Designation: D7994 – 17

Standard Test Method for
Total Fluorine, Chlorine, and Sulfur in Liquid Petroleum Gas (LPG) by Oxidative Pyrohydrolytic Combustion Followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)[1]

This standard is issued under the fixed designation D7994; 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 liquid petroleum gas (LPG), low molecular weight hydrocarbons, their mixtures, and dimethyl ether (DME) in the range of 1 mg/kg to 300 mg/kg fluorine and sulfur and 5 mg/kg to 300 mg/kg for chlorine. This test method is applicable to products described in Specifications D1835 and D7901 and it can be applicable to process streams with similar properties to LPG and other materials such as butylene, propylene, and olefins.

1.2 This test method can also be applied to the measurement of the bromine and iodine in samples covered by the scope of this test method, but the precision and bias statement of this test method is not applicable to these halides.

1.3 This test method can be applied to sample concentrations outside the scope of this test method through adjustments of sample injection volume or number of injections combusted (or both), adjustment of injection volume to the ion chromatograph, and adjustment of the final dilution volume of the absorbing solution prior to injection to the ion chromatograph. The precision and scope of this test method is not applicable to samples that are outside the scope of the method.

1.4 The values stated in SI units are to be regarded as standard.

1.4.1 *Exception*—Values given in parentheses are for information only.

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.

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
D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
D1835 Specification for Liquefied Petroleum (LP) Gases
D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder
D6849 Practice for Storage and Use of Liquefied Petroleum Gases (LPG) in Sample Cylinders for LPG Test Methods
D7901 Specification for Dimethyl Ether for Fuel Purposes
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E288 Specification for Laboratory Glass Volumetric Flasks
E969 Specification for Glass Volumetric (Transfer) Pipets

2.2 *OSHA Standards:*[3]
29 CFR Part 1910.1000 Air Contaminants
29 CFR Part 1910.1200 Hazard Communication

3. Terminology

3.1 *Definitions:*

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

3.1.2 *halogen (X), n*—a generic term which includes the elements fluorine, chlorine, bromine, and iodine.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.H0 on Liquefied Petroleum Gas.

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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.

[3] Available from Occupational Safety and Health Administration (OSHA), 200 Constitution Ave., NW, Washington, DC 20210, http://www.osha.gov.

3.1.3 *hydrogen halide (HX), n*—inorganic compounds with the formula HX where X is one of the halogens: fluoride, chloride, bromide, and iodide.

3.1.3.1 *Discussion*—Hydrogen halides are gases that dissolve in water to give acids.

3.1.4 *nitrogen oxides (NO_X), n*—one or more of the following compounds: nitric oxide (NO), nitrogen dioxide (NO_2).

3.1.5 *oxidative pyrohydrolytic combustion, n*—a process in which a sample is burned in an oxygen-rich environment at temperatures greater than 900 °C and in the presence of excess water vapor not originating from the combustion of the sample.

3.1.5.1 *Discussion*—In oxidative pyrohydrolytic combustion, the sample is converted into carbon dioxide, water, hydrogen halides (HX), and elemental oxides such as NO_X and SO_X.

3.1.6 *sulfur oxides (SO_X), n*—one or more of the following chemical species: sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfate (SO_4^{2-}).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *LPG calibration blank, n*—the LPG (usually butane or propane) used in the preparation of the LPG calibration standards (3.2.2).

3.2.2 *LPG calibration standard, n*—a material, usually prepared in butane or propane, and subsequently used for calibration the CIC System (3.1.1).

3.2.3 *LPG check standard, n*—a reference material, usually prepared in butane or propane, which is used to verify instrument calibration and performance of the CIC system prior to sample analysis but is not used in the instrument calibration procedure.

3.2.4 *LPG QC sample, n*—a pressurized sample previously analyzed and used to verify instrument calibration and performance of the CIC system prior to sample analysis.

3.2.5 *LPG system blank, n*—the area of the anion(s) of interest of a combustion ion chromatography (CIC) analysis of the LPG calibration blank (3.2.1) used for preparation of the LPG calibration standards (3.2.2). The same combustion conditions, chromatography, time protocols, and injection volumes are used as for the analysis of a LPG sample.

3.2.6 *non-LPG liquid check standard, n*—a liquid hydrocarbon sample not in an LPG matrix that is used to troubleshoot and check the performance of the CIC system (3.1.1) prior to sample analysis. (See Appendix X1 for preparation.)

3.2.7 *non-LPG liquid sample, n*—a hydrocarbon sample that is in liquid phase at 15 °C and atmospheric conditions.

3.2.8 *system blank, n*—the area of the anion(s) of interest of a combustion ion chromatography (CIC) analysis in which the same combustion, chromatography, and time protocols are used as for a sample analysis, but without the combustion of an LPG sample, LPG calibration blank, or LPG calibration standard.

3.3 *Abbreviations:*

3.3.1 *CIC*—combustion ion chromatography

3.3.2 *conc.*—concentration

3.3.3 *CRM*—certified reference material

3.3.4 *DME*—dimethyl ether

3.3.5 *HCl*—hydrogen chloride

3.3.6 *HF*—hydrogen fluoride

3.3.7 *HX*—hydrogen halide

3.3.8 *IC*—ion chromatograph or ion chromatography

3.3.9 *MW*—molecular weight

3.3.10 *LPG*—liquefied petroleum gas

3.3.11 NO_X—nitrogen oxides (NO and NO_2)

3.3.12 *NO*—nitric oxide

3.3.13 NO_2—nitrogen dioxide

3.3.14 PO_4^{3-}—phosphate

3.3.15 *RSD*—relative standard deviation

3.3.16 *SRM*—standard reference material

3.3.17 SO_X—sulfur oxides (SO, SO_2, SO_3, SO_4, S_2O_3, and S_2O_7)

3.3.18 SO_2—sulfur dioxide

3.3.19 SO_3—sulfur trioxide

3.3.20 SO_4^{2-}—sulfate

4. Summary of Test Method

4.1 Using an LPG sampling device with a fixed volume liquid injection loop, a pressurized sample is introduced at a controlled rate into a high-temperature combustion tube where the sample is combusted in an oxygen-rich pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in a liquid absorption solution 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 by 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 LPG calibration standards containing known amounts of fluorine, chlorine, and sulfur and then analyzing unknown pressurized samples under the same conditions as the standards.

5. Significance and Use

5.1 The total fluorine, chlorine, and sulfur contained in LPG, similar low molecular weight hydrocarbons, and DME can be harmful to many catalytic chemical processes, lead to corrosion, and contribute to pollutant emissions. While LPG specifications limit sulfur, some specifications also contain precautionary statements about fluorine. Chlorine has been known to contaminate LPG with detrimental consequences. This test method can be used to determine total fluorine (as fluoride), chlorine (as chloride), and sulfur (as sulfate ion) in process streams, intermediate and finished LPG products, similar low molecular weight hydrocarbons, and DME (1.1).

6. Interferences

6.1 Substances that co-elute with the elements (anions) of interest will interfere. A high concentration of one or more elements (anions) can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks. The potential for interference from specific elements (anions) by means of co-elution is largely dependent on the manufacturer and type of anion separation column used in the ion chromatograph.

6.2 Improper sample containers that react with fluorine, chlorine, or reactive sulfur species can give erroneously low results (Section 10).

7. Apparatus

7.1 *LPG Sampling System:*

7.1.1 *LPG Sampling Device,* capable of accurately delivering under pressure a known volume or aliquot of pressurized sample, typically in the range of 5 µL to 30 µL. The system and sample injection loop is swept by inert carrier gas and shall be capable of allowing the quantitative delivery of a known aliquot of pressurized sample into the oxidation zone at a controlled rate.

7.2 *Pyrohydrolytic Combustion Unit:*

7.2.1 *Furnace,* an electric furnace that can maintain a minimum temperature of 900 °C.

7.2.2 *Gas Flow Control,* the apparatus shall be equipped with flow controllers capable of maintaining a constant flow of oxygen and inert carrier gas (argon or helium).

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

7.2.4 *Pyrohydrolytic Combustion Tube,* made of quartz and capable of withstanding temperatures up to 1100 °C. The combustion tube shall 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.

7.3 *Gas Absorption Unit:*

7.3.1 *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.

7.4 *Ion Chromatograph:*

7.4.1 *Ion Chromatograph (IC),* (see Note 1) an analytical system with all required accessories including columns, suppressor and detector.

NOTE 1—Many different companies manufacture automatic ion chromatographs. Consult the specific manufacturer's instruction manual for details regarding setup and operation.

7.4.2 *Injection System,* capable of delivering a minimum of 5 µL to 200 µL with a precision better than 1 % or as recommended by the manufacturer for this determination. It is recommended to use an IC chromatograph configured for pre-concentration or matrix elimination (7.4.5) for injection volumes greater than 500 µL.

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

7.4.4 *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 via in-line dilution of a stock solution have been found satisfactory for this test method. Other continuous eluent generation devices may be used if the precision, bias, recovery, and accuracy of this test method are met.

7.4.5 *Anion Pre-Concentration Column (Optional),* used for anion pre-concentration and matrix elimination. Pre-concentration enables larger volumes of absorbing solution (1 mL 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 could potentially interfere with the fluoride peak resolution.

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

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

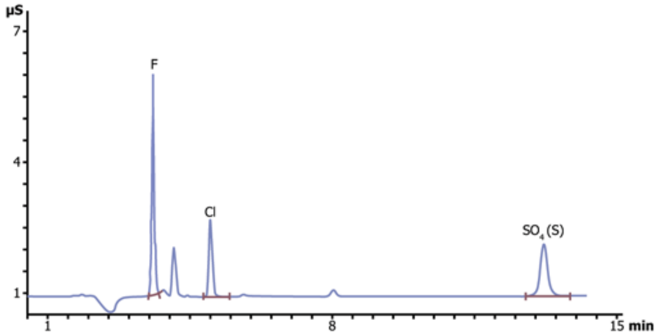

FIG. 1 Anion Peaks of Interest

7.4.8 *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 test method.

Other anion suppressor devices may be used as long as the precision and accuracy of the method are not degraded.

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

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

7.5 *Balance,* analytical, with sensitivity to 0.0001 g used for preparation of standards and reagents.

7.6 *Optional Apparatus and Accessories:*

7.6.1 *(Optional) Boat Inlet System*—The system provides a sampling port for the introduction of non-LPG liquid samples (3.2.7) into the sample boat and is connected to the inlet of the combustion tube. The system is swept by an inert carrier gas and shall be capable of allowing the quantitative delivery of the non-LPG liquid sample into the oxidation zone at a controlled rate. The optional boat inlet system may be used for QC testing and troubleshooting of the system with non-LPG liquid check standards (3.2.6) or non-LPG liquid samples (3.2.7) and is not required for routine pressurized sample analysis.

7.6.2 *(Optional) Boat Inlet Cooler*—The volatility of non-LPG liquid samples requires an apparatus capable of cooling the sample boat prior to injection of the non-LPG liquid sample into the boat. The boat inlet cooler may be used in conjunction with the optional boat inlet system (7.6.1) for QC testing and troubleshooting of the CIC system with non-LPG liquid check standards (3.2.6) or non-LPG liquid samples (3.2.7) and is not required for routine pressurized sample analysis.

7.6.3 *(Optional) Quartz or Ceramic Sample Boats,* of sufficient size to hold 10 µL to 100 µL and used in conjunction with the optional boat inlet system (7.6.1). The boat is filled with quartz wool or other suitable material (8.3) to wick any remaining drops of non-LPG liquid sample from the tip of the gas-tight syringe needle prior to introduction into the furnace. The optional boat inlet system (7.6.1) and quartz or ceramic sample boats (7.6.3) may be used for QC testing and troubleshooting of the system with non-LPG liquid check standards (3.2.6) or non-LPG liquid samples (3.2.7) but are not required for routine pressurized sample analysis.

7.6.4 *(Optional) Gas-Tight Sampling Syringe,* capable of accurately delivering microliter quantities up to 100 µL. The gas-tight syringe may be used for QC testing and troubleshooting of the system with non-LPG liquid check standards (3.2.6) or liquid samples (3.2.7) and is not required for routine pressurized sample analysis.

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, eluents, 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.[4] 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 is of particular importance when performing trace analysis of pressurized samples containing 1 mg⁄kg or less in concentration of the elements (anions) of interest. The LPG system blank (3.2.5) should provide a chromatographic area response no greater than 50 % of the lowest LPG calibration standard (3.2.2) used for calibration.

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

TABLE 1 Type I Reagent Water Key Specifications

	Specification D1193 Standards for Reagent Water		
Measurement (unit)	Type I	Type II	Type III
Resistivity (MΩ·cm) at 25 °C	>18	>1	>4
Total organic carbon (µg/kg)	<50	<50	<200
Sodium (µg/kg)	<1	<5	<10
Chloride (µg/kg)	<1	<5	<10
Total silica (µg/kg)	<3	<3	<500

8.3 *Quartz Wool (Fine Grade) (Optional),* or other suitable material that is stable and capable of withstanding the temperatures inside the furnace may be used.

NOTE 3—Materials meeting the requirements in 8.3 may be used in the pyrohydrolytic combustion tube (7.2.4) to provide increased surface area or to ensure a uniform injection of non-LPG liquid samples into the sample boat (7.6.3) of the optional boat inlet system (7.6.1) by wicking any remaining drops of non-LPG liquid sample from the tip of the syringe needle prior to introduction of the sample boat into the furnace. Consult instrument manufacturer recommendations for further guidance.

8.4 *Inert Carrier Gas,* such as argon or helium, minimum 99.98 % purity.

8.4.1 Purification scrubbers or filters are recommended to ensure the removal of contaminants, such as a molecular sieve for moisture and activated charcoal (or equivalent) for hydrocarbons.

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

8.6 *Nitrogen,* inert gas, minimum 99.75 % purity, used to pressurize the calibration standards and samples in the pressurized sample cylinders prior to analysis. Other inert gases such argon or helium (8.4) meeting the same minimum purity specification may also be used.

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[4] *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.

8.7 *Gas Regulators,* two-stage gas regulators capable of regulating the pressures in the range of 275 kPa to 415 kPa (40 psi to 60 psi) shall be used for the carrier and combustion gases. Follow instrument manufacturer's recommendations for pressure regulation.

8.8 *LPG Calibration Standards,* certified calibration standards gravimetrically prepared and traceable by weight to a national metrology institute (NMI) from commercial sources covering the desired calibration range and containing the elements (anions) of interest with the reported values verified by one or more analytical techniques. The certified calibration standards are normally prepared in butane or propane but may be prepared in LPG or other appropriate pressurized sample matrices. The calibration standard shall be pressurized to a constant pressure of 2000 kPa to 2760 kPa (300 psig to 400 psig) with inert gas to ensure sampling consistency and uniformity. Check pressure prior to analysis and re-pressurize as needed.

8.8.1 *Recommended Primary Organic Compounds,* used as sources for the elements (anions) of interest in the preparation of the LPG calibration standards (8.8):

8.8.1.1 *Fluorine:*

(1) Fluorobenzene, MW 96.103 g/mole, 19.77 % by mass F.

(2) Fluoropropane, MW 62.09 g/mole, 30.60 % by mass F.

8.8.1.2 *Chlorine:*

(1) Chlorobenzene, MW 112.56 g/mole, 32.16 % by mass Cl.

8.8.1.3 *Sulfur:*

(1) Dimethyl sulfide, MW 62.13 g/mole, 51.16 % by mass S.

8.8.2 Other primary organic compounds may be used.

8.8.3 LPG calibration standards typically have a useful shelf life between three months and twelve months if properly stored. Follow the manufacturer's instructions for proper storage and use. LPG calibration standards shall not be used beyond the declared shelf life on the calibration standard's certificate.

8.8.3.1 It is highly recommended when purchasing LPG calibration standards (3.2.2) to ensure the LPG calibration blank (3.2.1) is from the same LPG lot number that was used in the preparation of the LPG calibration standards (3.2.2) and to use the LPG calibration blank when calibrating the CIC system. The purity of the LPG used in the preparation of the LPG calibration standards is often not fully known and the background values for the elements (anions) of interest can vary considerably from lot to lot of LPG.

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

8.9.1 Fluka TraceSelect Ultra (trademarked), Fluka TraceSelect (trademarked), and EMD Suprapur (trademarked) have all proven to work well for this test method.[5]

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

8.11 *Suppressor (Chemical and Electrolytic):*

8.11.1 *Chemical Suppressor Regenerant Solution*—Follow the specific manufacturer's guidelines for the preparation and use of the suppressor solution. The manufacturer's recommended solutions may be purchased from qualified vendors as long as the performance, precision, and accuracy are not degraded.

8.11.2 *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.

8.12 *Absorbing Solution*—Dilute a sufficient amount of hydrogen peroxide stock solution listed in 8.9 to achieve a final concentration of approximately 100 mg/kg or µg/mL.

8.12.1 Approximately 0.7 mL of 30 % hydrogen peroxide added to 2 L (two liters) of absorbing solution will give a final approximate concentration of 100 mg/kg or µg/mL.

8.12.2 The use of hydrogen peroxide in the absorbing solution ensures that all SO_X species are converted to SO_4^{2-} prior to detection by the IC. Hydrogen peroxide is not required if the measurement of sulfur is not being determined.

8.12.3 Other concentrations of hydrogen peroxide may be used as long as the performance of the method is met.

8.12.4 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 at low concentrations. It has been observed that results for pressurized samples at concentrations below 5 mg/kg sulfur typically do not require hydrogen peroxide. If the differences in area counts of the sulfate peaks are less than 5 % with and without hydrogen peroxide at the maximum LPG calibration standard used (3.2.2), then one may assume that the use of hydrogen peroxide is not necessary.

8.13 *Phosphate Stock Solution (Optional) (1.00 mL = 1.00 mg phosphate)*—Dissolve 1.433 g of potassium dihydrogen phosphate (KH_2PO_4) in water and dilute to 1 L with water

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[5] The sole source of supply of the apparatus (Fluka TraceSelect Ultra, Fluka TraceSelect, and EMD Suprapur) known to the committee at this time is MilliporeSigma, a division of Merck KGaA, Darmstadt, Germany. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

in a Class A volumetric flask and mix well. This material is used in the absorbing solution for volume correction to check/verify IC stability and performance. The use of commercially available phosphate stock solution at the same or similar concentrations may be used. Follow manufacturer's recommendation for inclusion as an internal standard.

8.13.1 A known anion at a fixed concentration not present in the LPG calibration standards or samples may be used to verify the performance of the ion chromatograph during routine calibration and analysis. It is recommended to use a concentration of anion in the absorbing solution equal to half the area count of the maximum LPG calibration standard. Phosphate anion (PO_4^{3-}) at 1 mg/kg to 3 mg/kg is commonly used. Follow the manufacturer's instructions for specific recommendations.

9. Hazards

9.1 Consult the current version of OSHA (or equivalent national health and safety) regulations, supplier's safety data sheets, and local regulations for all materials used in this test method.

9.2 High temperatures and flammable hydrocarbons are used in this 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 (which may be used in the eluent solution preparation) is a caustic alkali, which in an anhydrous or concentrated solution is a hazardous material. In contact with the skin it produces burns that can be serious unless promptly treated. Its action is insidious since it produces no immediate stinging or burning sensation and damage to the skin can result before its presence is realized. Eyes are particularly vulnerable to severe damage from alkalis.

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

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

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

10. Sampling

10.1 Collect and store samples in accordance with Practices D1265, D3700, or D6849.

10.1.1 Pressurized sample containers/cylinders need to have interior surfaces that are inert to the analytes of interest. Some coatings, such as Sulfinert (trademarked), may be suitable for sampling cylinders used for samples containing reactive sulfur species, but can react with free hydrofluoric acid. Cylinders fabricated from Monel (trademarked) or similar grade material may be suitable for samples containing reactive species such as HF or HCl. PTFE coatings may be suitable for samples containing reactive fluorine and chlorine species, but care shall be taken to avoid damaging or abrading the coating and introducing particles of PTFE to the sample. Additionally, PTFE contains fluorine and can leach fluorine into the sample contained within the cylinder, contaminating the sample and resulting in higher results, especially in samples with low fluorine concentrations.

10.2 To preserve sample integrity, analyze samples as soon as possible after sampling to minimize prolonged contact with pressurized sample containers/cylinders.

10.3 Thoroughly mix the sample container/cylinder prior to connecting to the LPG sampling system (7.1) if the pressurized sample is not analyzed immediately after sampling.

10.4 Prior to analysis and connection to the LPG sampling system, it is recommended to pressurize the sample container/cylinder to a constant pressure of 2000 kPa to 2760 kPa (300 psi to 400 psi) with inert gas (8.6) to ensure sampling consistency and uniformity.

10.5 To ensure successful trace analysis, take care that the pressurized sample container/cylinders used for both sample and standards are clean and do not contaminate the LPG calibration blank, LPG calibration standards, and pressurized samples.

11. Preparation of Apparatus

11.1 Set up the system in accordance with the manufacturer's instructions. A typical block diagram of a CIC system for analysis of a pressurized sample is shown in Fig. 2.

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 and Standardization

12.1 Prior to sample injection, it is recommended to flush the LPG sampling device and sample injection loop with the pressurized sample to be analyzed to minimize carryover from the previous sample and remove any bubbles from the sampling train and injection loop. Follow the manufacturer's recommendations on the procedure for operation of the specific LPG sampler used.

12.2 Prior to calibration of the CIC system, run a series of system blanks (3.2.8) and LPG system blanks (3.2.5) to ensure cleanliness of the system. Follow the manufacturer's recommendation for this process. (See 12.3.)

12.3 Analyze a series of system blanks (3.2.8) repeatedly until a stable baseline response is achieved. Normally three to five system blanks are required.

12.3.1 A stable background is considered achieved when the analysis of three consecutive system blanks have area counts equal to or less than 5 % RSD for the elements (anions) of

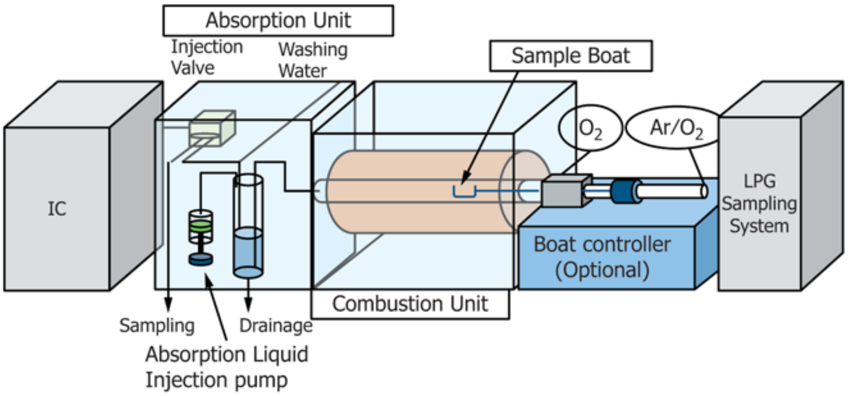

FIG. 2 Combustion IC Diagram with LPG Sampling System on the Right

interest. If a stable baseline response is not obtained, follow the manufacturer's recommendations to check for sources of contamination.

12.3.2 The system blank (3.2.8) shall be equal to or less than 50 % of the area counts of the lowest LPG calibration standard (3.2.2) used for calibration and a maximum of 50 % of the area count of the LPG system blank (3.2.5) used in the preparation of the LPG calibration standards (3.2.2) for the elements (anions) of interest.

12.3.3 LPG system blank (3.2.5) area count shall be less than or equal to two times (2×) the system blank (3.2.8) and 50 % or less than the area counts of the lowest LPG calibration standard (3.2.2) used in the calibration of the system for the anions of interest.

12.4 Select a series of LPG calibration standards (3.2.2) covering the range of samples to be analyzed. The LPG calibration standards shall include the LPG calibration blank (3.2.1) as one of the LPG calibration standards.

12.4.1 A minimum of three LPG calibration standards (3.2.2) are required to calibrate the system, of which one of the LPG calibration standards is the LPG calibration blank (3.2.1). The concentration of the LPG calibration standards should bracket the expected concentration of the LPG samples being analyzed.

12.4.2 It is recommended to use three calibration curves to cover the scope of this test method with four LPG calibration standards (3.2.2) for each calibration curve used. One of the LPG calibration standards (3.2.2) should be the LPG calibration blank (3.2.1). Recommended concentrations of LPG calibration standards (3.2.2) for the three calibration curves covering the range and scope of this test method are listed in Table 2, Table 3, and Table 4.

TABLE 2 Recommended Concentration for LPG Calibration Standards 0 mg⁄kg to 10 mg⁄kg Calibration Curve

NOTE 1—All concentrations in mg/kg.

Element	Std #1 (LPG Blank)	Std #2	Std #3	Std #4
Fluorine	0.00	1.00	5.00	10.0
Chlorine	0.00	1.00	5.00	10.0
Sulfur	0.00	1.00	5.00	10.0

TABLE 3 Recommended Concentration for LPG Calibration Standards 0 mg⁄kg to 100 mg⁄kg Calibration Curve

NOTE 1—All concentrations in mg/kg.

Element	Std #1 (LPG Blank)	Std #2	Std #3	Std #4
Fluorine	0.00	10.0	50.0	100
Chlorine	0.00	10.0	50.0	100
Sulfur	0.00	10.0	50.0	100

TABLE 4 Recommended Concentration for LPG Calibration Standards 0 mg⁄kg to 300 mg⁄kg Calibration Curve

NOTE 1—All concentrations in mg/kg.

Element	Std #1 (LPG Blank)	Std #2	Std #3	Std #4
Fluorine	0.00	30.0	150	300
Chlorine	0.00	30.0	150	300
Sulfur	0.00	30.0	150	300

12.4.3 Alternative number and concentrations of LPG calibration standards and calibration curves may be used so long as the concentration range properly brackets the response and concentration range of the pressurized samples analyzed and adhere to the scope of the method.

12.4.3.1 When calibrating the system, two types of data regression curves may be used: first order (linear) or second order (polynomial). Linear or first order regression is most commonly used and requires a minimum of three (3) calibration points or standards. If polynomial or second order regression is used, a minimum of five (5) calibration points or standards should be used and it is recommended the standards be equally distributed over the concentration range of the calibration curve.

12.5 Measure the LPG calibration standards covering the analytical range of the expected pressurized sample concentrations to be analyzed and determine the peak areas corresponding to the fluoride, chloride, and sulfate elements (anions) of interest.

12.6 Introduce an aliquot of absorbing solution following the combustion of each LPG standard into the IC for separation and quantification. Retention times vary with operating conditions. The LPG calibration standards shall therefore be analyzed by the IC in the same manner as the pressurized samples and corresponding absorbing solutions. Consult the manufacturer's recommendations for analyte (anion) retention time(s) and elution order for the specific separation column and flow rate used by the IC.

12.7 After the LPG calibration standards have been analyzed, determine a calibration curve using a "best-fit" regression by plotting concentration versus the integrated instrument response (area) for the element (anion) of interest. Instrument response is calculated and defined according to the manufacturer's recommendations. Refer to 12.4.3 and 12.4.3.1 for details. A typical calibration includes a series of four LPG calibration standards (including the LPG calibration blank (3.2.1)) containing the elements (anions) of interest and bracketing the corresponding concentrations in the samples. The calibration curve should have a correlation coefficient (r^2) greater than or equal to 0.995.

13. Procedure

13.1 Obtain a pressurized sample using the procedure described in Section 10. The concentrations of analytes of interest in the pressurized sample shall be less than the concentration of the highest LPG calibration standard and greater than the lowest LPG calibration standard used in the calibration.

13.2 Special precautions shall be taken in order to attain the detection limit of 1.0 mg/kg. Prior to the start of analysis the instrument shall be clean and properly maintained to address potential sources of contamination, carryover from previous samples, or both.

13.3 It is recommended that multiple system blank injections (3.2.8) should be analyzed until a stable background is attained. A stable background is typically considered to be achieved when the analysis of three consecutive system blanks (3.2.8) have area counts equal to or less than 5 % RSD for the elements (anions) of interest, or the area count of a system blank is equal to or less than the area count of the system blank measured during the calibration of the CIC system in Section 12 for the anions of interest.

13.4 Verify the calibration by running an LPG check standard (3.2.3). Recovery of the check standard should be within ±10 % of the known or certified value.

NOTE 4—If the LPG check standard used is at the lower level or limit of the calibration curve, the recovery may be greater than ±10 % of the known or certified value. At these lower concentration levels, ±20 % of the known or certified value is typically allowed.

13.5 Prior to the start of sample analysis, analyze a system blank (3.2.8) to verify the criteria as outlined in 12.3.2 and run a LPG system blank (3.2.5) to verify the criteria as outlined in 12.3.3.

13.5.1 Both system blank and LPG system blank should be equal to or less than the area counts measured during the calibration of the system for the anions of interest. Follow the manufacturer's recommendations for corrective actions if either value is not met.

13.6 Analyze the LPG samples using identical instrument conditions and procedures as used for the calibration in Section 12.

13.7 Inspect the combustion tube and other flow path components to verify complete oxidation of the pressurized sample after combustion and analysis. Reduce or decrease the LPG sample introduction rate into the combustion tube if coke or soot is observed on the exit of the combustion tube. Follow the specific manufacturer's recommendations, including one or more of the variables in 13.7.1, 13.7.2, and 13.7.3 below:

13.7.1 Reduce the inert gas flow rate through the LPG sampling system.

13.7.2 Reduce the volume (size) of the LPG injection loop.

13.7.3 Reduce the frequency or number of repeated injections.

13.8 Clean any coke or soot according to 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 program, follow the manufacturer's 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 by mass) using the peak area(s) and calibration curve(s) generated in Section 12 and using Eq 1:

$$\text{Element of Interest (F, Cl, or S) mg/kg} = \frac{(A - b)(K)(1000)}{m \times V \times D} \qquad (1)$$

where:

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

14.3 Calculation of the absorbing solution final volume (K) if using the internal phosphate method (see 8.13):

$$K = (\text{Initial Abs Soln (mL)} \times \text{IC Area } PO_4^{3-} \text{ Peak (Direct)}) / \text{IC Area } PO_4^{3-} \text{ Peak (After Combustion), mL} \qquad (2)$$

15. Report

15.1 Reference this test method and report the following information to the nearest 0.01 mg/kg or to three significant figures for results greater than 9.99 mg/kg for elements analyzed.

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. Interim Precision and Bias

16.1 The interim precision of this test method is based on a ruggedness study conducted in January/February 2014. A total of three laboratories tested seven different pressurized samples including propane, a butylene/propylene mixture, and DME. Every test result represents an individual determination and all participants were asked to report test results in triplicate. Details are available in ASTM Research Report No. RR:D02-1853.[6]

16.1.1 *Interim Repeatability* (r)*:*

16.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions that are accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.2 *Repeatability Limit (*r*)*—See Table 5.

$$\text{Fluorine} = 1.799\text{E-}02(X+25.1754)\ \text{mg/kg}$$
$$\text{Chlorine} = 2.394\text{E-}03(X+200.077)\ \text{mg/kg}$$
$$\text{Sulfur} = 2.313\text{E-}02 \times X^{0.8902}\ \text{mg/kg}$$

TABLE 5 Predicted Repeatability Limits of Fluorine, Chlorine, and Sulfur in LPG by CIC

Conc (mg/kg)	Fluorine (*r*)	Chlorine (*r*)	Sulfur (*r*)
1	0.471	0.481	0.023
5	0.543	0.491	0.097
10	0.633	0.503	0.180
100	2.252	0.718	1.395
250	4.950	1.077	3.154
300	5.850	1.197	3.709

16.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions that are accepted as plausible due to random causes under normal and correct operation of the test method.

16.1.3 *Reproducibility Limit (*R*)*—To be determined.

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 can be made.

17. Quality Guidelines

17.1 Confirm the performance of the instrument or the test procedure by analyzing an LPG check standard (3.2.3) after each calibration and either the LPG check standard (3.2.3) or LPG QC sample (3.2.4) at least each day of use thereafter (see 13.2).

17.2 When QC/quality assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

18. Keywords

18.1 analysis; anions; bromide; bromine; butane; butylene; chloride; chlorine; CIC; combustion; combustion ion chromatography; dimethyl ether; DME; fluoride; fluorine; halogens; hydrolysis; iodide; iodine; ion chromatography; liquefied petroleum gas; LPG; n-butane; olefins; oxidative pyrohydrolytic combustion; petroleum; propane; propylene; pyrohydrolytic; sulfate; sulfur

APPENDIX

(Nonmandatory Information)

X1. PREPARATION OF NON-LPG LIQUID CHECK STANDARDS

X1.1 **Non-LPG Liquid Check Standards (Optional)**—Prepare a non-LPG liquid check standard(s) for troubleshooting and checking the performance of the CIC system prior to running pressurized sample analyses.

X1.1.1 *Solvent,* the solvent of choice should be capable of dissolving the primary organic standard used to prepare the non-LPG liquid check standard. The solvent should contain less than 0.05 mg⁄kg of the anions of interest. The blank value shall be determined for each new bottle of solvent. Suggested solvents include, but are not limited to, *iso*octane, xylene, toluene, and methanol.

X1.1.2 *Volumetric Flasks,* Type Class A, per Specification E288 at the volume required for the preparation of standards, reagents, and solutions.

X1.1.3 *Volumetric Pipets,* Type Class A, per Specification E969 at the volume required for preparation of standards, reagents, and solutions.

X1.1.4 *Stock Non-LPG Liquid Check Standard(s) of Approximately 1000 µg⁄mL*—Prepare stock standard solution(s) by accurately weighing to within 10 % of the target masses for any or all of the target standard compound(s) listed in X1.2.1, X1.2.2, and X1.2.3 into a 100 mL Class A volumetric flask. Dilute to volume with the selected solvent listed in X1.1.1. Calculate the actual concentration of the stock standard solution(s) for each element by using Eq X1.1 with the actual recorded weight(s) of the target compound(s) used for each element. This stock standard solution may be further diluted to other desired concentrations. Other suitable materials, weights, and volumes may be substituted in preparing stock calibration solution(s) as long as the performance of the method is not degraded.

X1.1.4.1 Stock non-LPG liquid check standard from commercial sources may be used if the accuracy, precision, and performance criteria of the method are not degraded.

X1.2 Target Standard Compounds

X1.2.1 *Fluorobenzoic Acid (Fluorine),* 0.7375 g target mass.

X1.2.2 *2,4,5 Trichlorophenol (Chlorine),* 0.1856 g target mass.

X1.2.3 *Dibenzothiophene (Sulfur),* 0.5748 g target mass.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1853. Contact ASTM Customer Service at service@astm.org.

X1.3 Calculation—Concentration of Stock Non-LPG Liquid Check Standard

$$\text{Stock non-LPG liquid check standard } (\mu g/mL) = (A)(B)(10^6)(D)/(C)(K) \quad (X1.1)$$

where:

A = mass of the target compound in grams, g,
B = concentration of the elements in the respective target compounds listed in X1.2.1, X1.2.2, and X1.2.3, %,
C = final diluted volume, mL,
D = purity of target standard compounds listed in X1.2.1, X1.2.2, and X1.2.3, %, and
K = 100 (factor to convert percent to µg/g).

X1.4 **Working Non-LPG Liquid Check Standard Solution**—Calculate the correct concentration obtained from the stock standard solution(s) in X1.1.4 and prepare a working standard by diluting the stock standard solution(s) with solvent (X1.1.1).

X1.4.1 Prepare a 100.0 µg/mL of working non-LPG liquid check standard by using a 10.0 mL Type Class A volumetric pipet (Specification E969) and pipet 10.0 mL of the 1000 mg/L stock standard solution(s) (X1.1.4) into a 100 mL Type Class A volumetric flask (Specification E288) and dilute to mark with solvent (X1.1.1).

X1.5 **Non-LPG Liquid Check Standard(s)**—Prepare one or more non-LPG liquid check standards to the desired concentrations by pipetting known volumes of working non-LPG check standards to the desired final concentrations with the appropriate Class A volumetric pipets into one or more 100 mL Class A volumetric flasks and dilute to the mark with solvent (X1.1.1). The final concentrations of the non-LPG liquid check standards should be in the approximate range of the lower and upper LPG calibration standards used for calibration of the CIC system and bracket the expected concentration of the LPG samples being analyzed. The final dilution volumes are determined using Eq X1.2. A summary table outlining the preparation of recommended non-LPG liquid check standards (total volume of 100 mL) is shown in Table X1.1.

X1.5.1 Final dilution volumes may be calculated using Eq X1.2:

TABLE X1.1 Preparation of Non-LPG Check Standards from 100 ug/mL Working Non-LPG Liquid Check Standard

Target Concentration (µg/mL)	Working Std Volume (mL)[A]	Final Dilution Volume (mL)[B]
100	...	...
50	50	100
10	10	100
5	5	100
1	1	100

[A] Use Class A volumetric pipets or equivalent meeting Specification E969.
[B] Use Class A volumetric flasks or equivalent meeting Specification E288.

$$\text{Vol}_{\text{Non-LPG Liq Chk Std}}(\text{mL}) = \frac{\text{Conc}_{\text{Working Chk Std}} \times \text{Vol}_{\text{Working Chk Std}}}{\text{Conc}_{\text{Non-LPG Liq Chk Std}}} \quad (X1.2)$$

where:

$Conc_{Working\ Chk\ Std}$ = concentration of working non-LPG liquid check standard, µg/mL,
$Vol_{Working\ Chk\ Std}$ = volume of working non-LPG liquid check standard, mL,
$Conc_{Non\text{-}LPG\ Liq\ Chk\ Std}$ = concentration of stock non-LPG liquid standard, µg/mL, and
$Vol_{Non\text{-}LPG\ Liq\ Chk\ Std}$ = final dilution volume of non-LPG liquid check standard, mL.

X1.5.2 Alternative volumes and concentrations of stock non-LPG liquid check standards (X1.1.4), working non-LPG liquid check standards (X1.4), and non-LPG liquid check standards (X1.5) may be prepared so long as the preparation meets the concentration range needed to properly bracket the response of the pressurized samples.

X1.5.3 Working non-LPG check standards should be prepared on a regular basis depending upon the frequency of use and age. The working non-LPG check standard can be retained, if refrigerated, for up to three months.

X1.5.4 Alternatively, non-LPG liquid check standards may be prepared by gravimetric dilution provided the same solvents are used throughout. The solvent used for the stock non-LPG liquid check standard, working stock non-LPG liquid check standard, and stock non-LPG liquid check standard shall all be the same. In this case, the final concentration unit for the stock non-LPG liquid check standard will remain µg/mL even though the dilutions were performed gravimetrically.