



Designation: D6228 – 98 (Reapproved 2003)

Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection¹

This standard is issued under the fixed designation D6228; 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 individual volatile sulfur-containing compounds in gaseous fuels by gas chromatography (GC) with flame photometric detection (FPD). The detection range for sulfur compounds is from 20 to 20 000 picograms (pg) of sulfur. This is equivalent to 0.02 to 20 mg/m³ or 0.014 to 14 ppmv of sulfur based upon the analysis of a 1-mL sample.

1.2 This test method describes a GC-FPD method using a specific capillary GC column. Other GC-FPD methods, with differences in GC column and equipment setup and operation, may be used as alternative methods for sulfur compound analysis with different range and precision, provided that appropriate separation of the sulfur compounds of interest can be achieved.

1.3 This test method does not intend to identify all individual sulfur species. Total sulfur content of samples can be estimated from the total of the individual compounds determined. Unknown compounds are calculated as monosulfur-containing compounds.

1.4 The values stated in SI units are to be regarded as standard. The values stated in inch-pound units are for information only.

1.5 *This standard does not purport to address all 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.*

2. Referenced Documents

2.1 ASTM Standards:²

¹ This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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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.

- 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
 - D1945 Test Method for Analysis of Natural Gas by Gas Chromatography
 - D3609 Practice for Calibration Techniques Using Permeation Tubes
 - D4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry
 - D4626 Practice for Calculation of Gas Chromatographic Response Factors
 - D5287 Practice for Automatic Sampling of Gaseous Fuels
 - D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
 - E840 Practice for Using Flame Photometric Detectors in Gas Chromatography
- 2.2 EPA Standards:
- EPA-15 Determination of Hydrogen Sulfide, Carbonyl Sulfide and Carbon Disulfide Emissions from Stationary Sources, 40 CFR, Chapter 1, Part 60, Appendix A
 - EPA-16 Semicontinuous Determination of Sulfur Emissions from Stationary Sources, 40 CFR, Chapter 1, Part 60, Appendix A

3. Terminology

3.1 Abbreviations:

3.1.1 A common abbreviation of a hydrocarbon compound is to designate the number of carbon atoms in the compound. A prefix is used to indicate the carbon chain form, while a subscript suffix denotes the number of carbon atoms, for example, normal decane = n-C₁₀, isotetradecane = i-C₁₄.

3.1.2 Sulfur compounds commonly are referred to by their initials, chemical or formula, for example, methyl mercaptan = MeSH, dimethyl sulfide = DMS, carbonyl sulfide = COS, di-*t*-butyl trisulfide = DtB-TS, and tetrahydrothiophene = THT or thiophane.

4. Summary of Test Method

4.1 Sulfur analysis ideally is performed on-site to eliminate potential sample deterioration during storage. The reactive nature of sulfur components may pose problems both in sampling and analysis. Samples should be collected and stored in containers that are nonreactive to sulfur compounds, such as Tedlar³ bags. Sample containers should be filled and purged at least three times to ensure representative sampling. Laboratory equipment also must be inert, well conditioned, and passivated with a gas containing the sulfur compounds of interest to ensure reliable results. Frequent calibration and daily verification of calibration curve using stable standards are required. Samples should be analyzed within 24 h of collection to minimize sample deterioration. If the stability of analyzed sulfur components is proved experimentally, the time between collection and analysis may be lengthened.

4.2 A 1-mL sample of the fuel gas is injected into a gas chromatograph where it is passed through a 60-m, 0.53-mm inside diameter (ID), thick film, methyl silicone liquid phase, open tubular partitioning column, or a similar column capable of separating sulfur components.

4.3 *Flame Photometric Detectors*—When combusted in a hydrogen-rich flame, sulfur compounds emit light energy characteristic to all sulfur species. The light is detected by a photomultiplier tube (PMT). The PMT response is proportional to the concentration or the amount of sulfur. All sulfur compounds including sulfur odorants can be detected by this technique.

4.4 *Other Detectors*—This test method is written primarily for the flame photometric detector. The same gas chromatographic (GC) method can be used with other sulfur-specific detectors provided they have sufficient sensitivity and selectivity to all sulfur compounds of interest in the required measurement range.

4.5 *Other GC Test Methods*—The GC test methods using sulfur chemiluminescence, reductive rateometric, and electrochemical detectors are available or under development.

5. Significance and Use

5.1 Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds, which are odorous, corrosive to equipment, and can inhibit or destroy catalysts used in gas processing. Their accurate measurement is essential to gas processing, operation, and utilization.

5.2 Small amounts, typically, 1 to 4 ppmv of sulfur odorant compounds, are added to natural gas and liquefied petroleum (LP) gases for safety purposes. Some odorant compounds can be reactive and may be oxidized, forming more stable compounds having lower odor thresholds. These gaseous fuels are analyzed for sulfur odorants to help ensure appropriate odorant levels for safety.

5.3 This test method offers a technique to determine individual sulfur species in gaseous fuel and the total sulfur content by calculation. Gas chromatography is used commonly and extensively to determine other components in gaseous fuels

including fixed gas and organic components (see Test Method D1945). This test method dictates the use of a specific GC technique with one of the more common detectors for measurement.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph that has the following performance characteristics can be used.

6.1.1 *Sample Inlet System*—Gas samples are introduced to the gas chromatograph using an automated or manually operated stainless steel gas sampling valve enclosed in a heated valve oven, which must be capable of operating continuously at a temperature of 50°C above the temperature at which the gas was sampled. TFE-fluorocarbon tubing made of fluorinated ethylene propylene (FEP), 316 stainless steel tubing, or other tubing made of nonpermeable, nonsorbing, and nonreactive materials, as short as possible and heat traced at the same temperature, should be used for transferring the sample from a sample container to the gas-sampling valve. A 1.0-mL sampling loop made of nonreactive materials, such as deactivated fused silica or 316 stainless steel is used to avoid possible decomposition of reactive sulfur species. Other size fixed-volume sampling loops may be used for different concentration ranges. A 1- to 2-m section of deactivated precolumn attached to the front of the analytical column is recommended. The precolumn is connected directly to the gas sampling valve for on-column injection. The inlet system must be well conditioned and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds, such as *tert*-butyl mercaptan.

6.1.2 *Digital Pressure Transmitter*—A calibrated stainless steel pressure/vacuum transducer with a digital readout may be equipped to allow sampling at different pressures to generate calibration curves.

6.1.3 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range from 30 to 200°C, in programmed rate settings of 0.1 to 30°C/min. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.05 min (3 s).

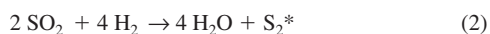
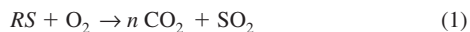
6.1.4 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical to optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. The gas flow rate is measured by any appropriate means and the required gas flow indicated by the use of a pressure gage. Mass flow controllers, capable of maintaining gas flow constant to $\pm 1\%$ at the required flow rates also can be used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa (10 psi) greater than the regulated gas at the instrument to compensate for the system back pressure. In general, a supply pressure of 552 kPa (80 psig) will be satisfactory.

6.1.5 *Detector*—A flame photometric detector calibrated in the sulfur-specific mode is used for this test method. Other detectors as mentioned in 4.4 will not be covered in this test method. This detector may be obtained from various manufacturers; however, there are variations in design. The pulsed flame photometric detector (PFPD) is one of the new FPD

³ Registered trademark. Available from DuPont de Nemours, E. I., & Co., Inc., Barley Mill Plaza, Bldg. 10, Wilmington, DE 19880-0010.

designs. The pressure and flow rate of the hydrogen and air gases used in the detector may be different. The selection of which detector to use should be based on its performance for the intended application. The detector should be set according to the manufacturer's specifications and tuned to the best performance of sensitivity and selectivity as needed.

6.1.5.1 When sulfur-containing compounds are burned in a hydrogen-rich flame, they quantitatively produce a S_2^* species in an excited state (Eq 1 and Eq 2). The light emitted from this species is detected by a photomultiplier tube (PMT) (Eq 3). A 393-nm bandpass optical filter is normally used to enhance the selectivity of detection. The selectivity normally is about 10^4 to 1 by mass of sulfur to mass of carbon.



where:

$h\nu$ = emitted light energy.

6.1.5.2 The intensity of light is not linear with the sulfur concentration but is proportional approximately to the square of the sulfur concentration. The relationship between the FPD response (R_D) and the sulfur concentration (S) is given by Eq 4 and Eq 5. The n -factor usually is less than 2.0.

$$R_D \propto [S]^n \quad (4)$$

$$\text{Log } [S] \propto 1/n \text{ Log } R \quad (5)$$

where:

n = exponential factor (1.7 to 2.0).

6.1.5.3 The linear calibration curve can be made using a log-log plot. Some instruments use an electronic linearizer to produce a signal with direct linear response. The dynamic range of this linear relationship is about 1×10^3 .

6.2 *Column*—A 60- by 0.53-m ID fused silica open tubular column containing a 5- μm film thickness of bonded methyl silicone liquid phase is used. The column shall provide adequate retention and resolution characteristics under the experimental conditions described in 7.3. Other columns, which can provide equivalent separation, can be used as well.

6.3 Data Acquisition:

6.3.1 *Recorder*—A 0- to 1-mV range recording potentiometer, or equivalent, with a full-scale response time of 2 s or less can be used.

6.3.2 *Integrator*—The use of an electronic integrating device or computer is recommended. The device and software must have the following capabilities:

6.3.2.1 Graphic presentation of the chromatogram.

6.3.2.2 Digital display of chromatographic peak areas.

6.3.2.3 Identification of peaks by retention time or relative retention time, or both.

7. Reagents and Materials

7.1 *Sulfur Permeation Tube Standards*—Gaseous standards generated from individual or a combination of certified permeation tubes at a constant temperature and flow rate shall be used for all calibrations. Each permeation tube will be weighed to the nearest 0.1 mg on a periodic basis after the permeation rate has equilibrated and remains constant. The standard concen-

tration is calculated by mass loss and dilution gas flow rate. Impurities permeated from each tube must be detected, measured, and accounted for in the mass loss, if they are present above a level of 0.1 % of the permeated sulfur species. See Practice D3609.

7.2 *Compressed Cylinder Gas Standards*—As an alternative, blended gaseous sulfur standards may be used if a means to ensure accuracy and stability of the mixture is available. These mixtures can be a source of error if their stability during storage cannot be guaranteed. (**Warning**—Sulfur compounds may be flammable and harmful or fatal if ingested or inhaled.)

7.3 *Carrier Gas*—Helium or nitrogen of high purity (99.999 % min purity). (**Warning**—Helium and nitrogen are compressed gases under high pressure.) Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate (see 6.1.4).

7.4 *Hydrogen*—Hydrogen of high purity (99.999 % min purity) is used as fuel for the flame photometric detector (FPD). (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

7.5 *Air*—High-purity (99.999 % min purity) compressed air is used as the oxidant for the flame photometric detector (FPD). (**Warning**—Compressed air is a gas under high pressure that supports combustion.)

8. Preparation of Apparatus and Calibration

8.1 *Chromatograph*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

8.2 *FPD*—Place the detector in service in accordance with the manufacturer's instructions. Hydrogen and air flows are critical and must be adjusted properly in accordance with the instruction furnished by the manufacturer. With the FPD flame ignited, monitor the signal to verify compliance with the signal noise and drift specified by the manufacturer. The FPD flame should be maintained to give consistent and optimum sensitivity for the detection range.

8.2.1 *Sample Injection*—A sample loop of 1.0 mL of suitable size for sample injection may be used for performance check. A linear calibration curve may be determined by using standards of varying concentrations or by injecting a single calibration standard at different pressures from 13.3 to 133 kPa (100 to 1000 torr). If the latter method is used, the concentration of sulfur component for calibration is calculated using the following equation.

$$S_n = (P_s/P_o) \times C_n \quad (6)$$

TABLE 1 Gas Chromatographic Operating Parameters

Gas Sample Loop:	1.0 mL at 120°C
Injection Type:	On-column
Carrier Gas:	He at 11.0 mL/min or at a flow rate allowing CH_4 elutes at approximately 2.1 min
Column Oven:	30°C hold 1.5 min, 15°C/min to 200°C, hold 8 min, or as needed
Detector:	H_2 /air ratio specified by manufacturer, 250°C, 20 mL/min, helium make-up gas