



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 (SO₂) 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 SO₂ absorbs the energy from the UV light and is converted to an excited sulfur dioxide (SO₂*). Fluorescence emitted from the excited SO₂* as it returns to a stable state SO₂ 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 °C ± 25 °C) sufficient to pyrolyze the entire sample and oxidize sulfur to SO₂.

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

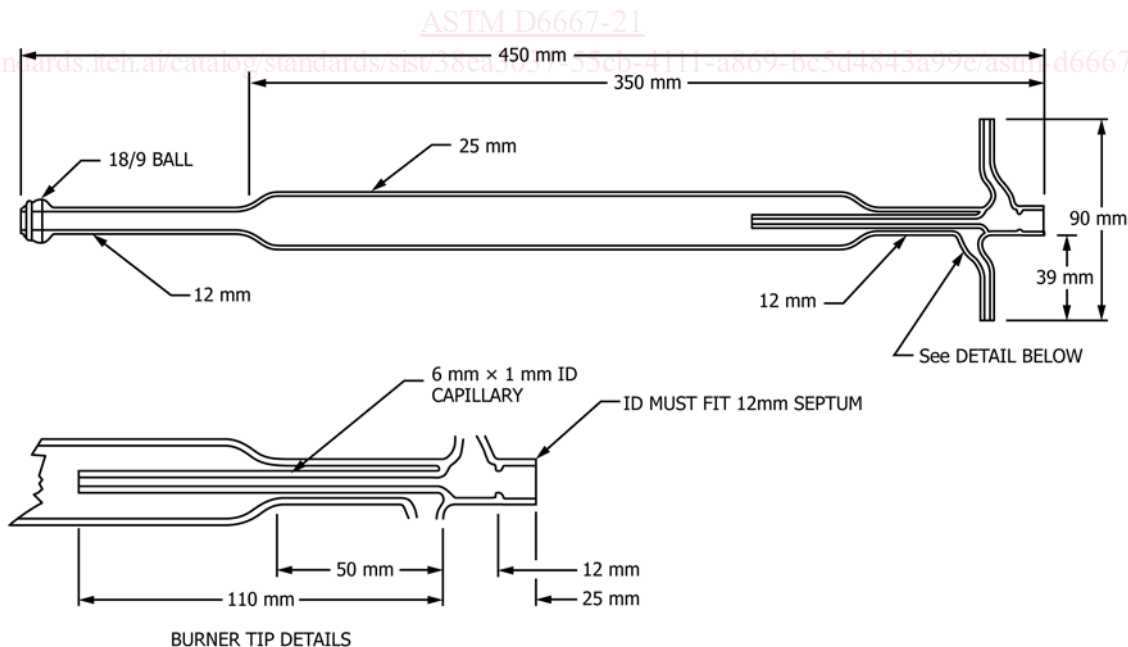


FIG. 1 Example of a Typical Direct Inject Quartz Pyrolysis Tube

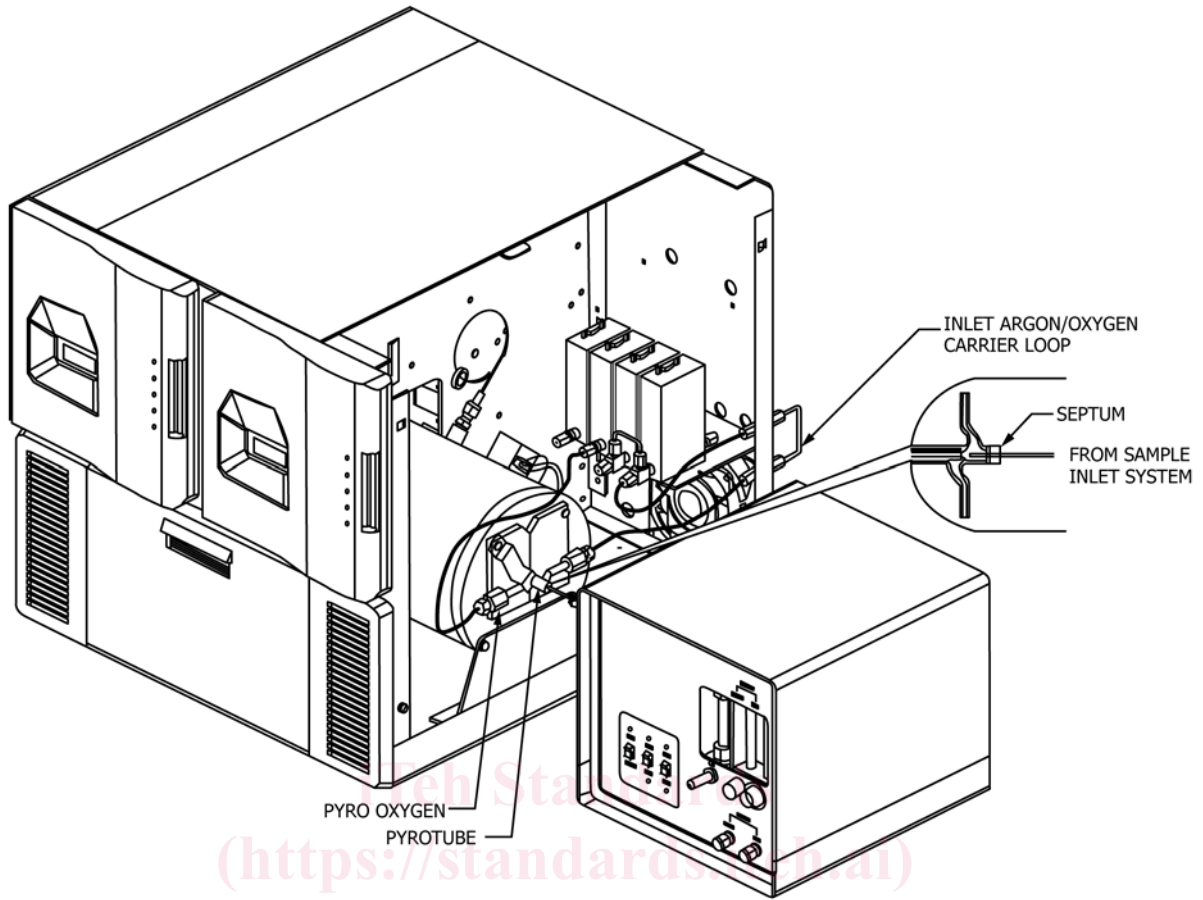


FIG. 2 Example of Orientation of Total Sulfur Analyzer and Gas or Liquid Sampling Valve

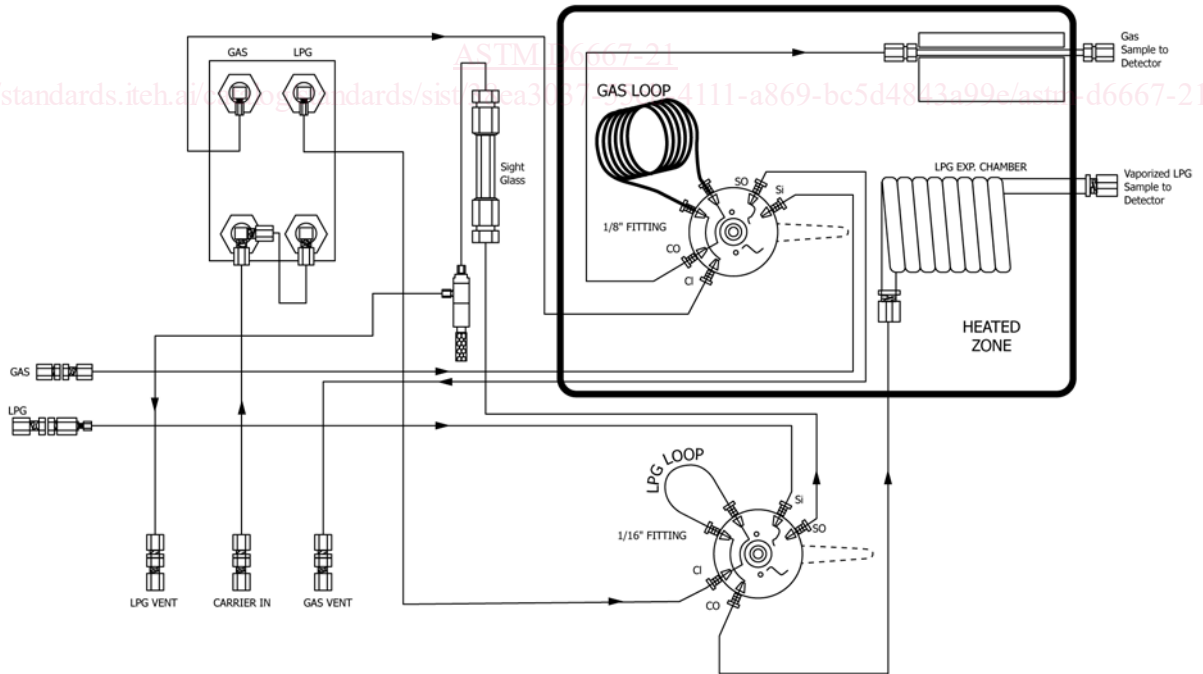


FIG. 3 Sample Inlet System Flow Path

reagents shall conform to the specifications of the Committee

on Analytical Reagents of the American Chemical Society,⁶ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Inert Gas*—Argon or helium only, high purity grade (that is, chromatography or zero grade), 99.998 % min purity, moisture 5 mg/kg max. (**Warning**—Argon or helium may be a compressed gas under high pressure (7.1)).

6.3 *Oxygen*—High purity (that is chromatography or zero grade), 99.75 % min purity, moisture 5 mg/kg max, dried over molecular sieves. (**Warning**—Oxygen vigorously accelerates combustion and may be compressed gas under high pressure (7.1)).

6.4 *Calibration Standards*—Certified calibration standards from commercial sources or calibration gases prepared using certified permeation tube devices are required. Table 1 lists the sulfur source material and diluent matrices used during the inter-laboratory study (Notes 2 and 3).

NOTE 2—Other sulfur sources and diluent materials may be used if precision and accuracy are not degraded.

NOTE 3—Calibration standards are typically re-mixed and re-certified on a regular basis depending upon frequency of use and age. These calibration standards may have a useful life of about 6 months to 12 months.

6.5 *Quality Control (QC) Samples*—preferably are portions of one or more gas or LP gas materials that are stable and representative of the samples of interest.

7. Hazards

7.1 High temperature, flammable hydrocarbons, and gases under high pressures occur in the test method. Use materials that are rated for containing these pressurized hydrocarbons in all sample containers and sample transfer apparatus. Exercise extra care when using flammable materials near the oxidative furnace.

8. Sampling

8.1 Obtain a sample in accordance with Practices F307, D1265, D3700, D5287, or GPA 2174 or GPA 2166. Analyze samples as soon as possible after taking from bulk supplies to prevent loss of sulfur or contamination due to exposure or contact with sample containers.

⁶ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

TABLE 1 Typical Standard Materials

Sulfur Source	Diluent
Dimethyl sulfide	n, butane iso-butane propylene propane

8.2 If the sample is not used immediately, then thoroughly mix it in its container prior to taking a test specimen. The use of segregated or specially treated sample containers can help reduce sample cross-contamination and improve sample stability.

9. Preparation of Apparatus

9.1 Assemble and check the apparatus for leaks according to manufacturer's instructions.

9.2 Typical apparatus adjustments and conditions are listed in Table 2.

9.3 Adjust instrument sensitivity and baseline stability and perform instrument-blanking procedures following manufacturer's guidelines.

10. Calibration and Standardization

10.1 Consult Table 3 and select a calibration range based on the anticipated sulfur concentrations present in samples to be analyzed, preferably using a sulfur compound and a diluent type representative of the samples to be analyzed (Note 4). Table 3 is representative of typical ranges, but narrower ranges than those indicated may be used if desired. However, the method precision using narrower ranges than those indicated has not been determined. Ensure the standards used for calibration bracket the concentrations of the samples being analyzed.

NOTE 4—The number of standards used per curve may vary.

10.2 With the sample valve in the load position, connect the pressurized sample container to the sample valve of the sample inlet system.

10.3 Obtain a quantitative measurement of the injected material by filling the sample loop of the sample valve system for the matrix being analyzed (see Table 2) (Notes 5 and 6).

NOTE 5—Injection of a constant or similar sample size for all materials analyzed in a selected operating range promotes consistent combustion conditions and may simplify result calculations.

NOTE 6—An automatic sample transfer and injection device may be used.

10.3.1 Flush the sample loop with sufficient calibrant to assure that the material to be injected is representative.

10.3.2 For LPG samples, if bubbles are present in the viewable portion of the liquid column, flush the sample loop to introduce a new liquid-full sample portion.

10.4 Start the analyzer and inject the calibration material according to the manufacturer's instructions.

10.5 Calibrate the instrument using one of the following techniques.

TABLE 2 Typical Operating Conditions

Sample inlet system temperature	85 °C ± 20 °C
Sample injection system carrier gas	25 mL/min to 30 mL/min
Furnace temperature	1075 °C ± 25 °C
Furnace oxygen flow meter setting	375 mL/min to 450 mL/min
Inlet oxygen flow meter setting	10 mL/min to 30 mL/min
Inlet carrier flow meter setting	130 mL/min to 160 mL/min
Gas sample size	10 mL to 20 mL
LPG sample size	15 µL

TABLE 3 Typical Sulfur Calibration Ranges and Standard Concentrations

Curve I Sulfur (mg/kg)	Curve II Sulfur (mg/kg)	Curve III Sulfur (mg/kg)
Blank	Blank	Blank
5	10	50
10	50	100
	100	200

TABLE 4 Repeatability (r) and Reproducibility (R)

Concentration S (mg/kg)	Repeatability		Reproducibility	
	Gaseous Hydrocarbons	LPG	Gaseous Hydrocarbons	LPG
1	0.1	0.3	0.3	2.3
5	0.6	0.8	1.6	7.2
25	2.9	2.6	7.8	22
50	5.8	4.2	16	36
100	12	6.8	31	58
150	N/A ^A	9	N/A	77
196	N/A	11	N/A	93

^AN/A—Not applicable to the scope of Gaseous Hydrocarbons.

10.5.1 Multi-point Calibration:

10.5.1.1 When the apparatus features an internal self-calibration routine, analyze the calibration standards and blank three times using the procedures described in 10.2 – 10.4.

10.5.1.2 Calibrate the analyzer according to the manufacturer’s instructions to yield sulfur concentration (see Section 14). This curve is typically linear and system performance shall be checked at least once per day, each day of use. (Note 7).

NOTE 7—Other calibration curve techniques may be used when accuracy and precision are not degraded. The frequency of calibration may be determined by the use of quality control charts or other quality assurance/quality control techniques.

10.5.2 One-point Calibration:

10.5.2.1 Utilize a calibration standard (6.4) with a sulfur content close to that of the samples to be analyzed (±25 % max.).

10.5.2.2 Follow the instrument manufacturer’s instructions to establish an instrument zero (instrument blank) by conducting an analysis run without injection of the calibration standard.

10.5.2.3 Perform measurements of the calibration standard a minimum of three times.

10.5.2.4 Calculate a calibration factor *K*, in counts per nanogram of sulfur (counts/ng S) as described in 12.2.

11. Procedure

11.1 Obtain a test specimen using the procedure described in Section 8. Typically the sulfur concentration in the test specimen is less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration.

11.2 Measure the response for the test specimen using one of the procedures described in 10.2 – 10.4.

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

11.3.1 Reduce the rate of injection or the sample size, or both, of the specimen into the furnace when coke or sooting is observed.

11.4 *Cleaning and Re-calibration*—Clean any coked or sooted parts according to the manufacturer’s instructions. After any cleaning or adjustment, assemble and check the apparatus for leaks. Repeat instrument calibration prior to reanalysis of the test specimen.

11.5 To obtain one result, measure each test specimen three times and calculate the average detector response.

11.6 Density values needed for calculations are to be measured using Test Methods D1070 or equivalent or calculate according to 12.2.3, at the temperature at which the sample was tested (Note 8).

NOTE 8—When sample matrix compositions are known, other techniques may be used to derive sample density, provided accuracy and precision are not degraded.

12. Calculation

12.1 This section describes the calculation procedure for different calibration options and for correction of the sulfur result when the sample is different from the composition of the calibration material. When the sample is injected in the liquid phase, the density of the calibration mixture and the sample are required to calculate the results (12.2 – 12.4). When the sample is injected in the gas phase, the molecular weight of the calibration mixture and the samples are required to calculate the results (12.5 – 12.7).

12.2 To calculate the density of the liquid calibration mixture and/or the sample:

12.2.1 Interconversion to Liquid Volume% from Mass% According to Practice D2421:

$$Liquid\ Volume\ \%_x = 100 \times \frac{(Mass\ \%_x / Relative\ Density_x)}{\sum_{N=1}^{#comp} (Mass\ \%_n / Relative\ Density_n)} \tag{1}$$

where:

- Liquid Volume%* = liquid volume percent of all determined components in the sample of which *x* is one,
- #comp* = the number of determined components in the sample of which *x* is one,
- Relative Density_x* = the value (taken from Practice D2421, Table 2, Column 3) given for each determined component *x* as a liquid,
- Mass%_x* = the weight percent of each determined component taken from GC analysis such as D2163, and
- $\sum_{N=1}^{#comp}$ = the sum of the quotients Mass% divided by the relative density for all determined components.

12.2.2 Interconversion to Liquid Volume% from Mole% According to Practice D2421:

$$\text{Liquid Volume}\%_x = 100 \times \frac{(\text{Mole}\%_x \times \text{Volume Ratio}_x)}{\sum_{N=1}^{\#comp} (\text{Mole}\%_n \times \text{Volume Ratio}_n)} \quad (2)$$

where:

Liquid Volume %_x = liquid volume% of all determined components in the sample of which x is one,

#comp = the number of determined components in the sample of which x is one,

*Volume Ratio*_x = the value (taken from Practice D2421, Table 2, Column 2) given for each determined component x,

Mole%_x = the mole percent of each determined component taken from GC analysis (equivalent to gas volume percent assuming an ideal gas), and

$\sum_{N=1}^{\#comp}$ = the sum of the quotients *Mole*%_n multiplied by the volume ratio for all determined components.

12.2.3 Relative Density Calculation According to Practice D2598:

$$\text{Relative Density}_{mix} = \frac{\sum_{x=1}^{\#comp} (\text{Liquid Volume}\%_x \times \text{Relative Density}_x)}{100} \quad (3)$$

where:

*Relative Density*_{mix} = relative density of the LPG mixture,

#comp = the number of determined components in the sample of which x is one,

*Relative Density*_x = liquid relative density of each component of which x is one,

Liquid Volume %_x = liquid volume% of all determined components in the sample of which x is one, and

$\sum_{N=1}^{\#comp}$ = the sum of the relative density of each component of which x is one.

12.3 For analyzers calibrated using an internal self-calibration and when the sample is injected in liquid phase, calculate the sulfur content in the test specimen as follows:

$$\text{Sulfur (mg / kg)} = \frac{G \times d}{s} \quad (4)$$

where:

d = density of standard mixture, g/mL,

s = density of sample, g/mL, and

G = sulfur found in test specimen, mg/kg.

12.4 For analyzers calibrated using a one-point calibration and when the sample is injected in liquid phase, calculate the calibration factor, (10.5.2.4).

$$K = \frac{A_c}{m_c \times S_{cg}} \quad (5)$$

or

$$K = \frac{A_c}{V_c \times S_{cv}} \quad (6)$$

where:

A_c = integrated detector response for calibration standard, in counts, and

m_c = mass of calibration standard injected, in milligrams, either measured directly or calculated from measured volume injected and density.

$$m_c = V \times D_c \quad (7)$$

where:

D_c = density of calibration standard at measurement temperature, g/mL,

V_c = volume of calibration standard injected, μL,

S_{cg} = sulfur content of calibration standard, mL/kg, and

S_{cv} = sulfur content of calibration standard, mg/L.

12.4.1 Calculate the average of the calibration factor (*K*) and check that the standard deviation is within the tolerance accepted. This calibration factor shall be established every day.

12.4.2 Calculate the sulfur content, *S*, of the sample, in mg/kg, using the following equation:

$$S = \frac{A}{m \times K \times F_g} \quad (8)$$

or

$$S = \frac{A}{V \times K \times F_v} \quad (9)$$

where:

K = calibration factor, in counts per nanogram of sulfur, and

m = mass of test specimen solution injected, in milligrams, either measured directly or calculated from measured volume injected and density.

$$m = V \times D \quad (10)$$

where:

D = density of test specimen solution at measurement temperature, g/mL,

V = volume of the test specimen solution injected, μL,

A = integrated detector response for sample, in counts number,

F_g = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g, and

F_v = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL.

12.5 To calculate the molecular weight of the gas calibration mixture or sample, or both:

12.5.1 Inter-conversion to mole (gas vol) % from mass % according to Practice D2421:

$$\text{Mol}\%_x = 100 \times \frac{(\text{Mass}\%_x / \text{Molecular Mass}_x)}{\sum_{n=1}^{\#comp} (\text{Mass}\%_n / \text{Molecular Mass}_n)} \quad (11)$$

where:

Mol%_x = mole percent of all determined components in the sample of which x is one,

#comp = the number of determined components in the sample of which *x* is one,
Molecular Mass = the value (taken from Practice D2421, Table 2, Column 1) given for each determined component *x*,
*Mass%*_{*x*} = the weight percent of each determined component taken from GC analysis, and
 $\sum_{N=1}^{\#comp}$ = the sum of the quotients *Mass%* divided by the molecular mass for all determined components.

12.5.2 Calculation of the mole mass of the mixture:

$$\begin{aligned} \text{Molecular Weight}_{\text{mixture}} (\text{g/mol}) \\ = \frac{(x_1 \times M_1 + x_2 \times M_2 + \dots x_n \times M_n)}{100} \end{aligned} \quad (12)$$

where:

x = mole% of all components, and
M = the molecular mass of each gas.

12.6 For analyzers calibrated using an internal self-calibration and when the sample is injected in gas phase, calculate the sulfur content in the test specimen as follows:

$$\text{Sulfur (mg/kg)} = \frac{G \times \text{Molecular Mass}_x}{\text{Molecular Mass}_y} \quad (13)$$

where:

*Molecular Mass*_{*x*} = molecular weight of standard mixture, g/mol,
*Molecular Mass*_{*y*} = molecular weight of sample, g/mol, and
G = sulfur found in test specimen, mg/kg.

12.7 For analyzers calibrated using a one-point calibration and when the sample is injected in gas phase, calculate the calibration factor, (10.5.2.4).

$$K = \frac{A_c}{m_c \times S_{cg}} \quad (14)$$

or

$$K = \frac{A_c}{V_c \times S_{cv}} \quad (15)$$

where:

A_c = integrated detector response for calibration, in counts, and
m_c = mass of calibration standard injected, in milligrams, either measured directly or calculated from measured volume injected and molecular mass.

$$m_c = V \times \text{Molecular Mass}_x \quad (16)$$

where:

*Molecular Mass*_{*x*} = molecular weight of calibration standard, g/mol,
V_c = volume of calibration standard injected, μL,
S_{cg} = sulfur content of calibration standard, mL/kg, and
S_{cv} = sulfur content of calibration standard, mg/L.

12.7.1 Calculate the average of the calibration factor (*K*) and check that the standard deviation is within the tolerance accepted. This calibration factor shall be established every day.

12.7.2 Calculate the sulfur content, *S*, of the sample in mg/kg, using the following equation:

$$S = \frac{A}{m \times K \times F_g} \quad (17)$$

or

$$S = \frac{A}{V \times K \times F_v} \quad (18)$$

where:

K = calibration factor, in counts per nanogram of sulfur, and
m = mass of test specimen solution injected, in milligrams, either measured directly or calculated from measured volume injected and molecular mass.

$$m = V \times \text{Molecular Mass}_y \quad (19)$$

where:

*Molecular Mass*_{*y*} = molecular weight of test specimen solution, g/mol,
V = volume of the test specimen solution injected, μL,
A = integrated detector response for sample, in counts number,
F_g = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g, and,
F_v = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL.

NOTE 9—Calculation examples are described in Appendix X4.

13. Report

13.1 For results equal to or greater than 10 mg/kg, report the sulfur results to the nearest mg/kg. For results less than 10 mg/kg, report the sulfur results to the nearest 0.1 mg/kg. State that the results were obtained according to Test Method D6667.

14. Quality Control

14.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 6.5) after each calibration and at least each day of use thereafter (see 11.5).

14.1.1 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.

14.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

15. Precision and Bias

15.1 The following precision and bias data was derived from two separate interlaboratory studies.^{2,3}

15.2 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under