



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 containing sulfur in the range of 1 to 100 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 inter-laboratory study on precision can be referenced in the ASTM research report.²

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.

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 3.1 and Sections 6 and 7 for specific warning statements.*

2. Referenced Documents

2.1 ASTM Standards:³

D1070 Test Methods for Relative Density of Gaseous Fuels

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

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:⁴

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 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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products 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.

³ 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.

⁴ Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145.

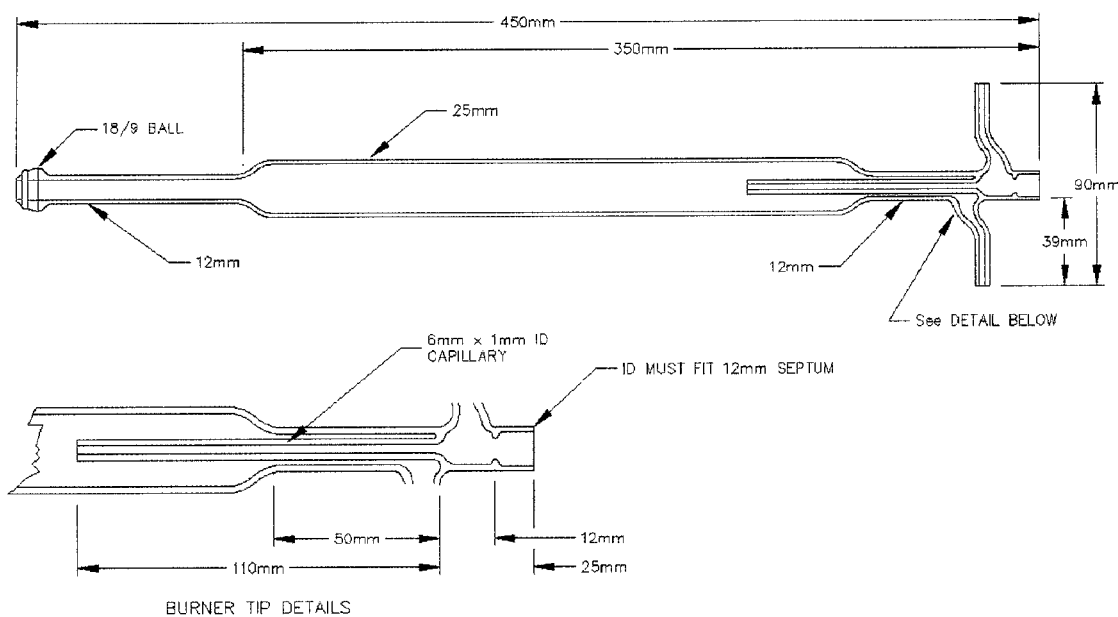


FIG. 1 Example of a Typical Direct Inject Quartz Pyrolysis Tube

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 ($1075 \pm 25^\circ\text{C}$) 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 reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,⁵ 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.

⁵ 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.

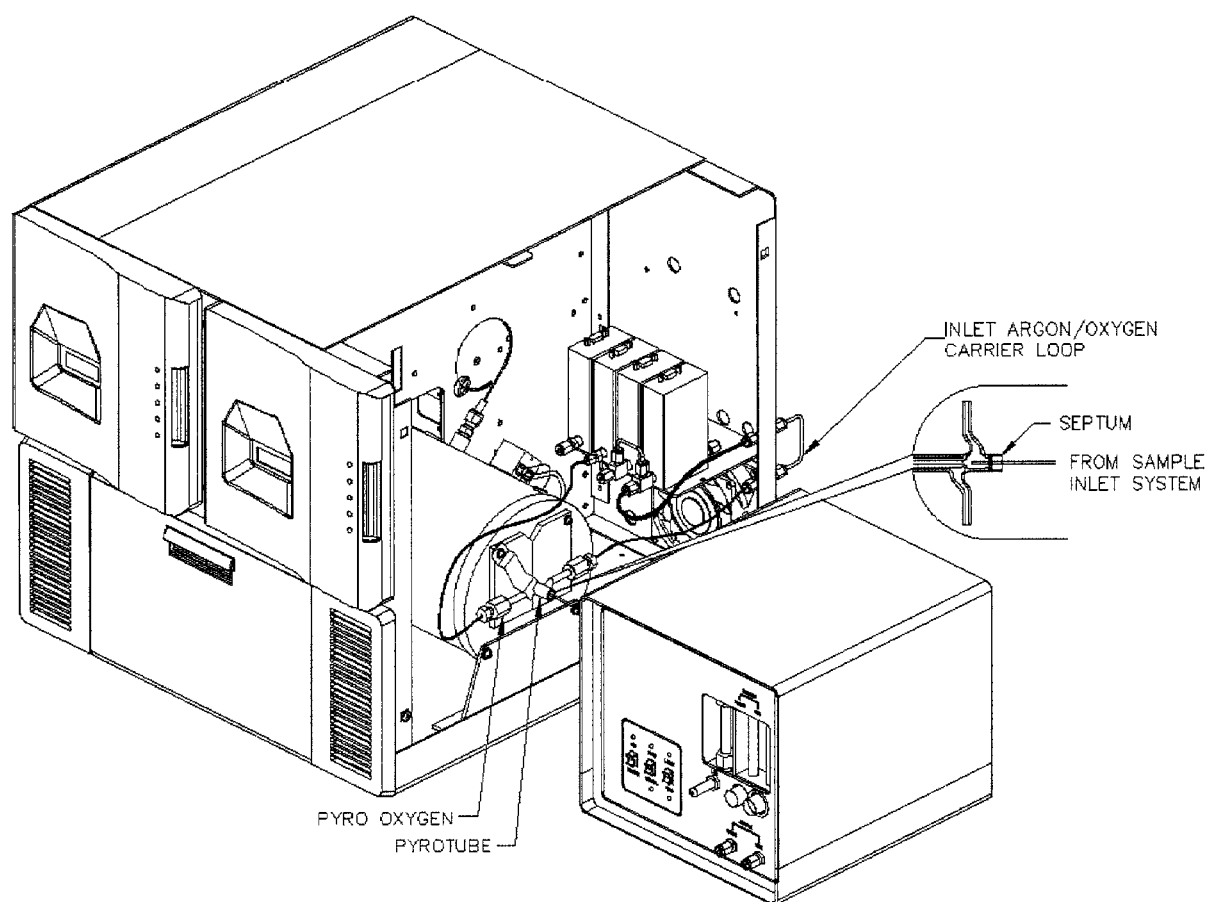


FIG. 2 Example of Orientation of Total Sulfur Analyzer and Gas or Liquid Sampling Valve

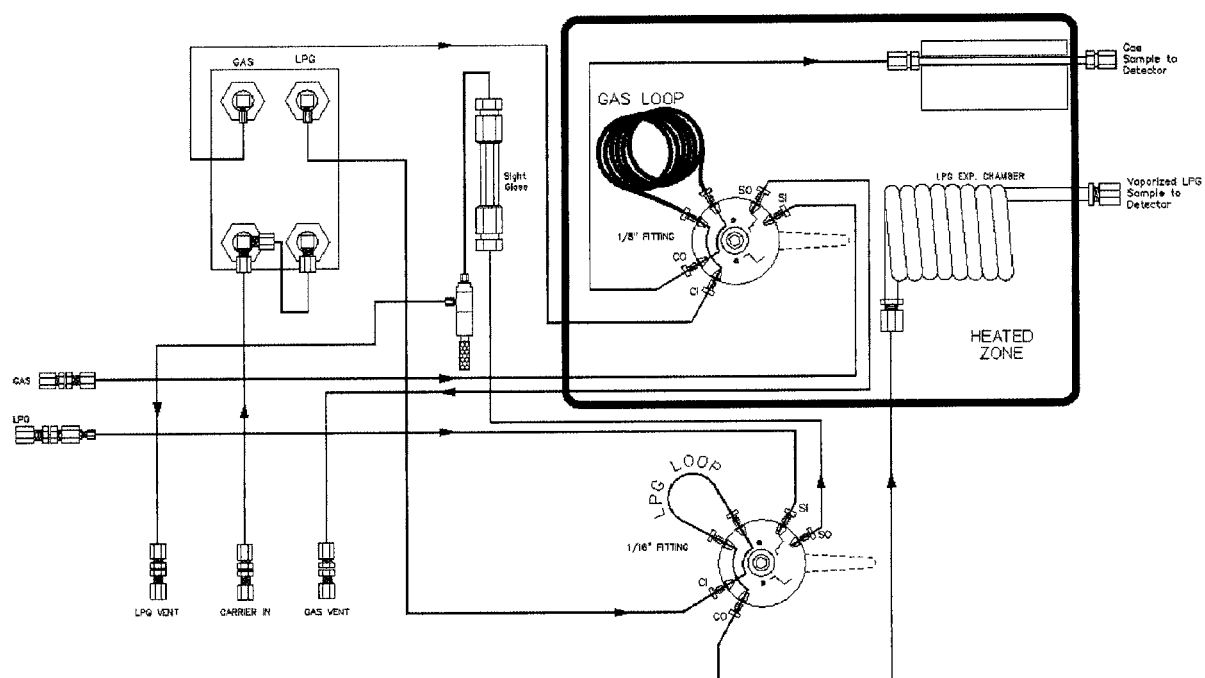


FIG. 3 Sample Inlet System Flow Path

TABLE 1 Typical Standard Materials

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

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 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.

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

TABLE 3 Typical Sulfur Calibration Ranges and Standard Concentrations

Curve I Sulfur mg/kg	Curve II Sulfur mg/kg
Blank	Blank
5.00	10.00
10.00	50.00
	100.00

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.

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:

TABLE 2 Typical Operating Conditions

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

TABLE 4 Repeatability (*r*) and Reproducibility (*R*)

Concentration (mg/kg S)	<i>r</i>	<i>R</i>
1	0.1	0.3
5	0.6	1.6
10	1.2	3.1
25	2.9	7.8
50	5.8	15.6
100	11.5	31.3

10.5.2.1 Utilize a calibration standard (6.4) with a sulfur content close to that of the samples to be analyzed ($\pm 25\%$ 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, 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 For analyzers calibrated using an internal self-calibration, calculate the sulfur content in the test specimen as follows:

$$\text{Sulfur, mg/kg} = \frac{G \times d}{s} \quad (1)$$

where:

d = density of standard mixture, g/mL,

s = density of sample, g/mL, and

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

12.2 For analyzers calibrated using a one point calibration, calculate the calibration factor, (10.5.2.4).

$$K = \frac{A_c}{M_c \times S_{cg}} \quad (2)$$

or

$$K = \frac{A_c}{V_c \times S_{cv}} \quad (3)$$

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.

$$M_c = V \times D_c \quad (4)$$

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.

12.2.1 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.

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

$$S = \frac{A}{M \times K \times F_g} \quad (5)$$

or

$$S = \frac{A}{V \times K \times F_v} \quad (6)$$

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.

$$M = V \times D \quad (7)$$

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.

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 an inter-laboratory study that included samples in n-butane, isobutane, and propane/propylene mix.^{2,6}

15.2 *Repeatability*—The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where X = the average of the two test results.

$$r = 0.1152(X) \quad (8)$$

⁶ The following equipment, as listed in RR:D02-1506, was used to develop this precision statement: (Antek Model 9000 Total Sulfur Analyzer configured with Model 734 Sample Inlet System, manufactured by Antek Instruments, 300 Bammel Westfield Rd, Houston, TX, 77090. To date no other equipment has demonstrated, through ASTM interlaboratory testing, the ability to meet the precision of this test. This is not an endorsement or certification by ASTM.

15.3 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where X = the average of the two test results,

$$R = 0.3130(X) \quad (9)$$

15.4 *Bias*—Bias for this test method was studied during the inter-laboratory study by analysis of certified-gravimetrically prepared calibration standards and sample materials and published in 2000 as a research report.² This report indicated that the results obtained were within the repeatability of the test method.

15.5 Examples of the above precision estimates for selected absolute values of X are set out in **Table 4**.

16. Keywords

16.1 analysis; butane; fluorescence; gases; hydrocarbon; isobutane; LP; LPG; liquefied; petroleum; propane; sulfur; ultraviolet

APPENDIXES

(Nonmandatory Information)

X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See Practice **D6299** and MNL7.⁷

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice **D6299** and MNL7.⁷ Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

NOTE X1.1—In the absence of explicit requirements given in the test method, **X1.4** provides guidance on QC testing frequency.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality. See Practice **D6299** and MNL7.⁷

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice **D6299** and MNL7⁷ for further guidance on QC and control charting techniques.

⁷ MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., Section 3, ASTM International.

X2. OPERATION HINTS AND SAFETY CONSIDERATIONS

X2.1 Prior to sample injection, fully stabilize and ready the apparatus for analysis according to the manufacturers' instructions.

X2.2 Valves in the sample inlet system typically remain in the load position except during sample analysis.

X2.3 Once the sample valve has been filled and allowed to equilibrate, accomplish sample injection by executing a prompt and full rotation to the sample valve to the inject position.

X2.4 Leave the sampling valve in the inject position until analysis has completed (instrument has returned to baseline and integration has finished.)

X2.5 The length of time required for detector response will depend upon the type of pyrotube utilized, carrier gas, sample size or sulfur concentration, or both. From 20 s to 1 min can be typical (see Fig. X2.1).

X2.6 Sample inlet system carrier gas flows can be used to manipulate sample combustion and detection characteristics. However, excessive carrier flow rates (greater than 30 mL/min) can cause incomplete sample combustion (sooting).

X2.7 Allow time for return of signal to baseline between injections.

X2.8 For sample cylinders containing liquefied petroleum gases, use sufficient pressure (typically greater than 200 psig container pressure) to allow the transfer of sample to the sample inlet system without the formation of bubbles in the transfer tubing and sight glass.

X2.9 Use standard gas flow conditions for your analyzer. See Section 9 of the test method.

X2.10 The use of a filtering device prior to sample introduction is strongly recommended. This can greatly extend valve service and prevent transfer line (tubing) blockage.

X2.11 The use of low or iron-free alloys and/or inert treated materials can enhance the analysis for low level sulfur contamination.

X2.12 The use of a strip-chart recorder or a software peak display can aid in the set up and normal operation of the sample inlet system.

X2.13 Quality analytical results are best obtained when calibration materials match the matrix of the samples analyzed. Injection of solvent (room temperature) liquids as calibrants or samples is discouraged and can cause severe coking (sooting) of sample flow path components and yield poor analytical results.

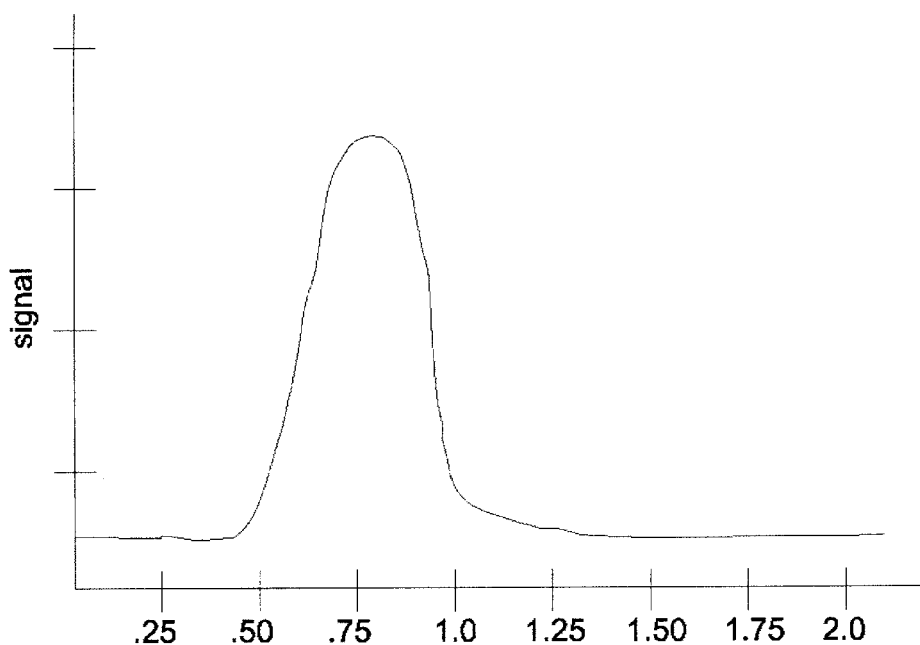


FIG. X2.1 Typical Injection Profile

X3. SAFETY CONSIDERATIONS

X3.1 Routinely inspect transfer lines and fittings used to connect the sample container to the sample inlet system for leaks and stress weakening that can be caused by frequent bending, age, or use.

X3.2 Inspect *Quick-Connect* fittings and other sample transfer and venting apparatus routinely for leaks and proper operation.

X3.3 Vent waste gases from the sample inlet system to an area away from the instrument operating environment and potential ignition sources.

X3.4 Pressures employed to maintain contents of sampling cylinders and to enable sample transfer are typically less than 750 psig. Do not exceed the general overall pressure rating (900 psig) of the sample inlet system or the capacity of the

sample transfer apparatus being employed.

X3.5 Use slow to moderate purge rates when filling the sample loops during the sample-loading phase of the sampling procedure.

X3.6 After sample loop loading, allow pressure within the loop and vent system to equilibrate. Use of a secure gas-bubble monitoring device that vents to an area free of potential ignition sources can provide visual confirmation and aid in ensuring the injection of consistent sample sizes.

X3.7 After sampling is complete, a controlled venting or relief of pressure of the sample transfer line is advised.

X3.8 After analysis, with the sample valves in the load position, an inert gas connected to the sample inlet system can be utilized to purge sample residue.

SUMMARY OF CHANGES

Subcommittee D02 has identified the location of selected changes to this standard since the last issue (D6667–04(2010)) that may impact the use of this standard.

(I) Added Section 13, Report.

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