Designation: D7359 – 23

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)[1]

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 (ε) 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 mg⁄kg to 10 mg⁄kg of each element can be analyzed.

1.2 This method can be applied to sample concentrations 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.

1.2.1 Special considerations must be made in order to attain detection limits below 1.0 mg⁄kg in a sample. The instrument must be clean and properly maintained to address potential sources of contamination, or carryover, or both. Multiple sequential injections shall be completed until a stable background is attained. A stable background is considered to be achieved when the analysis of a minimum of three consecutive system blanks have area counts equal to or less than 5 % RSD for the anions of interest.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* See Section 9.

1.6 *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]

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
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
E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E288 Specification for Laboratory Glass Volumetric Flasks
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E969 Specification for Glass Volumetric (Transfer) Pipets

[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.

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

2.2 *Other Documents:*

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

3. Terminology

3.1 *Definitions:*

3.1.1 *combustion ion chromatography, n*—an analytical system consisting of pyrohydrolytic combustion followed by ion chromatographic detection.

3.1.2 *oxidative pyrohydrolytic combustion, n*—a process in which a sample undergoes combustion at temperatures greater than 900 °C in an oxygen-rich environment and in the presence of excess water vapor not originating from the combustion of the sample. In oxidative pyrohydrolytic combustion, the sample is pyrolyzed into carbon dioxide, water, hydrogen halides, and residual ash; typically elemental oxides.

3.1.3 *halogens (X), n*—the elements fluorine, chlorine, bromine, and iodine.

3.1.4 *hydrogen halide (HX), n*—inorganic compounds with the formula HX where X is one of the halogens: fluorine, chlorine, bromine, and iodine. Hydrogen halides are gases that dissolve in water to give acids.

3.1.5 *sulfur oxide (SO_x), n*—refers to one or more of the following compounds:

3.1.5.1 *sulfur dioxide (SO_2)*

3.1.5.2 *sulfur trioxide (SO_3)*

3.1.5.3 *sulfate (SO_4)*

3.1.6 *system blank, n*—a combustion ion chromatography (CIC) analysis with no solvent or sample injection in which the same combustion, chromatography and time protocols are used as for the sample analysis, but without the combustion of a sample or solvent blank. The system blank must be equal to or less than 50 % (1/2) the area counts of the lowest calibration standard used for calibration and a maximum of 50 % (1/2) of the area count of the solvent blank used in the preparation of the calibration standards for the anions of interest.

3.1.7 *solvent blank, n*—a combustion ion chromatography (CIC) analysis of the solvent used for preparation of the calibration standards in which the same combustion, chromatography, time protocols and injection volumes are used as for the sample analysis. The solvent blank area count must be less than or equal to two times (2×) the system blank and 50 % (1/2) or less than the area counts of the lowest calibration standard used in the calibration of the system for the anions of interest.

3.1.8 *stock standard solution, n*—standard prepared from primary standards and subsequently used to prepare the working standard.

3.1.9 *working standard solution, n*—standard prepared from the stock standard solution and subsequently used to prepare the calibration standards.

3.1.10 *calibration standard, n*—standard prepared from the working standard and subsequently used to calibrate the instrument.

3.2 *Abbreviations:*

3.2.1 *CIC*—combustion ion chromatography

3.2.2 *Conc*—concentration

3.2.3 *CRM*—certified reference material

3.2.4 *HCI*—hydrogen chloride

3.2.5 *HF*—hydrogen fluoride

3.2.6 *HX*—hydrogen halide

3.2.7 *IC*—ion chromatograph or ion chromatography

3.2.8 *SO_x*—sulfur oxide (SO_2 and SO_3)

3.2.9 *SO_2*—sulfur dioxide

3.2.10 *SO_3*—sulfur trioxide

3.2.11 *SO_4*—sulfate

3.2.12 *SRM*—standard reference material

3.2.13 *Std*—standard

4. Summary of Test Method

4.1 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^- while the sulfur oxides (SO_X) formed are further oxidized to SO_4^{2-} in the presence of an oxidizing agent. An aliquot of known volume of the absorbing solution is then automatically injected into an ion chromatograph (IC) by means of a sample injection valve. The halide and sulfate anions are separated on the anion separation column of the IC. The conductivity of the eluent is reduced with an anion suppression device prior to the ion chromatograph's 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).

5. Significance and Use

5.1 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 in aromatic hydrocarbons and their mixtures. The results can be used for compliance determinations when acceptable to a regulatory authority using performance based criteria.

[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.