alkalis and avoid spillage on clothing. These materials rapidly attack wool and leather.

9.4 Use all appropriate safety precautions to clean up and discard waste materials in accordance with all federal, state, and local health and environmental regulations.

10. Sampling, Test Specimens, and Test Units

10.1 Sample the material in accordance with Practice D3437.

11. Preparation of Apparatus

11.1 Install the instrument in accordance with manufacturer's instructions.

11.2 Adjust gas flows and pyrolysis temperature to the operating conditions as recommended by the manufacturer.

11.3 The actual operation of introducing a sample will vary depending upon the instrument manufacturer and the type of inlet system used.

12. Calibration/Recovery Factor and Standardization

12.1 Prepare a series of calibration standards covering the range of samples to be analyzed by diluting the chloride standard working solution (8.15) to the desired final concentrations. Recommended calibration standards and injection volumes are listed in Table 1.

TABLE 1 Recommended Calibration Standards and Injection Volume

Concentration	Solvent Blank	0.100 µg/mL	1.00 µg/mL	5.00 µg/mL
Theoretical µg-Cl	0.0000	0.0100	0.1000	0.5000
Injection Volume	100 µL	100 µL	100 µL	100 µL

NOTE 6—It is recommended to calibrate the instrument with a minimum of three different concentration standards and a solvent blank. Other numbers of concentration of calibration standards can be used as long as the accuracy and precision of the method is not degraded.

NOTE 7—The selected concentrations of standards should bracket the expected concentrations of the samples to be analyzed.

12.2 Quantitatively inject 90 to 240 µL of the first calibration standard into the instrument for analysis covering the analytical range of the samples to be analyzed. Follow the instrument manufacturer's recommendation for introducing samples into the instrument.

12.3 Repeat the measurement for the calibration standard a minimum of two times, average the result and report the average result of the measurements as the reported result.

12.4 Repeat the steps outlined in 12.2-12.4 for each concentration of calibration standard used for calibrating the instrument. Use the same sampling and flushing procedures for all standards. See Note 1.

12.5 If the absolute µg chloride value for the calibration standards is outside the range of 80 to 120 %, prepare fresh standards. If the absolute µg chloride value for the calibration standards is still outside the range of 80 to 120 %, follow the instrument manufacturer's recommendations to correct.

12.6 Construct a calibration curve following the recommendations of the instrument manufacturer.

NOTE 8—A typical calibration would include a series of three to four standards containing the elements of interest and bracketing the concentrations that are in the samples. The calibration curve should be linear and have a minimum $r^2 = 0.999$.

13. Procedure

13.1 Clean the syringe to be used for the sample by flushing in the same manner as the standards used for the calibration. It is recommended to rinse the syringe a minimum of two times with sample or solvent, or both.

13.2 Analyze the sample following the same procedure as used for the calibration of the instrument. Determine the chloride concentration following the procedures outlined in 12.2-12.4.

13.3 Chloride determination for different samples may require slight modifications or changes in the titration parameters, adjustments in sample size, or both. Follow manufacturer's recommendations for samples whose matrices differ from the calibration standards.

TABLE 2 Ruggedness Study Data

	Ruggedness Study Data					
Location	Houston/Germany		Chigasaki, JP			
Sample	Toluene Blk	0.10 mg/kg	(0.10 mg/L) 0.12 mg/kg	(0.50 mg/L) 0.58 mg/kg	(1.00 mg/L) 1.16 mg/kg	5.0 mg/L) 5.81 mg/kg
n	80	40	40	40	40	20
Ave	0.02	0.12	0.13	0.60	1.20	6.042
SD	0.024	0.0273	0.0217	0.0267	0.0341	0.0767
% RSD	109.1 %	23.3	17.2 %	4.4 %	2.8 %	1.3 %
Repeatability (r)	0.065	0.076	0.060	0.074	0.095	0.212
LOD	0.07	0.08	0.07	0.08	0.10	0.23
LOQ	0.24	0.27	0.22	0.27	0.34	0.77
Max Range	5.80 mg/kg	1.00 mg/kg	5.80 mg/kg	5.80 mg/kg	5.80 mg.kg	5.80 mg/kg

Repeatability (r) = SD * 2.77
Limit of detection (LOD) = SD * 3.0
Limit of Quantification (LOQ) = SD * 10

14. Calculation of Result

14.1 Measurement utilizing volume and known specific gravity in mg per kg as follows:

$$Chloride, \left[mg/kg\right] = \frac{(M - B)}{V \times \rho} * \frac{1}{RF} * K \qquad (2)$$

where:

M = measured chloride value, µg,
B = blank chloride value, µg,
V = sample injection volume, mL,
ρ = density (g/mL),
RF = recovery factor = measured values of chlorides titrated / theoretical value, and
K = (1 mg/1000 µg)/(1000 g/kg).

14.2 If this equation does not apply to your instrument, then follow instrument manufacturer's recommendations.

15. Report

15.1 Report the chloride results as mg/kg chloride to two decimal points (X.XX mg/kg).

15.2 Use densities as stated in Test Method D1555M.

16. Precision and Bias[5]

16.1 *Repeatability*—Two ruggedness studies were performed on two different manufacturers' instruments. In the first study, two instruments analyzed samples containing 0.00 mg/kg and 0.10 mg/kg chloride 20 times each. In the second study, one instrument with a vertical furnace analyzed samples containing 0.00, 0.12, 0.58, 1.20 and 5.80 mg/kg chloride 20 times each and a second instrument with a horizontal furnace analyzed samples containing 0.00, 0.12, 0.58 and 1.20 mg/kg chloride 20 times each. Data from the two ruggedness studies were combined and the LOD (limit of detection) and LOQ (limit of quantification) were calculated in accordance with ASTM Committee D16 Editorial Guidelines (June 25, 2009). The LOD was determined to be 0.07 mg/kg and the LOQ to be 0.24 mg/kg. Summary of the data of the two ruggedness studies and the corresponding temporary precision statements are summarized in Table 2. The final precision statement and reproducibility will be determined within five years time.

16.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

16.2 *Reproducibility*—To be determined.

16.2.1 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

16.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for this test method, bias has not been determined.

17. Quality Guidelines

17.1 Laboratories shall have a quality control system in place.

17.1.1 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.

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

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

17.1.4 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.

18. Keywords

18.1 aromatic hydrocarbon; density; electrolysis; electrolyte; evaporation; microcoulometry; potential; pyrolysis; recovery; titration; total chloride

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1041.

ANNEX

(Mandatory Information)

A1. COMBUSTION AND TITRATION MEASUREMENT PRINCIPLES

A1.1 *Oxidative Pyrolysis*:

A1.1.1 The sample is injected by a 100-µL syringe, into a quartz boat, which is driven into a pyrolysis tube. Here, the sample is first evaporated, and then swept by a carrier gas further into the furnace, where it is combusted in a flow of oxygen gas. Hydrogen atoms from the breakdown of the hydrocarbon sample react with the chlorine atoms liberated by combustion to form hydrogen chloride. Hydrocarbons break down and form the following combustion products:

$$R-X \xrightarrow{O_2,\,\Delta°C} HX \quad (X=Cl, Br, I, F) \tag{A1.1}$$

$$R-S \xrightarrow{O_2,\,\Delta°C} SO_2 \tag{A1.2}$$

$$R-H \xrightarrow{O_2,\,\Delta°C} H_2O+CO_2 \tag{A1.3}$$

$$R-N \xrightarrow{O_2,\,\Delta°C} NO_x \quad (NO_x=NO, NO_2) \tag{A1.4}$$

A1.1.2 *Oxidative Pyrolysis*—These product gases are swept into a drying vessel to remove water, and then introduced into the titration cell.

A1.2 *Titration*:

A1.2.1 Before hydrogen chloride is introduced into the cell, the electrolysis potential is kept at the end point potential, and the following equilibrium equation is maintained:

$$Ag \rightarrow Ag^{+} + e^{-} \tag{A1.5}$$

A1.2.2 When hydrogen chloride is introduced into the cell, the following reaction takes place:

$$Ag^{+} + HCl \rightarrow AgCl\downarrow + H^{+} \tag{A1.6}$$

A1.2.3 When the potential changes, electrolysis current is applied to the working electrode to generate silver ions. Thus, the silver ions consumed are replaced coulometrically. The total current applied is a measure of the chlorine in the sample.