



Designation: D6667 – 21

Standard Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence¹

This standard is issued under the fixed designation D6667; 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 determination of total volatile sulfur in gaseous hydrocarbons and liquefied petroleum (LP) gases. It is applicable to analysis of natural, processed, and final product materials. Precision has been determined for sulfur in gaseous hydrocarbons in the range of 1 mg/kg to 100 mg/kg and for sulfur in LP gases in the range of 1 mg/kg to 196 mg/kg (**Note 1**).

NOTE 1—An estimate of pooled limit of quantification (PLOQ), information regarding sample stability and other general information derived from the interlaboratory studies on precision can be referenced in the ASTM research reports.^{2,3}

1.2 This test method may not detect sulfur compounds that do not vaporize under the conditions of the test.

1.3 This test method is applicable for total volatile sulfur determination in LP gases containing less than 0.35 % (mass/mass) halogen(s).

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. See 3.1 and Sections 6 and 7 for specific warning statements.*

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:⁴

D1070 Test Methods for Relative Density of Gaseous Fuels
D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D2163 Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography

D2421 Practice for Interconversion of Analysis of C₅ and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Mass Basis

D2598 Practice for Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis

D3700 Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

D5287 Practice for Automatic Sampling of Gaseous Fuels

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

F307 Practice for Sampling Pressurized Gas for Gas Analysis

2.2 Gas Processor Association (GPA) Standards:⁵

GPA 2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography

GPA 2174 Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography

3. Summary of Test Method

3.1 A heated sample valve is used to inject gaseous samples. Liquefied petroleum gas (LPG) samples are injected by a

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 D02.03 on Elemental Analysis.

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² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1506. Contact ASTM Customer Service at service@astm.org.

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1784. Contact ASTM Customer Service at service@astm.org.

⁴ 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.

⁵ Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145.

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

sample valve connected to a heated expansion chamber. The gaseous sample then enters a high temperature combustion tube where sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to an excited sulfur dioxide (SO_2^*). Fluorescence emitted from the excited SO_2^* as it returns to a stable state SO_2 is detected by a photomultiplier tube, the resulting signal is a measure of the sulfur contained in the sample. (**Warning**—Exposure to excessive quantities of ultraviolet light is injurious to health. The operator shall avoid exposing their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.)

4. Significance and Use

4.1 The sulfur content of LPG, used for fuel purposes, contributes to SO_x emissions and can lead to corrosion in engine and exhaust systems. Some process catalysts used in petroleum and chemical refining can be poisoned by sulfur bearing materials in the feed stocks. This test method can be used to determine sulfur in process feeds, to measure sulfur in finished products, and can also be used for compliance determinations when acceptable to a regulatory authority.

5. Apparatus

5.1 *Furnace*—An electric furnace held at a temperature ($1075^\circ\text{C} \pm 25^\circ\text{C}$) sufficient to pyrolyze the entire sample and oxidize sulfur to SO_2 .

5.2 *Combustion Tube*—A quartz combustion tube constructed to allow the direct injection of the sample into the

heated oxidation zone of the furnace. The combustion tube shall have side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough (see Fig. 1) to ensure complete combustion of the sample (see 11.3). Fig. 1 depicts a typical combustion tube. Other configurations are acceptable when precision is not degraded.

5.3 *Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas at the specified rates.

5.4 *Drier Tube*—The apparatus shall be equipped with a mechanism for the removal of water vapor formed during sample combustion. This can be accomplished with a membrane drying tube, or a permeation dryer that utilizes a selective capillary action for water removal.

5.5 *UV Fluorescence Detector*—A quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

5.6 *Sample Inlet System*—The system provides a heated gas-sampling valve, or a LP gas-sampling valve, or both, with a heated expansion chamber, connected to the inlet of the oxidation area, Fig. 2. The system is swept by an 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 and repeatable rate of approximately 30 mL/min. Fig. 3 provides an example.

5.7 *Strip Chart Recorder*, equivalent electronic data logger, integrator or, recorder (optional).

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in tests. Unless otherwise indicated, it is intended that all

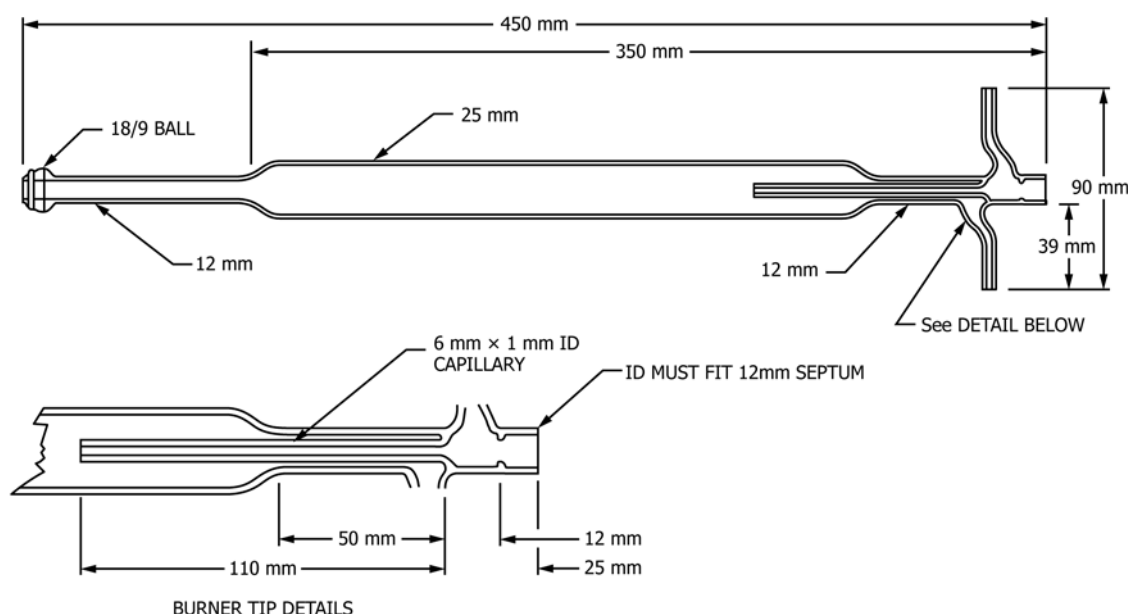


FIG. 1 Example of a Typical Direct Inject Quartz Pyrolysis Tube