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]

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

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

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.

[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.

Current edition approved Dec. 1, 2014. Published January 2015. Originally approved in 2008. Last previous edition approved in 2014 as D7359 – 14. DOI: 10.1520/D7359-14A.

[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**

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*—are 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 choloride

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 *Std*—standard

3.2.13 *SRM*—standard reference material

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.

6. Interferences

6.1 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.

7. Apparatus

7.1 *Autosampler,* capable of accurately delivering a known volume of sample, typically in the range of 10 to 100 µL, into the sample boat.

NOTE 1—The sample syringe should be rinsed with clean solvent followed by a rinse with the next sample when changing from one vial to another. Follow the manufacturer's recommendation to minimize carry-over.

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

7.3 *Boat Inlet System*—The system provides a sampling port for the introduction of liquid samples into the sample boat and is connected to the inlet of the 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 oxidation zone at a controlled rate.

7.4 *Boat Inlet Cooler*—Sample volatility requires an apparatus capable of cooling the sample boat prior to sample injection into the boat.

7.5 *Gas Flow Control*—The apparatus must be equipped with flow controllers capable of maintaining a constant flow of oxygen and argon or helium carrier gas.

7.6 *Furnace*—An electric furnace which can maintain a minimum temperature of 900°C.

7.7 *Gas Absorption Unit,* having an absorption tube with sufficient capacity to hold a minimum of 5 mL which is automatically filled with a known volume of absorption solution by a built-in burette or other similar device. The gas absorption unit is interfaced to the IC and injects an aliquot of the absorption solution into the IC after the sample is combusted and the by-products of combustion are absorbed. The gas absorption unit rinses the absorption tube and the transfer lines from the combustion tube to the gas absorption unit with Type I reagent water (8.2) or other appropriate absorption solution prior to sample combustion and after the absorption solution is injected into the IC to minimize cross contamination.

7.8 *Gas-Tight Sampling Syringe,* of 10, 25, 50, 100, or 250-µL capacity and capable of accurately delivering microliter quantities.

7.9 *Pyrohydrolytic Combustion Tube* made of quartz and capable of withstanding temperatures up to 1100°C. The combustion tube must be of ample volume and may include quartz wool or other suitable medium to provide sufficient mixing and surface area to ensure complete combustion of the sample.

7.10 *Humidifier Delivery System,* capable of delivering Type 1 reagent water (8.2) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

7.11 *Ion Chromatograph (IC),*[4]an analytical system with all required accessories including columns, suppressor and detector.

7.11.1 *Injection System,* capable of delivering 20 to 500 µL with a precision better than 1 % or as recommended for this determination by the manufacturer. Larger volumes can be used as long as the performance criteria of the method are not degraded.

7.11.2 *Pumping System,* capable of delivering mobile phase flows between 0.2 and 2.5 mL/min with a precision better than 2 %, or as recommended for this determination by the manufacturer.

[4] Many different companies manufacture automatic ion chromatographs. Consult the specific manufacturer instruction manuals for details regarding setup and operation.

7.11.3 *Continuous Eluent Generation (optional),* to automatically prepare and purify the eluent used in the ion chromatography. Electrolytic eluent generation and auto-buret preparation of eluent by means of in-line dilution of a stock solution have been found satisfactory for this method. Other continuous eluent generation devices may be used if the precision and accuracy of the method are not degraded.

7.11.4 *Anion Pre-concentration Column (optional),* used for anion pre-concentration and matrix elimination. Pre-concentration enables larger volumes of absorbing solution (1 to 3 mL) to be analyzed without the associated water dip. Matrix elimination refers to the elimination of any unreacted hydrogen peroxide in the absorbing solution prior to injection onto the guard and anion separator columns and potentially interfere with the fluoride peak resolution.

7.11.5 *Guard Column,* for protection of the analytical column from strongly retained constituents. Improved separation is obtained with additional theoretical plates.

7.11.6 *Anion Separator Column,* capable of producing satisfactory baseline separations of the anion peaks of interest as shown in Fig. 1.

7.11.7 *Anion Suppressor Device,* reduces the background conductivity of the eluent after separation by the anion separator column. Both chemical and continuous electrolytic suppressors have been found satisfactory for this method. Other anion suppressor devices may be used as long as the precision and accuracy of the method are not degraded.

7.11.8 *Conductivity Detector,* temperature controlled to 0.01°C, capable of at least 0 to 1000 µS/cm on a linear scale.

7.11.9 *Data Acquisition System,* an integrator or computer data handling system capable of integrating the peak areas of ion chromatograph

7.12 *Quartz or Ceramic Sample Boats* of sufficient size to hold 10 to 100 µL. The boat is filled with quartz wool or other suitable material (8.3) to wick any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or higher purity chemicals shall be used for the preparation of all samples, standards, eluent, and regenerator solutions. 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.[5] 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.

NOTE 2—Purity of reagents are of particular importance when performing trace analysis (samples containing 1 mg/kg or less in analyte concentration). A system reagent blank should provide a chromatographic area response no greater than 50 % (1/2) of the lowest calibration standard.

[5] *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.