



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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 standard-*

ization 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.

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 (NO₂).

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 (SO₂), sulfur trioxide (SO₃), sulfate (SO₄²⁻).

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 NO₂)

3.3.12 *NO*—nitric oxide

3.3.13 *NO₂*—nitrogen dioxide

3.3.14 *PO₄³⁻*—phosphate

3.3.15 *RSD*—relative standard deviation

3.3.16 *SRM*—standard reference material

3.3.17 *SO_x*—sulfur oxides (SO, SO₂, SO₃, SO₄, S₂O₃, and S₂O₇)

3.3.18 *SO₂*—sulfur dioxide

3.3.19 *SO₃*—sulfur trioxide

3.3.20 *SO₄²⁻*—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 SO₄²⁻ 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 $^{\circ}\text{C}$.

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 $^{\circ}\text{C}$. 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.

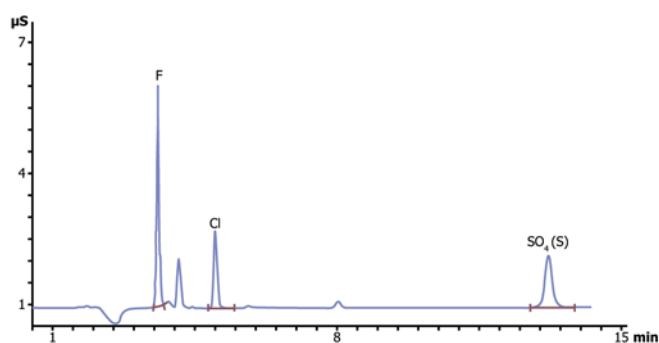


FIG. 1 Anion Peaks of Interest

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.