Designation: D 5808 – 95

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

This standard is issued under the fixed designation D 5808; 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 organic chlorides in aromatic hydrocarbons, their derivatives, and related chemicals.

1.2 This test method is applicable to samples with chloride concentrations from 1 to 25 mg/kg.

1.3 This test method is preferred over Test Method D 5194 for products, such as styrene, that are polymerized by the sodium biphenyl reagent.

1.4 The following applies to all specified limits in this standard: for purposes of determining conformance with this standard, an observed value or a calculated value shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit, in accordance with the rounding-off method of Practice E 29.

1.5 *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 Note 2 and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 3437 Practice for Sampling and Handling Liquid Cyclic Products[3]

D 5194 Test Method for Trace Chloride in Liquid Aromatic Hydrocarbons[3]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[4]

2.2 *Other Document:*

OSHA Regulations—29CFR paragraphs 1910.1000 and 1910.1200[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *dehydration tube*—a chamber containing concentrated sulfuric acid that scrubs the effluent gases from combustion to remove water vapor.

3.1.2 *oxidative pyrolysis*—a process in which a sample is combusted in an oxygen-rich atmosphere at high temperature to break down the components of the sample into elemental oxides.

3.1.3 *recovery factor*—an indication of the efficiency of the measurement computed by dividing the measured value of a standard by its theoretical value.

3.1.4 *reference sensor pair*—detects changes in silver ion concentration.

3.1.5 *test titration*—a process that allows the coulometer to set the endpoint and gain values to be used for sample analysis.

3.1.6 *titration parameters*—various instrumental conditions that can be changed for different types of analysis.

3.1.7 *working electrode (generator electrode)*—an electrode consisting of an anode and a cathode separated by a salt bridge; maintains a constant silver ion concentration.

4. Summary of Test Method

4.1 A liquid specimen is injected into a combustion tube maintained at 900°C having a flowing stream of 50 % oxygen and 50 % argon carrier gas. Oxidative pyrolysis converts the organic 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 organic halides in the specimen injected (see Annex A1).

5. Significance and Use

5.1 Organic as well as inorganic chlorine compounds can prove harmful to equipment and reactions in processes involving hydrocarbons.

---

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

Current edition approved Oct. 10, 1995. Published December 1995.

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

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

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 hydrotreating 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 %.

NOTE 1—To ensure reliable detectability, all sources of chloride contamination must be eliminated.

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

6.3 Organic chloride values of samples containing inorganic chlorides will be biased high due to partial recovery of inorganic species during combustion. Interference from inorganic species can be reduced by water washing the sample before analysis. This does not apply to water soluble samples.

7. Apparatus [6]

7.1 *Pyrolysis Furnace*, which can maintain a temperature sufficient to pyrolyze the organic matrix and convert all chlorine present in the sample to hydrogen chloride.

7.2 *Pyrolysis Tube*, made of quartz and constructed so that when a sample is volatilized in the front of the furnace, it is swept into the pyrolysis zone by an inert gas, where it combusts when 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 a reference electrode, a working electrode, and a silver sensor electrode, as well as a magnetic stirrer. An inlet from the pyrolysis tube is also required.

NOTE 2—**Caution:** Excessive stirring speed will decouple the stirring bar, and cause it to rise in the titration cell and possibly damage the electrodes. A slight vortex in the cell will be adequate.

7.4 *Microcoulometer*, capable of measuring the potential of the sensing-reference electrode pair, 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 *Automatic Boat Drive*, having variable stops, such that the sample boat may be driven into the furnace, and stopped at various points as it enters the furnace.

7.6 *Controller*, with connections for the reference, working, and sensor electrodes. The controller is used for setting of operating parameters and integration of data.

7.7 *Dehydration Tube*, positioned at the end of the pyrolysis tube so that effluent gases are bubbled through a sulfuric acid solution, and water vapor is subsequently trapped, while all other gases are allowed to flow into the titration cell.

7.8 *Gas-Tight Sampling Syringe*, having a 50 µl capacity, capable of accurately delivering 10 to 40 µl of sample.

7.9 *Quartz Boats*.

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.[7] 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 D 1193, Type II or III.

8.3 *Acetic Acid (sp gr 1.05)*—Glacial acetic acid (CH_3COOH).

8.4 *Argon or Helium*, 99.9 % minimum purity required as carrier gas.

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

8.6 *Cell Electrolyte Solution*—Dissolve 1.35 g sodium acetate ($NaCH_3CO_2$) in 850 mL of acetic acid (CH_3COOH), and dilute to 1000 mL with water.

NOTE 3—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every two weeks.

8.7 *Oxygen*, 99.6 % minimum purity is required as the reactant gas.

8.8 *Gas Regulators*, two-stage gas regulators must be used for the reactant and carrier gas.

8.9 *Potassium Nitrate (KNO_3)*, fine granular.

8.10 *Potassium Chloride (KCl)*, fine granular.

8.11 *Working Electrode Solution (10 % KNO_3)*—Dissolve 50 g potassium nitrate (KNO_3) in 500 mL of distilled water.

8.12 *Inner Chamber Reference Electrode Solution (1 M KCl)*—Dissolve 7.46 g potassium chloride (KCl) in 100 mL of distilled water.

8.13 *Outer Chamber Reference Electrode Solution (1 M KNO_3)*—Dissolve 10.1 g potassium nitrate (KNO_3) in 100 mL of distilled water.

8.14 *Sodium Chloride (NaCl)*, fine granular.

8.15 *Sulfuric Acid*, (sp gr 1.84), (H_2SO_4) concentrated.

8.16 *2,4,6-Trichlorophenol (TCP) ($C_6H_3OCl_3$)*, fine granular.

8.17 *Methanol (MeOH) (CH_3OH)*, 99.9 % minimum purity.

8.18 *Chloride Standard Stock Solution*—Weigh accurately 0.1 g of 2,4,6-Trichlorophenol to 0.1 mg. Transfer to a 500-mL volumetric flask. Dilute to the mark with methanol.

[6] Microcoulometer such as the TOX-10Σ and TOX-10, manufactured by Mitsubishi Chemical Corporation, and available through Cosa Instruments, 55 Oak Street, Norwood, NJ 07648, or equivalent instrument, has been found satisfactory for this purpose.

[7] *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.

$$\text{Cl/L mg MeOH (ppm)} = \frac{\text{g of TCP} \times 0.5386 \times 10^{3}}{\text{L of MeOH}} \quad (1)$$

where:
TCP = 2,4,6, Trichlorophenol, and
MeOH = Methanol.

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.

10. Sampling

10.1 Consult guidelines for taking samples from bulk in accordance with Practice D 3437.

11. Preparation of Apparatus

11.1 Carefully insert the quartz pyrolysis tube in the furnace and connect the oxygen and carrier gas lines.

11.2 Connect the boat drive to the pyrolysis tube and furnace.

11.3 Add the electrolyte solution to the titration cell, flushing several times. Maintain the electrolyte level at the highest marked line on the titration cell.

11.4 Add the proper solutions to the chamber of the working electrode and to the inner and outer chambers of the reference electrode.

11.5 Place the titration cell on the magnetic stirring device and connect the reference, working, and sensor electrodes to the controller.

11.6 Initiate a test titration of the titration cell according to the manufacturer's instructions.

11.7 Turn on the heating element of the pyrolysis furnace, and connect the dehydration tube to the outlet end of the pyrolysis furnace and to the cell.

11.8 Adjust the flow of the gases, the pyrolysis furnace temperature, and titration parameters to the desired operating conditions. Typical operational conditions are given in Table 1.

11.9 Prebake the sample boats to be used for the determination.

12. Calibration and Standardization

12.1 Using the chloride standard stock solution (see 8.18), make a series of three calibration standards covering the range of expected chloride concentration.

12.2 Into three 100-mL volumetric flasks, respectively pipet 1, 15, and 30 mL of chloride stock solution and dilute to the mark with methanol. (The standards are approximately 1 mg Cl/L MeOH, 15 mg Cl/L MeOH and 30 mg Cl/L MeOH).

12.3 Adjust the operational parameters for a three-point calibration. If instrument is not equipped for a three-point calibration, manually record the recovery factors and calculate.

12.4 The sample size can be determined either volumetrically, by syringe, or by mass. Make sure that the sample size is 80 % or less of the syringe capacity.

12.4.1 Volumetric measurement can be utilized by filling the syringe with standard, carefully eliminating all bubbles, and pushing the plunger to a calibrated mark on the syringe, and recording the volume of liquid in the syringe. After injecting the standard, read the volume remaining in the syringe. The difference between the two volume readings is the volume of standard injected. This test method requires the known or measured specific gravity or density, to the third decimal place. Several densities of various hydrocarbons are listed in Table 2. A sample size of 40 µL is suggested to start, and then this volume can be adjusted to accommodate more quickly or more accurate determinations.

12.4.2 Alternatively, the syringe may be weighed before and after the injection to determine the weight of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of ± 0.0001 g is used.

12.5 Insert the syringe needle through the septum and into the quartz boat inside the boat drive. Start the boat drive, and insert the standard into the pyrolysis furnace.

12.6 Repeat the measurement of each calibration standard at least three times.

12.7 If a low recovery factor (less than 95 %) occurs, prepare fresh standards. If the recovery factor remains low, prepare new electrolyte, or new electrode solutions, or both. If the recovery factor still does not fall in the proper range, review the procedural details.

12.8 Calculate the three-point calibration curve.

13. Procedure

13.1 Clean the syringe to be used for the sample. Flush it several times with the sample. Determine the chloride concentration in accordance with 12.4-12.6.

13.2 Chloride determination for the sample may require a change in titration parameters or adjustment in sample size, or both.

14. Calculation

14.1 Measurement utilizing volume and known specific gravity in milligrams per kilograms as follows:

$$\text{Chloride, mg/kg} = \frac{(M - B)}{v \times SG} \times \frac{1}{RF} \quad (2)$$

TABLE 1 Operating Parameters

Parameter	Value
End Point	290 to 315 mV
Gain 1	0.5 to 5.0
Gain 2	1.0 to 10.0
Gain 3	1.0 to 15.0
Sensitivity	0.5 to 1.5 mV
Furnace temperature	900 to 1100°C
Oxygen flow	200 mL/min
Carrier gas flow	250 mL/min

TABLE 2 Densities of Common Hydrocarbons[A]

Component	Density	Temperature °C
Benzene	0.879	20
Cyclohexane	0.779	20
Ethylbenzene	0.867	20
Isopropylbenzene	0.862	20
Toluene	0.867	20
m-Xylene	0.864	20
o-Xylene	0.880	20

[A] *Handbook of Chemistry and Physics*, 40th Edition,“ Table, Physical Constants of Organic Compounds”, Chemical Rubber Co.

14.2 Measurement utilizing weight of sample, considering dilution's in milligrams per kilograms as follows:

$$\text{Chloride, mg/kg} = \frac{(M - B)}{w} \times \frac{1}{RF} \quad (3)$$

where:

M = measured chloride value, µg,
B = blank chloride value, µg,
v = sample injection volume, mL,
w = weight of sample, g,
SG = relative density, and
RF = recovery factor = µg chlorides titrated/theoretical value.

15. Report

15.1 Report the chloride results as (mg/kg) of the sample.

16. Precision and Bias [8]

16.1 *Precision*—The results from six laboratories were used to generate statistical data. Three values were recorded for each sample. The standard used to calibrate a standard curve was provided with the samples and a volume of 40 µL was specified for all injections. For statistical calculations, the average value obtained on the neat (or blank) sample was subtracted from the average value for the 1 mg/kg, 5 mg/kg, and 25 mg/kg samples.

16.2 *Intermediate Precision*—Two successive test results generated by the same laboratory, on the same sample, by the same operator, with the same test equipment should not be considered suspect unless the difference is greater than 0.7 mg/kg, with 95 % confidence.

16.3 *Reproducibility*—Two tests generated in different laboratories, on the same sample, should not be considered suspect unless the difference is greater than 1.3 mg/kg, with 95 % confidence.

16.4 *Bias*—The results from the analysis by 6 different laboratories of gravimetrically prepared standard addition samples indicated that this procedure does not contain a measurable amount of bias nor systematic error that could contribute to a difference between a population mean and the accepted true value.

NOTE 4—Although the data in this report was compiled using an automatic boat drive, direct needle injections with a constant rate injector have been found to give satisfactory results.

17. Keywords

17.1 density; electrolysis; electrolyte; microcoulometry; potential; pyrolysis; recovery factor; relative density; titration; total chloride; volatilization

[8] Supporting data are available from ASTM International Headquarters. Request RR: D16-1017.

ANNEX

(Mandatory Information)

A1. COMBUSTION AND TITRATION MEASUREMENT PRINCIPLES

A1.1 *Oxidative Pyrolysis:*

A1.1.1 The sample is injected by a 50-µL syringe, into a quartz boat, which is driven into a pyrolysis tube. Here, the sample is first volatilized, 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:

X (Cl)	→	HX (HCl greater than Cl_2)
S	→	SO_2 greater than SO_3
C	$\xrightarrow{O_2/900°C}$	CO_2
H	→	H_2O
N	→	NO, NO_2
P	→	P_2O_5

A1.1.2 These product gases are swept into a dehydration tube 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:

$$Ag \rightleftarrows Ag^+ + e^- \quad (A1.1)$$

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

$$HCl + Ag^+ \rightleftarrows AgCl + H^+ \quad (A1.2)$$

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.