Designation: D7359 – 14a

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 *HCl*—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 carryover.

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.

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.

---

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

[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.

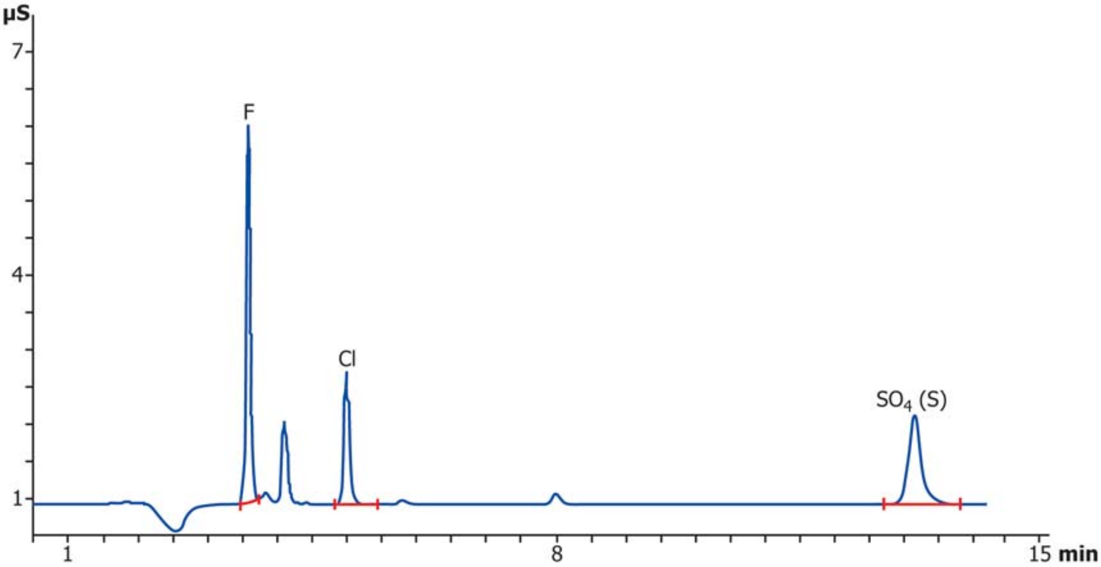

FIG. 1 Anion Peaks of Interest

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type 1 having 18 MΩ cm resistance and conforming to Specification D1193. Comply with all ion chromatograph instrument and column vendor requirements for eluent preparation and handling (for example, filtering, degassing, and the like). The reagent water is critical to the performance, repeatability, reproducibility and accuracy of the method. Therefore, the reagent water used must be of the highest quality available in the lab. A chart of critical specification parameters for Type I reagent water in accordance with Specification D1193–06 (2011) is listed in Table 1.

8.3 *Quartz Wool,* (fine grade) or other suitable absorbent material can be used that is stable and capable of withstanding temperatures inside the furnace.

NOTE 3—Materials meeting the requirements in 8.3 provide a more uniform injection of the sample into the boat by wicking any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace. Consult instrument manufacturer recommendations for further guidance.

8.4 *Argon or Helium,* carrier gas minimum 99.99 % purity.

NOTE 4—Purification scrubbers to ensure the removal of containments such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) are recommended.

8.5 *Oxygen,* combustion gas minimum 99.75 % purity.

8.6 *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. Follow instrument manufacturer's recommendations for pressure regulation.

TABLE 1 Type I Reagent Water Key Specifications

	Specification D1193–06 (2011)		
Measurement (unit)	Type I	Type II	Type III
Resistivity (MΩ·cm) at 25°C	>18	>1	>4
Total organic carbon (ppb)	<50	<50	<200
Sodium (ppb)	<1	<5	<10
Chloride (ppb)	<1	<5	<10
Total silica (ppb)	<3	<3	<500

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

NOTE 5—Other calibration standard sources and diluents may be used if precision and accuracy are not degraded.

NOTE 6—Calibration standards can have a useful shelf life of about three months if properly stored in a cool, dark place.

NOTE 7—A correction for chemical impurity can be used if deemed necessary.

8.8 *Dibenzothiophene,* FW 184.26, 17.40 % S.

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

8.10 *2,4,5 Trichlorophenol,* FW 197.46, 53.87 % Cl.

8.11 *Hydrogen Peroxide 30 %,* FW 34.01 H_2O_2 (see Section 9 regarding Hazards). Purity must be suitable for trace analysis. It is highly recommended that the concentration of each anion of interest be less than 1 mg/kg.

NOTE 8—Fluka TraceSelect Ultra, Fluka TraceSelect,[6] and EMD Suprapur[7] have all proven to work well for this method.

8.12 *Eluent Solution*—Follow the specific guidelines for the preparation and use of the eluent solution from the manufacturer of the columns being used. Other concentrations may be used if precision and accuracy of the method is not degraded. The solutions recommended by the column manufacturer can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded (see Section 9 regarding Hazards).

8.13 *Suppressor Solutions:*

8.13.1 *Chemical Suppressor Regenerant Solution*—Follow the specific manufacturer guidelines for the preparation and use of the suppressor solution. The manufacturer recommended

---

[6] Fluka TraceSelect Ultra and Fluka TraceSelect are registered trademarks of Sigma-Aldrich Co. LLC.

[7] EMD Suprapur is a registered trademark of EMD Millipore Corporation.

solutions can be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded.

8.13.2 *Electrolytic Suppressor Current Setting*—Follow the specific guidelines for the current setting from the vendor of the suppressor being used based upon the flow rate and eluent concentration being used for the analysis.

8.14 *Solvent*—The solvent of choice should be capable of dissolving the standard or sample. The solvent should contain less than 0.05 mg/kg of the elements or anions of interest. The blank value must be determined for each new bottle of solvent. Suggested solvents include, but are not limited to, *iso*-octane, xylene, toluene, and methanol.

8.15 *Volumetric Flasks–Type Class A,* in accordance with Specification E288 at the volume required for the preparation of standards, reagents, and solutions.

8.16 *Volumetric Pipets–Type Class A,* in accordance with Specification E969 at the volume required for preparation of standards, reagents, and solutions.

8.17 *Stock Standard Solution(s) of approximately 1000 µg/mL*—Prepare stock standard solution(s) by accurately weighing to within 10 % of the target weights for any or all of the target standard compound(s) listed in 8.17.1, 8.17.2, and 8.17.3 into a 100 mL Type Class A volumetric flask. Dilute to volume with the selected solvent listed in 8.14. Calculate the actual concentration of the stock standard solution(s) for each element by using the formula in Eq 1 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 standard solution(s) as long as the performance of the method is not degraded.

NOTE 9—Stock standard solutions from commercial sources can be used if the accuracy, precision, and performance criteria of the method are not degraded.

Target Standard Compound(s)

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

8.17.2 *2,4,5 Trichlorophenol, (Chlorine),* 0.1856 g target weight.

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

Calculation of Concentration of Stock Standard Solution

$$\text{Stock Standard Solution}(\mu g/mL) = (A)\,(B)\,(10^6)\,(P)/(V)\,(K) \tag{1}$$

where:

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

B = % concentration of the elements in the respective target compounds listed in 8.8, 8.9, and 8.10,

V = final diluted volume, mL,

P = % purity of target standard compounds listed in 8.8, 8.9, and 8.10, and

K = 100 (correction to convert % to µg/g).

8.18 *Absorbing Solution*—Dilute a sufficient amount of hydrogen peroxide stock solution listed in 8.11 to achieve a final concentration of approximately 100 µg/mL. (Approximately 0.7 mL of 30 % hydrogen peroxide added to 2 L of absorbing solution will give a final concentration of approximately 100 µg/mL.) The use of hydrogen peroxide in the absorbing solution ensures that all SO_X species are converted to SO_4 prior to detection by the IC. Hydrogen peroxide is not required if the measurement of sulfur is not being determined.

NOTE 10—Other concentrations of hydrogen peroxide can be used as long as the performance of the method is met.

NOTE 11—Hydrogen peroxide may not be necessary if the concentration of sulfur in the sample is low since the formation of SO_3 in the absorption solution becomes insignificant. It has been observed that results at concentrations below 5 mg/kg in aromatic compounds typically do not require hydrogen peroxide. If the differences in area counts of the sulfate peak is less than 5 % with and without hydrogen peroxide then one can assume that the use of hydrogen peroxide is not necessary.

8.19 *Working Standard Solution*—Calculate the correct concentrations obtained from the stock standard solution(s) in 8.17 and prepare a working standard by diluting the stock standard solution(s) with solvent (8.14).

8.19.1 Prepare a 10.0 µg/mL working standard by using a 1.0 mL Type Class A volumetric pipet (Specification E969) and pipet 1.0 mL of the 1000 µg/mL stock standard solution(s) (8.17) into a 100 mL Type Class A volumetric flask (Specification E288) and dilute to mark with solvent.

8.20 *Calibration Standards*—Prepare calibration standards by diluting the working standard solution (8.19.1) to create 0.1, 0.5, 1.0 and 5.0 µg/mL calibration standards by pipetting 1.0, 5.0, 10.0, and 50.0 mL of working standard solution with the appropriate Class A volumetric pipets into four separate 100 mL Class A volumetric flasks and dilute to the mark with solvent (8.14). The calibration standards used to calibrate the system will include the solvent (8.14) as zero, the working standard for the 10 µg/mL and encompass the following approximate concentrations: 0.0, 0.1, 0.5, 1.0, 5.0, and 10 µg/mL. The final dilution volumes are determined using the formula in Eq 2.

$$Vol_{calibration}(\mathrm{mL}) = \frac{Conc_{working} \times Vol_{working}}{Conc_{calibration}} \tag{2}$$

where:

$Conc_{working}$ = concentration of working standard, µg/mL,

$Vol_{working}$ = volume of working standard, mL,

$Conc_{calibration}$ = concentration of calibration standard, µg/mL,

$Vol_{calibration}$ = final dilution volume of calibration standard, mL.

8.20.1 A summary outlining the preparation of the calibration standards is shown in Table 2.

8.20.2 Final dilution volumes can be calculated using the formula in Eq 2.

NOTE 12—Alternate volumes and concentrations of working and calibration standards may be prepared so long as the preparation meets the concentration range needed to properly bracket the response of the samples and adhere to the scope of the method.

NOTE 13—Working standard solutions should be prepared on a regular basis depending upon the frequency of use and age. The working standard solution can be retained, if refrigerated, for up to three months. Do not refrigerate working standard solution if prepared in benzene as the benzene will freeze and cause erratic results.

NOTE 14—Alternatively, calibration standards may be prepared by

TABLE 2 Calibration Standards – Preparation from Working Standard Solution

Calibration Std Conc (µg/mL)	Working Standard Solution Conc (µg/mL)	Dilution Volume (mL)[A]	Final Vol (mL)[B]
10	10.0	100	100
5	10.0	50	100
1	10.0	10	100
0.5	10.0	5	100
0.1	10.0	1	100

[A] Use Class A volumetric pipets or equivalent meeting Specification E969.

[B] Use Class A volumetric pipets or equivalent meeting Specification E288.

gravimetric dilution provided the same solvents are used throughout. The solvent used for the stock standard solution, working standard and calibration standards must all be the same. In this case, the final concentration unit for the calibration standards will remain µg/mL even though the dilutions were performed gravimetrically.

9. Hazards

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

9.2 High temperature and flammable hydrocarbons occur in the 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 Potassium hydroxide is a caustic alkali, which in an anhydrous or strong solution forms, is a hazardous material. In contact with the skin, it produces burns that may be quite serious unless promptly treated. Its action is insidious since it produces no immediate stinging or burning sensation and damage to the skin may result before its presence is realized. Eyes are particularly vulnerable to severe damage from alkalis.

9.4 Hydrogen peroxide (used in the eluent solution preparation) is a strong oxidizer and hazardous material. In contact with the skin, it produces burns that may be quite serious unless promptly treated. Its action is insidious since it produces no immediate stinging or burning sensation and damage to the skin may result before its presence is realized. Eyes are particularly vulnerable to severe damage.

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

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

10. Sampling

10.1 Collect sample in accordance with Practice D3437.

10.2 To preserve sample integrity and prevent loss of volatile components that may be present in some samples, do not expose samples to the atmosphere any longer than necessary. Analyze samples as soon as possible after sampling from bulk supplies to prevent loss or contamination due to exposure to air or prolong contact with sample containers.

10.3 Thoroughly mix the sample in its container prior to withdrawing a sample for analysis if the sample is not analyzed immediately after sampling.

10.4 Care must be taken to ensure the standard and sample containers are clean and do not contaminate the sample to ensure successful trace analysis.

11. Preparation of Apparatus

11.1 Set up the instrument in accordance with the manufacturer's instructions. A typical diagram of a CIC system is shown in Fig. 2.

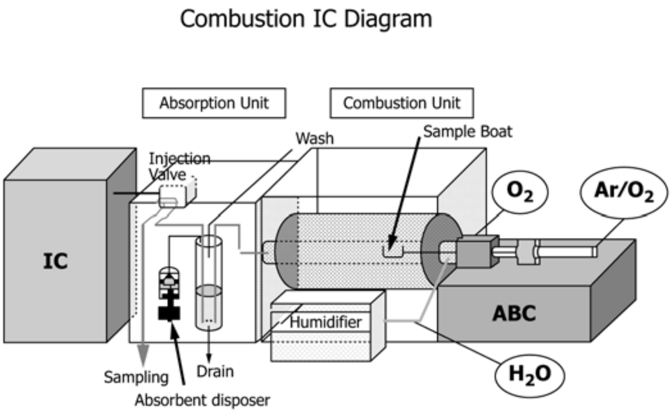

FIG. 2 Combustion IC Diagram

11.2 Set instrument parameters in accordance with the manufacturer's instructions.

11.3 Adjust gas flows and pyrolysis temperatures to the operating conditions as recommended by the instrument manufacturer.

12. Calibration

12.1 Prior to the analysis of standards or samples, it is necessary to run a series of system blanks (3.1.6) and solvent blanks (3.1.7) to ensure cleanliness of the system. Follow the manufacturer's recommendation for this process.

12.1.1 The series of system blanks should be analyzed repeatedly until a stable baseline response is achieved. Typically, 3 to 5 system blanks are all that is required. A stable background is considered 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. If a stable baseline response is not obtained, follow the manufacturer's recommendations to check for sources of contamination.

12.1.2 The system blank (3.1.6) 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.

12.1.3 The solvent blank (3.1.7) 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.

12.2 Prepare a series of calibration standards covering the range of samples to be analyzed by diluting the working standard (8.19) prepared from the stock standard solution (8.17) to the desired final concentrations.

NOTE 15—Commercially available standards may be used as long as the accuracy and precision of the method is not degraded.

12.3 Analyze the calibration standards covering the analytical range of the samples and determine the peak areas corresponding to the fluoride, chloride, and sulfate ions. The use of an automated sampling device is required to ensure accurate and repeatable injection volumes and techniques.

12.4 An aliquot of absorbing solution following the combustion of each standard is introduced into the IC for separation and quantification. Retention times vary with operating conditions. The standards, therefore, must be analyzed by the IC in the same manner as the sample solutions. Consult the manufacturer's recommendations for analyte elution order.

12.5 After the standards have been analyzed, a calibration curve is determined for each anion using a "best-fit" regression by plotting concentration versus the integrated instrument response (area) for the anion of interest. Instrument response is calculated and defined per the manufacturer's recommendations. A typical calibration includes a series of four standards containing the elements of interest and bracketing the concentrations that are in the samples. The calibration curve should have a correlation coefficient (r^2) greater than 0.995.

13. Procedure

13.1 Obtain a test specimen using the procedure described in Section 10. The concentrations in the test specimen must be less than the concentration of the highest standard and greater than the lowest standard used in the calibration. If required a dilution of the sample can be performed.

13.2 Analyze the samples using identical instrument conditions as used for calibration.

13.3 Inspect the combustion tube and other flow path components to verify complete oxidation of the test specimen after analysis.

13.4 If necessary, increase the residence time for the boat in the furnace if coke or soot is observed on the boat after combustion. Decrease the boat drive introduction rate or hold times in the furnace, or both, if coke or soot is observed on the exit end of the combustion tube.

13.5 Clean any coke or soot as per the manufacturer's instructions. After any cleaning or adjustment, assemble and leak check the apparatus. Run a check standard to determine if the instrument needs to be recalibrated.

14. Calculation

14.1 If the Ion Chromatograph has a Computer Based Data Handling Software, follow manufacturer procedures for calculation of sample concentration.

14.2 For analyzers calibrated manually, calculate the concentration(s) in the sample for the anion(s) of interest in mg/Kg (ppm) using the peak area(s) and calibration curve(s) generated in Section 12 using the formula in Eq 3.

$$Element\ of\ Interest\,(F,\ Cl,\ or\ S)\ mg/Kg = \frac{(A-b)(K)(1000)}{m \times V \times D \times Kg} \quad (3)$$

where:

D = density of test specimen, g/mL,
V = volume of sample analyzed (injected), µL,
A = area of anion peak of interest derived from the chromatogram of the absorbing solution, area,
Kg = gravimetric dilution factor, mass of sample/mass of sample plus solvent (total weight), g/g,
m = slope of standard curve, (area of anion of interest/concentration, (area/(µg/mL)),
b = y-intercept of standard curve, anion of interest, (area),
K = final volume of absorbing solution prior to injection into IC, mL,
1000 = factor to convert final concentration to mg/Kg.

15. Report

15.1 Report the following information to the nearest 0.01 mg/kg or to two significant figures.

15.1.1 Fluorine to the nearest 0.01 mg/kg.

15.1.2 Chlorine to the nearest 0.01 mg/kg.

15.1.3 Sulfur to the nearest 0.01 mg/kg.

16. Precision and Bias[8]

16.1 An ILS was conducted which included ten laboratories analyzing seven samples and one quality control sample two times each. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. RR:D16-1052.

16.1.1 *Repeatability (r)*—Results should not be suspect unless they differ by more than shown in Tables 3-5. Results differing by less than "*r*" have a 95 % probability of being correct.

TABLE 3 Total Fluoride (mg/kg)[A]

Material	Average[B] $\bar{X}$	Repeatability r	Reproducibility R
Sample 1: Benzene[C]	0.075	0.013	0.168
Sample 2: *p*-Xylene[C]	0.092	0.044	0.244
Sample 3: Toluene	0.136	0.047	0.188
Sample 4: *p*-Xylene	0.530	0.069	0.175
Sample 5: *p*-Xylene	1.041	0.046	0.197
Sample 6: Toluene	4.838	0.112	0.360
Sample 7: Benzene	10.073	0.449	1.195
QC – *p*-Xylene	1.043	0.089	0.217

[A] Data from 9 labs are included in the precision calculation.
[B] The average of the laboratories' calculated averages.
[C] Only 8 laboratories included in the precision calculations.

---

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D16-1052. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Total Chloride (mg/kg)[A]

Material	Average[B] $\bar{X}$	Repeatability r	Reproducibility R
Sample 1: Benzene	0.028	0.009	0.099
Sample 2: *p*-Xylene	0.047	0.028	0.114
Sample 3: Toluene	0.128	0.033	0.093
Sample 4: *p*-Xylene	0.511	0.077	0.175
Sample 5: *p*-xylene	1.060	0.127	0.316
Sample 6: Toluene	4.907	0.211	0.619
Sample 7: Benzene	10.246	0.796	1.190
QC – *p*-Xylene	1.048	0.158	0.258

[A] Data from 10 labs are included in the precision calculations.

[B] The average of the laboratories' calculated averages.

TABLE 5 Total Sulfur (mg/kg)[A]

Material	Average[B] $\bar{X}$	Repeatability r	Reproducibility R
Sample 1: Benzene	0.066	0.017	0.166
Sample 2: *p*-Xylene	0.095	0.025	0.284
Sample 3: Toluene	0.105	0.057	0.061
Sample 4: *p*-Xylene	0.525	0.101	0.262
Sample 5: *p*-Xylene	1.137	0.173	0.484
Sample 6: Toluene	4.974	0.343	0.601
Sample 7: Benzene	10.599	0.198	2.126
QC – *p*-Xylene	1.096	0.189	0.296

[A] Data from 10 labs are include in the precision calculations.

[B] The average of the laboratories' calculated averages.

16.1.2 *Reproducibility (R)*—Results submitted by two labs should not be considered suspect unless they differ by more than shown in Tables 3-5. Results differing by less than "*R*" have a 95 % probability of being correct.

16.1.3 Any judgment in accordance with statements 16.1.1 and 16.1.2 would have an approximate 95 % probability of being correct.

16.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

16.3 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

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 analysis; anions; aromatics; chloride; chlorine; CIC; combustion; combustion ion chromatography; fluoride; fluorine; hydrolysis; ion chromatography; oxidative pyrohydrolytic combustion; petroleum; pyrohydrolytic; sulfur

SUMMARY OF CHANGES

Committee D16 has identified the location of selected changes to this standard since the last issue (D7359–14) that may impact the use of this standard. (Approved December 1, 2014.)

(1) Updated Section 7, Apparatus, to include Section 7.11.8 outlining conductivity detector specification.

(2) Updated Section 16 in accordance with D16 Guidelines.

(3) Updated headers in Tables 3–5.

(4) Updated Section 17 in accordance with D16 Guidelines.

Committee D16 has identified the location of selected changes to this standard since the last issue (D7359–13) that may impact the use of this standard. (Approved July 1, 2014.)

(1) Extensive revisions were made throughout.

(2) Updated to reflect the results of an interlaboratory study.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/