



Designation: D7359 – 13

# Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)<sup>1</sup>

This standard is issued under the fixed designation D7359; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope\*

1.1 This test method covers the individual determination of total fluorine, chlorine and sulfur in aromatic hydrocarbons and their mixtures. Samples containing 0.10 to 50 mg/kg of each element can be analyzed.

1.2 This method can be applied to sample types outside the range of the scope by dilution of the sample in an appropriate solvent to bring the total concentrations of fluorine, chlorine and sulfur within the range covered by the test method. However, it is the responsibility of the analyst to verify the solubility of the sample in the solvent and that the diluted sample results conform to the precision and accuracy of the method.

1.3 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.

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

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. See Section 8.*

<sup>1</sup> 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. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D1193 Specification for Reagent Water

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:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200<sup>3</sup>

## 3. Summary of Test Method

3.1 A sample of known weight or volume is placed into a sample boat and introduced at a controlled rate into a high temperature combustion tube. There the sample is combusted in an oxygen rich pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in an absorption medium where the hydrogen halides (HX) formed during combustion disassociate into their respective ions, X<sup>-</sup> while the sulfur oxides (SO<sub>x</sub>) formed are further oxidized to SO<sub>4</sub><sup>2-</sup> in the presence of an oxidizing agent. An aliquot of known volume of the adsorbing solution is then automatically injected into an ion chromatograph (IC) by means of a sample injection valve. The halide and sulfate anions are separated into individual elution bands on the separator column of the IC. The conductivity of the eluent is reduced with an anion suppression

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

<sup>3</sup> 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

device prior to the ion chromatograph's thermal conductivity detector, where the anions of interest are measured. Quantification of the fluorine, chlorine and sulfur in the original combusted sample is achieved by first calibrating the system with a series of standards containing known amounts of fluorine, chlorine and sulfur and then analyzing unknown samples under the same conditions as the standards. The combined system of pyrohydrolytic combustion followed by ion chromatographic detection is referred to as Combustion Ion Chromatography (CIC).

#### 4. Significance and Use

4.1 The total fluorine, chlorine and sulfur contained in aromatic hydrocarbon matrices can contribute to emissions, be harmful to many catalytic chemical processes, and lead to corrosion. This test method can be used to determine total sulfur and halogens aromatic hydrocarbon matrices, in finished products and can be used for compliance determinations when acceptable to a regulatory authority using performance based criteria.

#### 5. Interferences

5.1 Substances that co-elute with the anions of interest will interfere. A high concentration of one anion can interfere with other constituents if their retention times are close enough to affect the resolution of their peak.

#### 6. Apparatus

6.1 *Autosampler (Optional)*, capable of accurately delivering 10 to 80  $\mu\text{L}$  of sample into the sample boat. The autosampler may be used as long as the accuracy and performance of the method is not degraded.

NOTE 1—Multiple rinsing with clean solvent between sample injections and/or sampling between different sample vials to minimize carryover contamination from previous samples is recommended. A solvent flush from a vial separate from the solvent wash, providing 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.

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

6.3 *Boat Inlet System*—The system provides a sampling port for the introduction of liquid and solid samples into the sample boat and is connected to the inlet of the Pyrohydrolytic Combustion Tube. The system is swept by a humidified inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analyzed into the pyrohydrolytic oxidation zone at a controlled and repeatable rate.

6.4 *Boat Inlet Cooler (Optional)*—Sample volatility and injection volume may require an apparatus capable of cooling the sample boat prior to sample introduction. Thermoelectric coolers (peltier) or recirculating refrigerated liquid devices are strongly recommended. Switching sample boats between each analysis may prove effective, provided sample size is not too large.

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

6.6 *Furnace* which can maintain a minimum temperature of 900°C.

6.7 *Gas Adsorption Unit*, having an adsorption tube of either 10 or 20 mL which is automatically filled with a known volume of absorption solution by a built-in burette or other similar device. The Gas Adsorption Unit is interfaced to the Ion Chromatograph and injects an aliquot of the adsorption solution into the Ion Chromatograph after the sample is combusted and the by-products of combustion are absorbed. The Gas Adsorption Unit rinses out the gas lines with Type I reagent water (7.2) from the pyrohydrolytic combustion tube after the completion of the sample combustion to ensure all the combustion by-products (HX and SO<sub>2</sub>) are absorbed. The Gas Adsorption Unit rinses the gas lines and adsorption tube with Type I reagent water (7.2) prior to sample combustion and after the absorption solution is injected into the Ion Chromatograph to minimize cross contamination from the previous analysis.

6.8 *Gas-Tight Sampling Syringe*, capable of accurately delivering 10 to 80  $\mu\text{L}$  of standard or sample.

6.9 *Pyrohydrolytic Combustion Tube* made of quartz and constructed such that when the sample is combusted in the presence of humidified oxygen, the by-products of combustion are swept into the humidified pyrohydrolytic combustion zone. The inlet end shall allow for the stepwise introduction and advancement of a sample boat into the heated zone and shall have a side arm for the introduction of the humidified carrier gas and oxygen. The pyrohydrolytic combustion tube must be of ample volume, and have a heated zone with quartz wool or other suitable medium providing sufficient surface area so that the complete pyrohydrolytic combustion of the sample is ensured.

6.10 *Humidifier Delivery System*, capable of delivering Type I reagent water (7.2) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

6.11 *Ion Chromatograph (IC)*<sup>4</sup>, equipped with:

6.11.1 High Performance inert PEEK- (polyetheretherketone) flow path system is required.

6.11.2 High Pressure eluent pump, capable of delivering 0.0 to 5 mL/min (without eluent generator; 0.1 to 3 mL/min (with eluent generator), in 0.01 mL/min increments. Flow rate accuracy of <1 % of the set value and precision of <2 % is required.

6.11.3 Conductivity Detector, capable of an operating range of 0 to 15 000  $\mu\text{S}$  with a linearity correlation coefficient of 0.999 and %RSD <5 % at 800  $\mu\text{S}$ . Detector cell constructed of PEEK and capable of maintaining an operating temperature of 30 to 55°C.

6.11.4 Injection valve, 2 position electrically actuated with wetted component material of PEEK (polyetheretherketone).

6.11.5 Anion Separator Column AS11HC (4x250mm) or equivalent, with sufficient capacity for disparate analyte concentrations and constructed of PEEK. Capacity of >290  $\mu\text{Equivalent}$ s/column with alkanol quaternary ammonium functional groups.

<sup>4</sup> Many different companies manufacture automatic ion chromatographs. Consult the manufacturer for details in setup and operation. Other systems may be used as long as precision is shown to be as good as or better than the precision in the method.

6.11.6 Guard Column AG11HC (4X50mm) or equivalent, packed with same material for protection of the anion separator column and constructed of PEEK.

6.11.7 Post-Column Chemical Suppression Device, capable of reducing the absolute conductivity of eluent concentrations of up to 200 mM KOH (or NaOH). Delivery of hydronium ions for suppression by electrolysis of recycled eluent through a cation exchange membrane.

6.11.8 Eluent Generator (Optional), an eluent generator capable of producing eluents of 10 to 100 mM KOH with continuous eluent purification can be employed.

6.11.9 Data Acquisition System, such as an integrator or computer data handling system capable of integrating the peak areas of ion chromatograph.

6.12 *Quartz or Ceramic Sample Boats* of sufficient size to hold 10 to 80  $\mu\text{L}$  or mg of sample.

## 7. Reagents and Materials

7.1 *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 specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type 1 conforming to Specification D1193.

7.3 *Quartz Wool*, (fine grade) or other suitable medium.

7.4 *Argon*, carrier gas minimum 99.9 % purity.

NOTE 2—Purification scrubbers to ensure the removal of containments are recommended such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) are recommended.

7.5 *Oxygen*, combustion gas minimum 99.6 % purity.

7.6 *Gas Regulators*, two-stage, gas regulators capable of regulating the pressures to 40 to 60 psi must be used for the carrier and combustion gases.

7.7 *Calibration Standards*, certified calibration standards from commercial sources or calibration standards prepared in the laboratory containing the elements of interest at the concentrations of interest.

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

NOTE 4—Calibration standards are typically re-mixed and re-certified on a regular basis depending upon frequency of use and age. Calibration standards can have a useful life of about 6 to 12 months if properly stored in a cool, dark place.

NOTE 5—A correction for chemical impurity can be used if deemed necessary.

<sup>5</sup> *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.

7.8 *Dibenzothiophene*, FW 184.26, 17.399 % S.

7.9 *Fluorobenzoic Acid*, FW 140.11, 13.56 % F.

7.10 *2,4,5 Trichlorophenol*, FW 197.46, 53.87 % Cl.

7.11 *Hydrogen Peroxide 30 %*, FW 34.01  $\text{H}_2\text{O}_2$  (see Section 8 regarding Hazards).

7.12 *Potassium Hydroxide*, for eluent preparation (see Section 8 regarding Hazards).

7.13 *Toluene, Xylene, Isooctane or Methanol, Reagent grade*. (Other solvents similar to those occurring in samples to be analyzed are also acceptable.) Correction for contaminate levels of elements of interest must be corrected for (solvent blank). Alternatively, using a solvent with non-detectable contamination relative to the sample makes the blank correction unnecessary.

7.14 *Volumetric Flasks-Type Class A*, at the volume specified to use in this method to prepare standards, reagents and solutions.

7.15 *Stock Standard Solutions of approximately-1000  $\mu\text{g}/\text{mL}$* —Prepare a stock standard solution by accurately weighing to within 10 % of the target weights for any or all of the target standard compound(s) listed in 7.15.1, 7.15.2, and 7.15.3 into a 100 mL class A volumetric flask. Dilute to volume with the selected solvent described in 7.13. Calculate the actual concentration of the stock standard solution(s) for each element by using the equation below with the actual recorded weight of the target compound used for each element. This stock standard solution can be further diluted to other desired concentrations. Other suitable materials, weights and volumes may be substituted in preparing stock calibration standards as long as the performance of the method is not degraded.

### Target Standard Compound(s)

7.15.1 *Fluorobenzoic Acid, (Fluorine)*, 0.7375 g target weight.

7.15.2 *2,4,5 Trichlorophenol, (Chlorine)*, 0.1856 g target weight.

7.15.3 *Dibenzothiophene, (Sulfur)*, 0.5748 g target weight.

### Calculation Formula

$$\text{Stock Standard Solution } (\mu\text{g}/\text{ml}) = (A) (B) (10^6)/(C) (K) \quad (1)$$

where:

A = weight of the target compound actually weighed in grams, g,

B = % concentration of the elements in the respective target compounds listed in 7.8, 7.9, and 7.10,

C = final diluted volume, mL, and

K = 100 (factor correction for %).

7.16 *Phosphate Stock Solution (1.00 mL = 1.00 mg Phosphate)*—Weigh to within 10 % 1.433 g of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) in water and dilute to 1 L with water in a class A volumetric flask and mix well.

7.17 *Absorbing Solution*—Dilute the Phosphate Stock Solution with water in a class A volumetric flask to a final concentration of approximately 1.00 ppm. The concentration of