Designation: D7994 – 25

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 225 mg⁄kg fluorine, 1 mg⁄kg to 281 mg⁄kg chlorine and 1 mg⁄kg to 248 mg⁄kg sulfur. 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* See Section 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
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
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
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

[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 www.astm.org/contact. 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.

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

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

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

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

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

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

3.1.6 *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.

3.1.6.1 *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.

3.1.7 *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 (3.1.2).

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 (3.1.2) 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.