



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

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1. Scope

1.1 This test method covers the determination of total volatile sulfur in gaseous hydrocarbons, Liquefied Petroleum Gases (LPG) and Liquefied Natural Gas (LNG). It is applicable to analysis of natural gaseous fuels, process intermediates, final product hydrocarbons and generic gaseous fuels containing sulfur in the range of 1 to 200 mg/kg. Samples can also be tested at other total sulfur levels using either pre-concentration methods or sample dilution using a diluent gas. The methodology for pre-concentration and dilution techniques is not covered in this test method. The precision statement does not apply if these techniques are used in conjunction with this test method. The diluent gas, such as UHP nitrogen, zero nitrogen or zero air, shall not have a significant total sulfur concentration.

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

1.3 This test method covers the laboratory determination and the at-line/on-line determination of total volatile sulfur in gaseous fuels, LPG, and LNG.

1.4 This test method is applicable for total volatile sulfur determination in gaseous hydrocarbons, LPG, and LNG containing less than 0.35 mole % halogen(s).

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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 Sections 4.1, 7.3, 7.4, 11.2, and Section 8.

2. Referenced Documents

2.1 ASTM Standards:²

- D1070 Test Methods for Relative Density of Gaseous Fuels
- D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration
- D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
- D3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels
- D3609 Practice for Calibration Techniques Using Permeation Tubes
- D4150 Terminology Relating to Gaseous Fuels
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4784 Specification for LNG Density Calculation Models
- D5287 Practice for Automatic Sampling of Gaseous Fuels
- D5503 Practice for Natural Gas Sample-Handling and Conditioning Systems for Pipeline Instrumentation
- D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
- D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D7166 Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels
- E617 Specification for Laboratory Weights and Precision Mass Standards
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- F307 Practice for Sampling Pressurized Gas for Gas Analysis

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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.

2.2 *ASTM Manuals*:³

ASTM MNL 7

2.3 *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. Terminology

3.1 *Definitions*:

For definitions of *at-line instrument* and *on-line instrument* see Terminology D4150.

3.2 *Acronyms*:

3.2.1 *LNG*—liquefied natural gas

3.2.2 *LPG*—liquefied petroleum gas

3.2.3 *NIST*—National Institute of Standards and Technology

3.2.4 *NMI*—Nederlands Meetinstituut

3.2.5 *NTRM*—NIST traceable reference material

3.2.6 *QA*—quality assurance

3.2.7 *QC*—quality control

3.2.8 *SO₂*—ground state sulfur dioxide

3.2.9 *SO₂**—excited state sulfur dioxide

3.2.10 *SO_x*—sulfur oxides

3.2.11 *SRM*—standard reference material

3.2.12 *UHP*—ultra high purity

3.2.13 *UV*—ultraviolet

3.2.14 *VSL*—Van Swinden Laboratorium

4. Summary of Test Method

4.1 A gaseous sample is injected into the analyzer, either by a sample valve, direct injection at a constant flow rate, or by syringe. A LPG or LNG sample is vaporized in an appropriate expansion chamber and injected into the analyzer by a sample valve or a syringe or a sample valve connected to an expansion chamber. The gaseous sample then enters into a high tempera-

ture combustion tube where the sulfur-containing compounds in the sample are oxidized to SO₂. Water produced during the sample combustion is removed, as required, and the sample combustion gases are then exposed to a source of continuous or pulsed UV light. The SO₂ absorbs the energy from the UV light to form SO₂*. Fluorescence emitted from SO₂* as it returns to 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 UV light is injurious to health. The operator shall avoid exposing any part of their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.

4.2 The design and installation details for the on-line/at-line process analyzer needs to conform to application-specific requirements including, but not limited to, acceptable design practices as described in Practice D7166, hazardous area classifications, safety practices, and regulatory requirements. Fig. 1 illustrates a general flow diagram applicable for an on-line/at-line process analyzer. Sample collection and conditioning, sample introduction and detection system are depicted. Modifications to meet site-specific and/or application specific requirements may be required.

5. Significance and Use

5.1 The sulfur content of gaseous hydrocarbons, LPG, and LNG used for fuel purposes contributes to total 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 trace amounts of sulfur-bearing materials in the feed stocks. This test method can be used to determine the total volatile sulfur content in process feeds, to control the total volatile sulfur content in finished products and, as applicable, to meet regulatory requirements. Practice D1072 has previously been used for the measurement of total sulfur in gaseous fuels.

6. Apparatus

6.1 *Furnace*—An electric furnace held at a constant temperature in accordance with the analyzer manufacturer's recommendations (nominally 1000 to 1125°C) sufficient to oxidize the entire sample to carbon dioxide and water and oxidize the sulfur in the sample to SO₂.

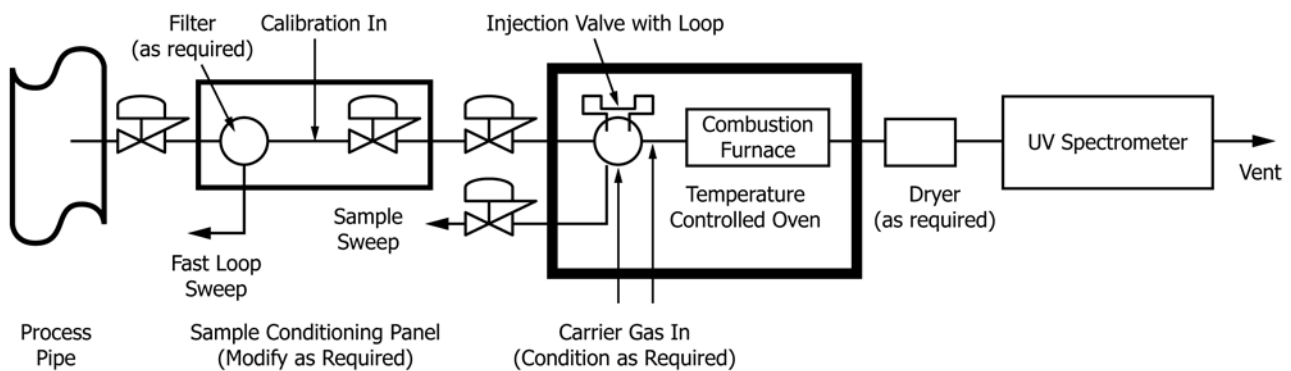


FIG. 1 General Flow Diagram—On-Line Analyzer

³ MNL 7A Manual on Presentation of Data and Control Chart Analysis, Seventh Edition, ASTM International, West Conshohocken, 2002.

⁴ Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, <http://www.gasprocessors.com>.

6.2 *Combustion Tube*—A quartz tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace by syringe or sample valve using either oxygen or air for the oxidation of the sample. Other tube materials suitable for use at the furnace operating conditions can be used so long as performance is not degraded. The oxidation section shall be large enough to ensure complete conversion of the sample to carbon dioxide and water and oxidize the sulfur in the sample to SO₂.

6.3 *Flow Control*—The apparatus shall be equipped with flow controllers capable of maintaining a constant volumetric flow rate of the carrier gases necessary for performing the total sulfur analysis.

6.4 *Drier*—The oxidation of the sample produces reaction products that include water vapor which, if in excess, must be removed prior to measurement by the detector. This can be accomplished with a membrane drying tube, or a permeation dryer that utilizes a selective capillary action for water removal.

6.5 *UV Fluorescence Detector*—A quantitative detector capable of measuring light emitted from the fluorescence of SO₂ generated by continuous or pulsed UV light.

NOTE 1—For an on-line analyzer, detection of uncombusted hydrocarbons in the UV Fluorescence Detector can be used to ensure complete conversion of the hydrocarbons to carbon dioxide and water and to minimize the potential for coke formation in the analytical system.

6.6 *Sample Inlet System*—Either of the following two types of sample inlet systems can be used.

6.6.1 *Sample Valve System*—The system provides a gas-sampling valve, or an LPG or LNG gas or liquid sampling valve with an expansion chamber, or both, with access to the inlet of the oxidation area. The system is swept by the carrier gas at the manufacturer's recommended flow rate.

6.6.2 *Sample Injection*—The sample inlet system for gaseous samples shall be capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. For a laboratory analysis, a syringe drive mechanism that discharges the sample from the syringe at a rate of approximately 1 mL/s is required. For at line and on-line analysis a constant volumetric flow rate delivery device is used.

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

7. Reagents

7.1 *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, 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.

7.2 *Inert Gas*—Argon or helium only, high purity grade (that is, chromatography or zero grade), 99.998 % minimum purity, moisture 5 mg/kg maximum, as required.

7.3 *Oxygen*—High purity, that is, chromatography or zero grade, 99.75 % minimum purity, moisture 5 mg/kg maximum, dried over molecular sieves, as required. **Warning**—Oxygen vigorously accelerates combustion.

7.4 *Air*—Use dry, sulfur free air, that is, chromatography grade or zero grade, -40°C dew point or lower, as required. Nitrogen/oxygen or helium/oxygen bottled gas blends containing no more than 30 % oxygen can also be used, as required. **Warning**—Never use pure oxygen as a substitute for air on analyzers designed to operate using air as a carrier gas.

7.5 *Calibration Standards*—Certified liquid or gas phase calibration standards from commercial sources or calibration gases prepared using certified permeation tube devices are required (see **Notes 2 and 3**). Accurate volatile sulfur containing standards are required for quantization of the volatile total sulfur content. Permeation tubes and compressed gas standards should be stable, of high purity, and of the highest available accuracy. Use of standards consisting of a sulfur compound and matrix similar to samples to be analyzed is recommended.

NOTE 2—Other sulfur sources and diluent materials can be used if precision and accuracy are not degraded. The use of solvent based calibration standards that are liquid at ambient temperatures and pressures is not recommended.

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

NOTE 4—Enhanced oxygen containing combustion gasses, such as 30 % Oxygen balance Helium, Nitrogen, and/or Argon, can be used if precision and accuracy are not degraded.

NOTE 5—**Warning:** Compressed gas cylinders as well as sulfur compounds contained in permeation tubes may be flammable and harmful or fatal if ingested or inhaled. Permeation tubes and compressed gas standards should only be handled in well ventilated locations away from sparks and flames. Improper handling of compressed gas cylinders containing air, nitrogen, helium, or other gasses can result in unsafe conditions that can cause severe damage to equipment and significant harm, including death, to people. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion.

7.5.1 *Permeation Devices*—Standards containing volatile sulfur compounds can be made from permeation tubes, one for each selected sulfur species, gravimetrically calibrated and certified at a convenient operating temperature. With constant temperature, calibration gases covering a wide range of concentration can be generated by varying and accurately measuring the flow rate of diluent gas passing over the permeation tubes. These calibration gases can be used to calibrate the analyzer system.

7.5.1.1 *Permeation System Temperature Control*—Permeation devices are maintained at the calibration temperature within $\pm 0.1^{\circ}\text{C}$.

7.5.1.2 *Permeation System Flow Control*—The permeation flow system measures diluent gas flow over the permeation tubes within an accuracy of $\pm 2\%$.

7.5.1.3 Permeation tubes are inspected and weighed to the nearest 0.01 mg on at least a monthly basis using a balance calibrated against Specification E617 Class 1 weights or equivalent. Analyte concentration is calculated by weight loss and dilution gas flow rate as per Practice D3609. Permeation tubes are replaced when the liquid contents are reduced to less than 10 % of the initial mass or when the permeation surface is

unusually discolored or otherwise compromised. Permeation tube disposal shall be in accordance with all applicable regulations.

7.5.2 Compressed Gas Standards—As an alternative to permeation tubes, blended gaseous standards containing volatile sulfur-containing compounds in nitrogen, helium methane or other base gas may be used. Care must be exercised when using compressed gas standards since they can introduce errors in measurement due to lack of uniformity in their manufacture or instability in their storage and use. The protocol for compressed gas standards contained in the appendix can be used to ensure uniformity in compressed gas standard manufacture and provide for traceability to a NIST or VSL (formerly NMI) reference material.

7.5.2.1 Compressed gas standard regulators must be appropriate for the delivery of sulfur containing gases and attached fittings must be passivated or inert to sulfur containing compounds in the compressed gas standards.

7.5.2.2 The following sulfur compounds, either singularly or together, are suggested for inclusion in a compressed gas standard:

Hydrogen sulfide (H₂S)
 Carbonyl sulfide (COS)
 Methyl mercaptan (CH₃SH)

7.5.2.3 The following substances can also be included, either singularly or together, in a compressed gas standard:

Ethyl mercaptan (CH₃CH₂SH)
 1-propanethiol (CH₃CH₂CH₂SH)
 2-propanethiol (CH₃CHSHCH₃)
 Dimethyl sulfide (CH₃SCH₃)

7.5.2.4 Other sulfur containing compounds can be used so long as the stability of the compressed gas standard is not compromised.

NOTE 6—Warning: The following compounds are not recommended for inclusion in mixed component standards due to their potential for promoting degradation:

Dimethyl disulfide (CH₃SSCH₃)
 Other disulfides

7.6 For calibration procedures utilizing one calibration standard, the sulfur concentration of the calibration standard should exceed the maximum sulfur content of the samples being analyzed. For laboratory analysis, the sulfur concentration in the test specimen shall be less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration. For at-line or on-line analysis, the concentration of the calibration standard is selected in accordance with manufacturer's recommendations for the full-scale concentration range of the test samples to be analyzed. This value is typically between 80 and 100 % of the full scale concentration.

7.7 QC samples preferably contain one or more gas, LPG, or LNG materials with a known volatile total sulfur content that are stable and representative of the samples of interest. These QC samples are to be used to check the validity of the testing process as described in Section 14.

8. Hazards

8.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this test method.

8.2 High temperature and flammable hydrocarbons under high pressures are employed in the test method. Exercise extra care when using flammable materials near the oxidative pyrolysis furnace.

9. Sampling

9.1 Laboratory Analyzers:

9.1.1 Obtain a sample in accordance with Practice [D1265](#), [D4177](#), [D5287](#), [D5503](#), [F307](#), GPA 2174 or GPA 2166. Samples should be analyzed as soon as possible after taking from bulk supplies to prevent loss of sulfur or contamination due to exposure or contact with sample container.

9.1.2 If the sample is not used immediately, thoroughly mix it in its container prior to taking a test specimen. The use of segregated or specially treated sample containers that minimize sulfur compound loss can be required (see [Note 7](#)).

NOTE 7—Floating-piston cylinders can be used.

9.2 At-Line and On-Line Analyzers:

9.2.1 Sampling considerations for at-line and on-line analyzers can be found in Practice [D7166](#).

10. Preparation of Apparatus

10.1 Place the analyzer into service in accordance with the manufacturer's instructions.

10.2 Adjust apparatus operational parameter settings, as required to meet the conditions suggested or specified by the manufacturer for the sample introduction method employed. Typical instrument parameters for laboratory instruments can be found in [Table 1](#). Typical instrument parameters for on-line analyzers can be found in [Table 2](#).

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

11. Calibration and Standardization

11.1 Based on the anticipated sulfur concentration, identify the number of, and sulfur concentration of, calibration standards required for all calibration curves in accordance with the manufacturer's recommendations. The number of standards used per curve can vary from the manufacturer's recommendations, if equivalent results are obtained.

TABLE 1 Typical Operating Conditions Laboratory Instruments

Syringe Drive (Direct Inject) Drive Rate	1 mL/s
Sample Injection System carrier gas	25-30 mL/min
Furnace Temperature	1000-1125°C ± 25°C
Furnace Oxygen Flowmeter Setting	375-450 mL/min
Inlet Oxygen Flowmeter Setting	10-30 mL/min
Inlet Carrier Flowmeter Setting	130-160 mL/min

TABLE 2 Typical Operating Conditions At-Line and On-Line Instruments

Furnace Temperature	1000-1125 °C
Furnace Oxygen, as required	375-425 mL/min
Inlet Oxygen Setting, as required	5-15 mL/min
Inlet Carrier Setting, as required	5-15 mL/min
Inlet Air Carrier Setting, as required	250-350 mL/min
Dryer sweep gas, plant air grade, (optional)	9 L/min
Dryer sweep gas, zero grade (optional)	325-375 mL/min

11.2 For laboratory analyzers flush the sample valve or syringe several times with the calibrant prior to analysis. For at-line and on-line analyzers flush the appropriate sample conditioning components with the calibrant before beginning the analysis. If bubbles are present in the liquid column of LPG samples, flush the sample loop to introduce a new sample and ensure that there is enough back-pressure on the sample loop to prevent bubble formation. **Warning**—Over-pressurization of an injection valve can cause it to fail. For compressed liquid samples this can result in excessive amounts of hydrocarbon being introduced into the furnace or the atmosphere due to the volume change when a compressed liquid vaporizes. Massive introduction of hydrocarbons into the furnace can result in soot formation and contamination of the detector. A release of compressed liquids into the atmosphere represents a fire and/or explosion hazard as well as an exposure hazard.

11.3 Use sample loop sizes that are consistent with the manufacturer's recommendations. Typical sample loop sizes for gaseous samples range from 0.5 to 20 mL. Typical sample loop sizes for compressed liquid samples range from 1 to 100 μ L. Based upon the desired measurement levels, other sample sizes can be used. Larger sample sizes may require adjustment of some of the analyzer's operational parameter settings. Consultation with the manufacturer is recommended.

11.3.1 For direct syringe injection of gaseous materials into a laboratory analyzer, carefully fill, seal and insert the syringe into the inlet of the combustion tube and the syringe drive. Allow time for sample residues to be burned from the needle (needle burn-off). Once a stable baseline has reestablished, inject the contents of the syringe into the combustion tube and promptly start the analysis. Remove the syringe once the apparatus has returned to a stable baseline.

11.3.2 *Discussion*—Needle burn-off allows the laboratory analyzer baseline to stabilize before the sample is injected. Typically, a small amount of sample is contained in the needle after it is filled with sample. During needle burn-off the small residual amount of sample in the needle is burned out of the needle. Sample injection begins after a stable baseline is obtained.

11.4 Calibrate the instrument using one of the following techniques.

11.4.1 If the apparatus features an internal self-calibration or validation routine, measure the calibration standards and blank three times. For an at-line or on-line analyzer allow the analyzer reading to stabilize for at least ten minutes. After stabilization obtain three analytical results. To obtain one analytical result average the values obtained during the steady state operation of the test sample over one boxcar time interval.

11.4.1.1 *Discussion*—Calibrate the analyzer as per manufacturer's instructions (see **Note 8**). The calibration curve shall be linear within the manufacturer's published specifications. For laboratory analyzers, the system performance shall be checked at least once per day the analyzer is in use or in accordance with the manufacturer's recommendations or established QC protocols, or, in the absence of any established protocols, **Appendix X1** can be used. For at-line and on-line analyzers the calibration shall be checked at least once per quarter or in accordance with the manufacturer's recommendations, established QC protocols, or in the absence of any established protocols **Appendix X1** can be used. Validation routines require an operator to manually determine whether to accept or reject the reading of a particular calibration standard as a permanent adjustment to the analyzer's calibration.

11.4.1.2 *Discussion*—A boxcar average is the sum of an array of N adjacent data values divided by N . As a new data value is determined the oldest value in the array is dropped, the new data value is added and the boxcar average is recalculated. The boxcar time interval is based on the data collection rate, in units of data values collected per unit time. The boxcar time interval is calculated by dividing N by the data collection rate.

NOTE 8—Other calibration curve techniques can be used when accuracy and precision are not degraded. The frequency of calibration can be determined by the use of QC charts or other QA/QC techniques, operational considerations or regulatory requirements, or combinations thereof.

11.4.1.3 If analyzer calibration is performed using a calibration curve different from the original analyzer calibration consult the manufacturer's recalibration procedures.

11.4.2 *One-Point Calibration:*

11.4.2.1 Utilize a calibration standard in accordance with **Section 7**.

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

11.4.2.3 Perform measurements of the calibration standard a minimum of 3 times for laboratory analyzers. For at-line or on-line analyzers allow the analyzer to stabilize on the calibration standard for at least 10 minutes. After stabilization obtain three analytical results. To obtain one analytical result average the values obtained during the steady state operation of the test sample over one boxcar time interval.

11.4.2.4 Calculate a calibration factor K as described in **section 13.1**. Input this value into the analyzer as required. If the analyzer software is capable of performing the calibration factor calculation, record the calculated value, the units employed, and the date in a calibration log.

12. Procedure

12.1 *Laboratory Instruments:*

12.1.1 Obtain a test specimen using the procedure described in **Section 9**. If the sulfur concentration is outside the calibration standard sulfur concentration limits a recalibration of the analyzer is required.

12.1.2 Measure the response for the test specimen following **Section 11** as required.

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

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

12.1.3.2 *Cleaning and Recalibration*—Clean any coked or sooted parts per manufacturer’s instructions. After any cleaning or adjustment, assemble and leak check the apparatus. Repeat instrument calibration prior to reanalysis of the test specimen.

12.1.4 To obtain one result, measure each test specimen three times and calculate the average detector responses with the necessary precision to support the reported analytical accuracy.

12.1.5 Density values needed for calculations are to be measured using Test Methods **D1070**, **D3588**, **D4784**, or equivalent, at the temperature at which the sample was tested. When sample compositions are known, other techniques may be used to derive sample density.

12.2 *At-Line and On-Line Instruments:*

12.2.1 Select an appropriate sample injection size in accordance with manufacturer’s recommendations. Sample injection volumes of 1 to 5 μL are typical. The injection volume must be the same as used in the calibration procedure. Other injection sizes can be used if precision is not degraded.

12.2.2 The concentration of the calibration standard is selected in accordance with section **7.6**.

12.2.2.1 Prepare the instrument for calibration and load the calibration standard into the injection valve or auto-injector mechanism according to the manufacturer’s instructions.

12.2.2.2 Inject the calibration standard into the analyzer according to the manufacturer’s instructions.

12.2.2.3 After stabilization of at least 10 minutes analyze the calibration standard at least three times. To obtain one analytical result average the values obtained during the steady state operation of the test sample over one boxcar time interval.

12.2.2.4 Calculate the response factor for the sulfur concentration present.

12.2.3 *Cleaning and Recalibration*—Clean any coked or sooted parts per the manufacturer’s instructions. After any cleaning or adjustment, assemble and leak check the apparatus. Repeat the instrument calibration prior to reanalyzing the test specimens.

12.2.4 To obtain one analytical result average the values obtained during the steady state operation of the test sample over one boxcar time interval.

12.2.5 Density values needed for calculations are to be measured using Test Methods **D1070**, **D3588**, **D4784** or equivalent, at the temperature at which the sample was tested. When sample compositions are known, other techniques may be used to derive sample density.

13. Calculation

13.1 Analyzers that are capable of automatic calibration and result determination are acceptable if precision is not degraded. Software included with the instrumentation may perform the

required calculations. The user should be satisfied that the software is working properly and is accurately performing the calculations.

13.2 *Laboratory Instruments:*

13.2.1 For analyzers calibrated using self-calibration routine with blank correction, calculate the sulfur content in the test specimen in mg/kg as follows:

$$\text{Sulfur, } S, \text{ mg/kg} = \frac{G \cdot d}{\rho} \quad (1)$$

where:

d = density of standard mixture, g/mL,

ρ = density of sample, g/mL, and

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

13.2.2 For analyzers calibrated using a one point calibration:

13.2.2.1 Calculate the calibration factor, section **11.4.2.4**:

$$K = \frac{Ac}{Mc \times Scg} \quad (2)$$

or

$$K = \frac{Ac}{Vc \times Scv} \quad (3)$$

where:

K = calibration factor, in counts per ng of sulfur,

Ac = integrated detector response for calibration standard, in counts,

Mc = mass of calibration standard injected, in mg, either measured directly or calculated from measured volume injected and density: $Mc = Vc \times Dc$

Dc = density of calibration standard at measurement temperature, in gm/mL,

Vc = volume of calibration standard injected, in μL ,

Scg = sulfur content of calibration standard, in mg/kg, and

Scv = sulfur content of calibration standard, in mg/L.

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 at least once per day the analyzer is in use.

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

$$S = \frac{A}{M \times K \times Fg} \quad (4)$$

or

$$S = \frac{A}{V \times K \times Fv} \quad (5)$$

where:

K = calibration factor, in counts per ng of sulfur,

M = mass of test specimen solution injected, in mg, either measured directly or calculated from measured volume injected and density, $M = V \times D$

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

V = volume of the test specimen solution injected, in 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, in gm/gm, and

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

13.3 At-Line and On-Line Instruments:

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

$$S_M = RF_{SM} \times A_s \quad (6)$$

where:

A_s = detector response, counts,

RF_{SM} = response factor for sulfur, (mg/kg)/count, and

S_M = concentration of sulfur in the sample, mg/kg.

13.3.1.1 When reporting S in mg/kg but injecting the sample into the analyzer on a volume basis, a density correction is required, using the following equation, if the density of the sample is different from the density of the calibration standard:

$$S_{density\ corrected} = S_{uncorrected} * (\text{Density of Standard/Density of Sample}) \quad (7)$$

where:

$S_{density\ corrected}$ = density corrected concentration of sulfur in the sample, mg/kg, and

$S_{uncorrected}$ = reported concentration of sulfur in the sample prior to density correction, mg/kg.

13.3.2 Calculate the sulfur content, S , of the sample, in $\mu\text{L/L}$, using the following equation:

$$S_V = RF_{SV} \times A_s \quad (8)$$

where:

A_s = detector response, counts,

RF_{SV} = response factor for sulfur, ($\mu\text{L/L}$)/count, and

S_V = concentration of sulfur in the sample, $\mu\text{L/L}$.

14. Report

14.1 Report concentrations ≤ 200 mg/kg and ≥ 10 mg/kg to one or two significant figures consistent with the observed variability in the data.

14.2 Report concentrations below 10 mg/kg to two or three significant figures consistent with the observed variability in the data.

15. Quality Control

15.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample after each calibration. For

laboratory analyzers the QC sample should be analyzed at least each day of use thereafter. For at-line or on-line analyzers the QC sample should be analyzed at least weekly or in accordance with the manufacturer's recommendations.

15.1.1 When QC/QA protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

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

16. Precision

NOTE 9—Final statements of precision and bias for this method will be provided as a result of inter-laboratory testing to be conducted within 5 years of the publication date of this method.

16.1 The estimate of the repeatability standard deviation for the Ultraviolet Fluorescence total sulfur on-line analysis is set out in **Table 3**.

16.2 *Discussion*—The LPG results include both liquid and gas phase samples. A distinct analyzer result is either a liquid phase sample or a gas phase sample. The repeatability standard deviation, s_r , is defined by Equation (7) in Practice **E691**. The number of laboratories, p in Equation (7) in Practice **E691**, is taken to be the number of distinct analyzers used to generate the repeatability data. The cell standard deviation, s , was calculated using Equation (2) in Practice **E691**.

17. Keywords

17.1 analysis; at-line; butane; fluorescence; gases; hydrocarbon; laboratory; liquefied; LNG; LPG; on-line; petroleum; propane; sulfur; ultraviolet

TABLE 3 Estimated Repeatability Standard Deviation for On-Line Ultraviolet Fluorescence Total Sulfur Analyzer

Material	Nominal Sulfur Concentration mg/kg	Number of Analyzers	Number of Results per Analyzer	s_r
LPG (Propane or Butane)	5	5	6	0.038
	10	6	5	0.091
	25	3	10	0.068
	50	4	8	0.18
Methane	20	7	5	0.024
	40	4	8	0.036
	200	3	10	0.15

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 method needs to determine the average value and control limits of the QC sample. See Practice [D6299](#) and ASTM MNL 7³.

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.⁵ See Practice [D6299](#) and ASTM MNL 7³. Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

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 ASTM MNL 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 ASTM MNL 7 for further guidance on QC and Control Charting techniques.

⁵ In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

X2. PROTOCOL FOR COMPRESSED GAS CALIBRATION STANDARDS

X2.1 This protocol was developed to assist compressed gas sulfur standard users. It can provide calibration gas traceability to a NIST, VSL (formerly NMI), or similar standard reference material. This protocol requires the determination of the speciated and total sulfur using a NIST or VSL (formerly NMI) hydrogen sulfide SRM or a NTRM as the primary reference. This procedure will insure uniformity in measurement of sulfur content. This protocol was developed by compressed gas vendors and should be submitted to vendors when calibration gas is ordered.

X2.2 A standard is analyzed according to Test Method [D5504](#) or [D6228](#). The GC temperature program is designed to elute all sulfur species up to and including di-*n*-propyl sulfide. A minimum of three consecutive data points are collected with the necessary precision to support the reported analytical accuracy. The necessary precision is achieved with a percent relative standard deviation (% RSD) calculated from a minimum of three consecutive data points, less than or equal to 1 %. An average area for each component and the total sulfur area is calculated using all consecutive analyses.

X2.3 A hydrogen sulfide standard reference material is analyzed under identical conditions used in the analysis of the standard. Acceptable hydrogen sulfide reference standards include NIST or VSL (formerly NMI) traceable SRMs or NTRMs. A minimum three consecutive data points are collected with the necessary precision to support the reported analytical accuracy. An average area of the hydrogen sulfide is calculated using all consecutive analysis:

X2.4 The values for individual sulfur components and the total sulfur amount are calculated according to the formula:

$$\text{Sulfur calculated concentration} = \quad (X2.1)$$

$$\frac{\text{Average area as calculated in X2.2}}{\text{Average area as calculated in X2.3}} \times \text{H}_2\text{S Standard Concentration}$$


X2.5 The analysis for total reduced sulfur and individual components calculated as hydrogen sulfide ([X2.2 – X2.4](#)) is performed at least twice, with a minimum 48 hour incubation period between the two analyses. The difference in percent between the two values, for total reduced sulfur and individual components calculated as hydrogen sulfide must be less than 2 %. This is necessary to assure product stability. The reported total and individual sulfur concentrations are the value obtained in the second analysis.

X2.6 The values for total reduced sulfur and individual components are reported on the certificate of analysis as follows:

X2.6.1 The values for the total reduced sulfur and individual components from both the first and second analysis in [X2.5](#), along with the date of analyses.

X2.6.2 The cylinder number, concentration and NIST or VSL (formerly NMI) SRM/NTRM batch ID from the reference standard used in the standard analysis.

X2.6.3 The total sulfur reported must include all components including any unknowns. The total of the unknowns shall also be reported in ppm.

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