Standard Test Method for
Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection[1]

1. Scope

1.1 This test method covers the determination of individual volatile sulfur-containing compounds in gaseous fuels by gas chromatography (GC) with a flame photometric detector (FPD) or a pulsed flame photometric detector (PFPD). 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/m^3 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.~~

1.2 This test method describes a GC method using capillary column chromatography with either an FPD or PFPD.

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]

~~D1072~~ ~~Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration~~

~~D1265~~

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~~

D4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry

~~D4626~~

D4626 Practice for Calculation of Gas Chromatographic Response Factors

~~D5287~~

D5287 Practice for Automatic Sampling of Gaseous Fuels

~~D5504~~

D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

~~E840~~

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-C_{10}, isotetradecane = i-C_{14}.

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 tetrahydothiophene = THT or thiophane.

4. Summary of Test Method

4.1 *Sample Collection*—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 Tedlar[3] 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. See Practices D1265 and D5287.

4.2 *Sample Introduction*—A 1-mL ~~sample~~aliquot of the ~~fuel gas~~ sample 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~~capillary column capable of separating sulfur components.

4.3 *Flame Photometric Detectors (FPD and PFPD)*—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~~Most 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~~FPD and PFPD. Similar 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.~~ —The GC test using sulfur chemiluminescence (see Test Method D5504), reductive rateometric (see Test Method D4468), 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), passivated 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

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

passivated 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 entire inlet system must be well conditioned and evaluated frequently for compatiability with trace quantities of reactive sulfur compounds, such as *tert-~~butyl mercaptan.~~ —butyl mercaptan.*

6.1.1.1 *On-Column Injections*—For the FPD, 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.

6.1.1.2 *Split Injections*—For the PFPD, the column is connected to a heated flash vaporizing injector designed to provide a linear sample split injection (for example, 50:1). The associated carrier gas flow controls shall be of sufficient precision to provide reproducible column flows and split ratios in order to maintain analytical integrity.

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 gauge. Mass flow controllers, capable of maintaining gas flow constant to ± 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 (FPD) or pulsed flame photometric dectector (PFPD) 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 (see Practice E840). 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 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 *Principle of Operation*—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.~~ * 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).

6.1.5.2 *Flame Photometric Detector (FPD)*—in the FPD a 393-nm bandpass optical filter is normally used to enhance the selectivity of detection. The FPD selectivity normally is about 10^6 to 1 by mass of sulfur to mass of carbon.

6.1.5.3 *Pulsed Flame Photometric Detector (PFPD)*—In the PFPD the propagation of the flame produces gas phase reactions which result in light emissions with specific luminescent spectra and lifetimes. The differences in specific emission lifetimes combined with a broad-band optical filter and the kinetics of the propagating flame, allow both time and wavelength information to be used to improve the PFPD's selectivity and sensitivity. The PFPD selectivity relative to hydrocarbon is 10^6 or better, depending on gate settings and other factors. Using gated electronics permit the acquisition of two, simultaneous, mutually selective chromatograms (for example, sulfur and hydrocarbon).

$$RS + O_2 \rightarrow n\,CO_2 + SO_2 \tag{1}$$

$$2\,SO_2 + 4\,H_2 \rightarrow 4\,H_2O + S_2{}^* \tag{2}$$

$$S_2{}^* \rightarrow S_2 + h\nu \tag{3}$$

where:
$h\nu$ = emitted light energy.

6.1.5.~~2~~4 *Detector Response*—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~~detector 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.

$$R_D \; \alpha \; [S]^n \tag{4}$$

$$\text{Log}\,[S] \; \alpha \; 1/n \; \text{Log}\,R \tag{5}$$

where:
n = exponential factor (1.7 to 2.0).

6.1.5.~~3~~5 *Linearity*—The linear calibration curve can be made using a log-log plot. Some instruments ~~use an~~provide optional electronic ~~linearizer~~algorithims to produce a signal with direct linear response. The dynamic range of this linear relationship is about 1×10^3 .

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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~~ —The capillary column shall be chosen to be compatible with the detector and detector gas flow rate requirements.

6.2.1 *FPD Column*—A 60-m by 0.53-m ID fused silica open tubular column containing a 5-μm film thickness of bonded methyl silicone liquid phase is used.

6.2.2 *PFPD Column*—A fused silica capillary column with 0.32-mm ID or smaller and sufficient length (for example, 30-m or 60-m) and phase to separate the sulfur species is used. Helium carrier gas flow rate of 2.0 mL/minute or slower is used.

6.2.3 The column shall provide adequate retention and resolution characteristics under the experimental conditions described in 7.3. One example of a capillary column and operating conditions used with the FPD is shown in Table 1. Two examples of columns and operating conditions used with the PFPD are shown in Table 2. 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 concentration 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, hydrogen, or nitrogen of high purity (99.999 % min purity). (**Warning**—Helium, hydrogen, 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).

7.3.1 The FPD and PFPD have different requirements for the carrier gas flow rate. For example, with a PFPD the carrier gas flow rate should not exceed 2.0 mL/minute (He) to prevent cooling the flame. Consult the detector manufacturer for guidance.

7.3.2 When using hydrogen as the carrier gas, adjustments to the detector hydrogen flow rate may be necessary; consult the detector manufacturer for guidance.

7.3.3 Nitrogen should not be used as the carrier gas with the PFPD.

7.4 *Hydrogen*—Hydrogen of high purity (99.999 % min purity) is used as fuel for ~~the flame photometric detector (FPD).~~both detectors. (**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)~~both detectors. (**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 ~~.~~ (FPD) and Table 2 (PFPD).

TABLE 1 Gas~~Chromatographic~~-FPD Operating Parameters

Gas Sample Loop:	1.0 mL at 120°C
Injection Type:	On-column
Column:	60-m × 0.53–mm ID × 5μ film, fused silica open tublar column with bonded methyl silicone liquid phase
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:~~	~~H₂/air ratio specified by manufacturer, 250°C, 20 mL/min, helium makeup gas~~
Detector:	Flame Photometric Detector (FPD) H_2/air ratio specified by manufacturer, 250°C, 20 mL/min, helium makeup gas

TABLE 2 GC-PFPD Operating Parameters

Parameter	Column 1	Column 2
Gas Sample Loop:	1.0 mL at 150°C	1.0 mL at 150°C
Injection Type:	Split; split ratio 50:1	Split: split ratio 50:1
Column:	Agilent GS-GasPro PLOT column, 30–m× 0.32 mm ID	Agilent J&W Select Low-Sulfur column, 60–m×0.32-mm ID
Carrier Gas:	Helium at 2 mL/minute	Helium at 2 mL/minute
Oven Program	60 °C for 2 minutes, 20 °C/minute to 260 °C, hold for 5 minutes, total run time 17 minutes	50 °C for 5 minutes, 5 °C/minute to 200 °C, hold 0.1 minute, total run time 35.1 minutes
Detector:	Pulsed Flame Photometric Detector (PFPD) H_2/air ratio adjusted for sulfur analysis, 250 °C, 2-mm combustor, BG-12 optical filter, R1924 PMT	Pulsed Flame Photometric Detector (PFPD) H_2/air ratio adjusted for sulfur analysis, 200 °C, 2-mm combustor, BG-12 optical filter, R1924

8.2 ~~FPD~~Detector—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.

8.2.1 *Flame Photometric Detector (FPD)*—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~~8.2.2 *Pulsed Flame Phototmetric Detector (PFPD)*—Ensure that the sulfur emission, pulse frequency, electronic gating, and calculated dectectivity meet the manufacturer's specifications.

8.3 *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.

$$S_n = (P_s /P_o) \times C_n \tag{6}$$

where:
S_n = calculated concentration of the sulfur compound in the sampled gas on mole or volume basis,
P_s = sampling pressure as absolute,
P_o = laboratory ambient pressure as absolute, and
C_n = concentration of the sulfur compound in the calibration standard.

~~8.2.2~~

8.4 *Detector Response Calibration*—Analyze the calibration gas and obtain the chromatograms and peak areas. Determine the linear range of detector response using sample injection techniques illustrated in ~~8.2.1~~8.3. A log/log plot or a linearized plot may be constructed with the linear correlation factor calculated. Calculate the relative sulfur response factor (see Practice D4626) of each sulfur compound at ambient pressure by:

$$F_n = (S_n /A_n) \times L_n \tag{7}$$

where:
F_n = sulfur response factor of compound,
S_n = concentration of the sulfur compound in the sampled gas on mole or volume basis,
A_n = peak area of the sulfur compound measured, and
L_n = moles of sulfur in the compound.
Example:
Assume 1.0 ppmv of dimethyl sulfide (DMS) injected with a 1.0-mL sample loop.
1-ppmv DMS = 62.13/22.41 = 2.772 mg/m^3 (from ~~Table 2~~Table 3). 1.0 mL of 1-ppmv DMS = 2772-pg DMS = 2772 × 51.61 % = 1430-pg S. If the peak area of DMS response is 15 850 counts, the response factor F_n (S/peak) is 1430/15 850 × 1 = 9.02 × 10^2 (pg sulfur/unit area). The response factor (F_n) of 1.0-mL injection = 1.0/15 850 × 1 = 63 × 10^{-6} (ppmv DMS/unit area).

All ~~mono-sulfur~~sulfur compounds of the same class should have approximately the same response factor. The response factor (F_n) of each sulfur compound should be within 10 % of F_n for dimethyl sulfide. The day-to-day variation of F_n should not be greater than 5 %. The detector should be maintained and flow rates readjusted to optimize the detector performance if F_n exceeds this limitation. ~~Table 2~~ Table 3 lists common sulfur compounds found in gaseous fuel and their properties for calculation.

~~8.2.3~~

8.5 *Interferences*—There are two types of interferences that must be minimized for reliable quantitation.

~~8.2.3.1~~

8.5.1 *Hydrocarbon Quenching*—Hydrocarbons produce a quenching effect on sulfur detection as a result of the formation of a large amount of carbon dioxide in the flame suppressing the formation of SO_2. The quenching can be minimized by optimizing the chromatographic conditions to separate the sulfur components of interest from large hydrocarbons present in the sample matrix. A flame ionization detector (FID) or thermal conductivity detector (TCD) can be used to identify the presence of interfering hydrocarbons. If using a PFPD, the second channel can be configured to monitor for the presence of hydrocarbons, as shown in Fig. 2 and Fig. 3. Sample dilution or injection of a smaller volume of sample may be used to alleviate the quenching effect if sulfur

TABLE 2 3 Physical Properties of Common Sulfur Compounds

| Compound	Relative Molecular Mass (Molecular Weight)	%-5 Sulfur	Boiling Point, °C	Vapor Pressure kPa at 37.78°C
H₂S	34.08	94.09	−60.3	. . .
COS	60.08	53.37	−50.2	. . .
MeSH	48.11	66.65	6.2	214
EtSH	62.13	51.61	35.0	112
DMS	62.13	51.61	37.3	103
CS₂	76.14	84.23	46.5	. . .
iPrSH	76.16	42.10	52.6	61
TBM	90.19	35.55	64.0	41
nPrSH	76.16	42.10	67.0	35
MES	76.16	42.10	67.0	36
THT	88.17	36.37	120	4.6
di-EtS	90.19	35.55	92.0	. . .
DMDS	94.20	68.08	109.7	. . .
di-Et-DS	122.25	52.46	154.0	. . .
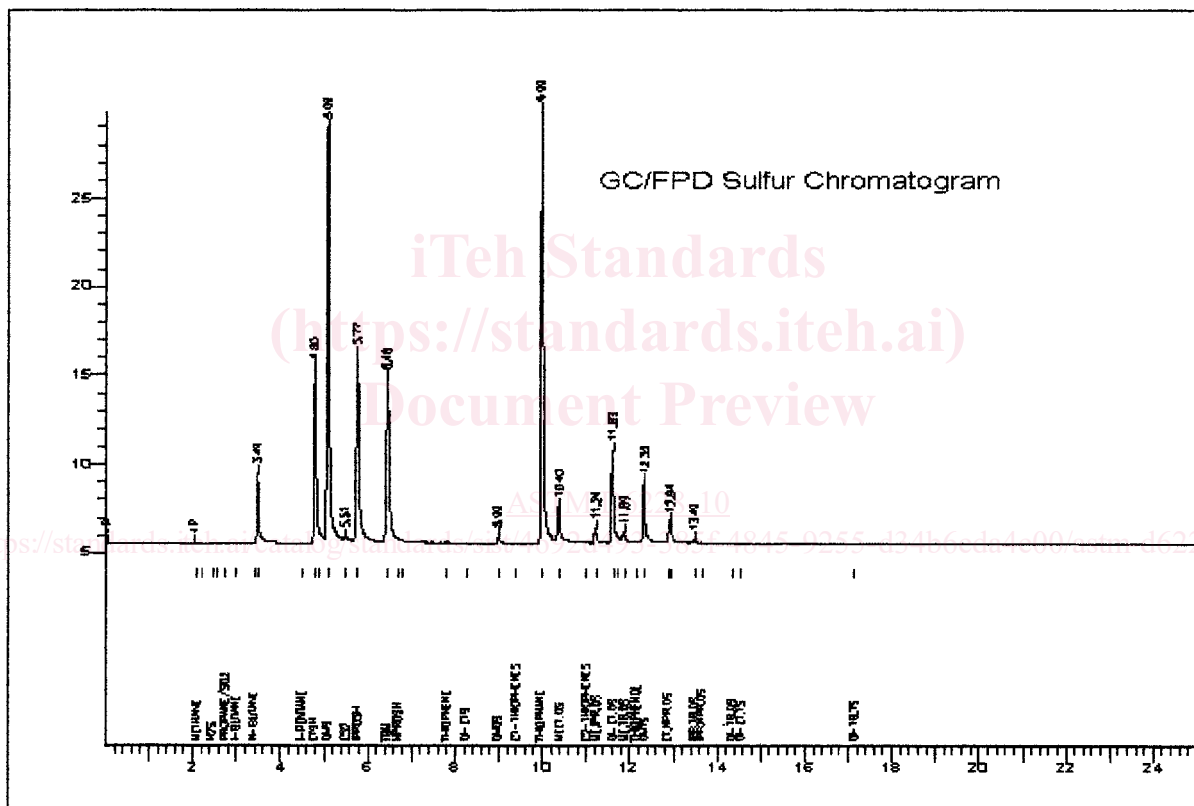
FIG. 1 Chromatogram of a Composite Odorized Natural Gas Acquired Using an FPD and Conditions Shown in Table 1

concentration is significantly higher than the method detection limit.

8.2.3.2 8.5.1.1 *Self-Quenching*—In other cases, the reverse of the reaction shown in Eq 3 produces self-quenching. This arises when the emitted light is reabsorbed before reaching the photomultiplier. It occurs when a very large concentration of any sulfur species is present in the flame above and beyond the linearity range of the detector. It often generates an M-shape peak with the inverted signal at a component's peak apex, which mistakenly can be identified as two close eluting compounds. Sample dilution or smaller sample injection may eliminate this effect.

8.3 8.6 *Chromatography*—A chromatogram of typical natural gas analysis is illustrated in —Chromatograms of typical natural gas analyses are illustrated in Fig. 1(relative response versus retention time). The retention times of selected sulfur components are listed for reference (Table 3, Fig. 2, and Fig. 3 (relative response versus retention time). The retention times of selected sulfur components in Fig. 1 are listed for reference in Table 4). They. Retention times may vary considerably depending on the chromatographic conditions. The eluting sequence and spread of sulfur peaks and their peak shape should remain the same. Adequate resolution defined as baseline separation of adjacent peaks shall be achieved. The baseline separation of two peaks is defined as the FPDdetector signal of the first compound returns to a point at least below 5 % of the smallest peak of two.