



Designation: D5504 – 12

Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence¹

This standard is issued under the fixed designation D5504; 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 is primarily for the determination of speciated volatile sulfur-containing compounds in high methane content gaseous fuels such as natural gas. It has been successfully applied to other types of gaseous samples including air, digester, landfill, and refinery fuel gas. The detection range for sulfur compounds, reported as picograms sulfur, is ten (10) to one million (1 000 000). This is equivalent to 0.01 to 1 000 mg/m³, based upon the analysis of a 1 cc sample.

1.2 The range of this test method may be extended to higher concentration by dilution or by selection of a smaller sample loop.

NOTE 1— Dilution will reduce method precision.

1.3 This test method does not purport to identify all sulfur species in a sample. Only compounds that are eluted through the selected column under the chromatographic conditions chosen are determined. The detector response to sulfur is equimolar for all sulfur compounds within the scope (1.1) of this test method. Thus, unidentified compounds are determined with equal precision to that of identified substances. Total sulfur content is determined from the total of individually quantified components.

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

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.*

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. Referenced Documents

2.1 ASTM Standards:²

- D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration
- 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
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 The analysis of gaseous sulfur compounds is challenging due to the reactivity of these substances. They are difficult to sample and analyze. Ideally, analysis is performed on-site to eliminate sample deterioration as a factor in analysis. Sampling must be performed using non-reactive containers, such as Silcosteel³ lined vessels, Tedlar⁴ bags with polypropylene fittings or the equivalent. Tedlar⁴ bag samples require protection from light and heat. Laboratory equipment must be inert or passivated to ensure reliable results.

3.2 A one cc (mL) sample is injected into a gas chromatograph where it is eluted through a megabore, thick film, methyl silicone liquid phase, open tubular partitioning column or other suitable column, and separated into its individual constituents.

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.

³ Silcosteel is a trademark of Restek Corporation, 110 Benner Circle Bellefonte, PA, 16823.

⁴ Tedlar is a trademark of DuPont.

3.3 *Sulfur Chemiluminescence Detection*—As sulfur compounds elute from the gas chromatographic column, they are processed in a flame ionization detector (FID) or a heated combustion zone. The products are collected and transferred to a sulfur chemiluminescence detector (SCD). This technique provides a sensitive, selective, linear response to volatile sulfur compounds and may be used while collecting hydrocarbon and fixed gas data from a FID.

3.3.1 *Detectors in Series with a SCD*—A SCD can frequently be used in series with other fixed gas and hydrocarbon detectors. However, regulatory bodies may question detector compatibility and require demonstration of equivalence between a SCD in a multi-detector system and a SCD operated using a FID or combustion zone. The user is referred to USEPA Method 301 for an example of a general equivalence procedure.

3.3.2 *Alternative Detectors*—This test method is written for the sulfur chemiluminescent detector but other sulfur specific detectors can be used provided they have sufficient sensitivity, respond to all eluted sulfur compounds, do not suffer from interferences and satisfy quality assurance criteria. Regulatory agencies may require demonstration of equivalency of alternative detection systems to the SCD.

4. Significance and Use

4.1 Many sources of natural and petroleum gases contain sulfur compounds that are odorous, corrosive, and poisonous to catalysts used in gaseous fuel processing.

4.2 Low ppm amounts of sulfur odorants are added to natural gas and LP gases for safety purposes. Some odorants are unstable and react to form compounds having lower odor thresholds. Quantitative analysis of these odorized gases ensures that odorant injection equipment is performing to specification.

4.3 Although not intended for application to gases other than natural gas and related fuels, this test method has been successfully applied to fuel type gases including refinery, landfill, cogeneration, and sewage digester gas. Refinery, landfill, sewage digester and other related fuel type gases inherently contain volatile sulfur compounds that are subject to federal, state, or local control. The methane fraction of these fuel type gases are occasionally sold to distributors of natural gas. For these reasons, both regulatory agencies and production and distribution facilities may require the accurate determination of sulfur to satisfy regulatory, production or distribution requirements. Fuel gases are also used in energy production or are converted to new products using catalysts that are poisoned by excessive sulfur in the feed gas. Industry frequently requires measurement of sulfur in these fuel type gases to protect their catalyst investments.

4.4 *Analytical Methods*—Gas chromatography (GC) is commonly used in the determination of fixed gas and organic composition of natural gas (Test Method D1945). Other standard ASTM methods for the analysis of sulfur in fuel gases include Test Methods D1072 and D4468 for total sulfur and Test Methods D4010 and D4884 for hydrogen sulfide.

5. Apparatus

5.1 *Chromatograph*—Any gas chromatograph of standard manufacture, with hardware necessary for interfacing to a chemiluminescence detector and containing all features necessary for the intended application(s) can be used. Chromatographic parameters must be capable of obtaining retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

5.1.1 *Sample Inlet System*—A sample inlet system capable of operating continuously at the maximum column temperature is used. A split/splitless injection system capable of splitless operation and split control from 10:1 up to 50:1 may be used with capillary columns, or when interferants are encountered. An automated gas sampling valve is required for many applications. The inlet system must be conditioned or constructed of inert material and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds.

5.1.2 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical for optimum and consistent analytical performance. Control is achieved by use of pressure regulators and fixed flow restrictors. The gas flow is measured by appropriate means and adjusted. Mass flow controllers, capable of maintaining gas flow constant to $\pm 1\%$ at the flow rates necessary for optimal instrument performance can be used.

5.1.3 *Detector*—Sulfur compounds are processed using a flame ionization detector (FID), a heated combustion zone or a similar device. The products are collected and delivered to a sulfur chemiluminescence detector (SCD).

5.1.3.1 *FID*—The detector must meet or exceed the specifications in Table 1 of Practice E594 while operating within manufacturers specifications. The detector must be capable of operating at the maximum column temperature. The flow path from the injection system through the column to the FID must remain at or above the column temperature throughout the analysis. The FID must allow for the insertion of a SCD sampling probe into the flame without compromising the ability of the FID to detect hydrocarbons. Flow rates of air and hydrogen or, alternatively of oxygen and hydrogen, must be optimized to produce a hydrogen rich flame or combustion zone that is capable of combusting hydrocarbons. This is necessary to minimize matrix effects. When performing the simultaneous detection of hydrocarbons is necessary, a FID and heated combustion zone can be used in series. Zero air is necessary when performing the simultaneous determination of sulfur gases and hydrocarbons.

5.1.3.2 *SCD*—The sulfur chemiluminescence detector shall meet or exceed the following specifications: (1) greater than 10^5 linearity, (2) less than 5 pg S/s sensitivity, (3) greater than 10^6 selectivity for sulfur compounds over hydrocarbons, (4) no quenching of sulfur compound response, and (5) no interference from co-eluting compounds at the usual GC sampling volumes.

5.1.3.3 *Heated Combustion Zone*—Sulfur compounds eluting from the chromatographic column are processed in a heated hydrogen rich combustion zone or a flame ionization detector fitted to the end of the column. Products are transferred under

reduced pressure to the reaction chamber of a chemiluminescence detector. An excess of ozone present in the chamber reacts with the sulfur combustion product(s) to liberate blue (480 nm) and ultraviolet light (260 nm).

5.1.3.4 SCD operation is based on the chemiluminescence (light emission) produced by the reaction of ozone with an unidentified sulfur species produced in a combustion zone, flame ionization detector or related device. The chemiluminescent sulfur species is the subject of on-going research. The appendix describes two chemiluminescence reaction models. The sulfur combustion product(s) and an excess of ozone are drawn into a low pressure (<20 Torr) reaction cell. The ozone reacts to produce blue light (480 nm), oxygen, and other products. A blue sensitive photomultiplier tube detects the emitted light which is then amplified for display or output to a data collection system.

5.2 Column—A variety of columns can be used in the determination of sulfur compounds. Typically, a 60 m × 0.54 mm ID fused silica open tubular column containing a 5 μm film thickness of bonded methyl silicone liquid phase is used. The selected column must provide retention and resolution characteristics such as listed in Table 2 and illustrated in Fig. 1. The column must be inert towards sulfur compounds. The column must also demonstrate a sufficiently low liquid phase bleed at high temperature such that loss of the SCD response is not encountered while operating the column at 200°C.

5.3 Data Acquisition:

5.3.1 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.

5.3.2 Integrator—An electronic integrating device or computer can be used. A dual channel system is necessary for simultaneous acquisition of both the FID and SCD signals. The device and software must have the following capabilities:

- 5.3.2.1 Graphic presentation of the chromatogram.
- 5.3.2.2 Digital display of chromatographic peak areas.
- 5.3.2.3 Identification of peaks by retention time or relative retention time, or both.
- 5.3.2.4 Calculation and use of response factors.
- 5.3.2.5 External standard calculation and data presentation.

6. Reagents and Materials

NOTE 2—Warning: Sulfur compounds contained in permeation tubes or compressed gas cylinders 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 or helium can result in explosion. Rapid release of nitrogen or helium can result in asphyxiation. Compressed air supports combustion.

6.1 Sulfur Standards—Accurate sulfur standards are required for sulfur gas quantitation. Permeation and compressed gas standards should be stable, of high purity, and of the highest available accuracy.

6.1.1 Permeation Devices—Sulfur standards can consist of 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

TABLE 1 Example Retention Times Using 4μ Capillary Column (30 m × 0.32 mm)

Conditions as in Table 2			
Compound	Ave. RT min	Compound	Ave. RT min
Methane	1.458	?S	16.363
Ethane	1.730	n-Octane	16.423
Ethylene	1.733	?S	16.425
Hydrogen Sulfide	2.053	?S	16.592
Propylene	2.550	?S	16.692
Carbonyl Sulfide	2.586	?-EtThiophene	16.983
Propane	2.679	?S	17.183
Sulfur Dioxide	2.815	?S	17.319
i-Butane	4.422	?S	17.631
Butene-1	5.263	?S	17.754
n-Butane	5.578q	m&p-Xylene	17.788
Methanethiol	5.804	?S	17.913
t-Butene-2	5.938	?S	18.063
2,2-DMO3	6.009	?S	18.139
c-Butene-2	6.409	o-Xylene	18.279
3-Me-Butene-1	7.463	n-None	18.448
i-Pentane	8.035	?S	18.450
Pentene-1	8.500	?S	18.567
Ethanethiol	8.583	?S	18.642
2-Me-Butene-1	8.717	DiEthylDiSulfide	18.767
n-Pentane	8.860	?S	18.911
Isoprene	8.983	?S	19.008
t-Pentene-2	9.096	?S	19.125
Dimethylsulfide	9.117	?S	19.292
o-Pentene-2	9.321	?S	19.979
2-Me-Butene-2	9.463	2,2,4-TriMeBz	20.227
Carbon Disulfide	9.617	n-Decane	20.308
2,2-DMO4	9.898	?S	20.550
i-Propanethiol	10.222	?S	21.396
Cyclopentene	10.392	?S	21.733
3-MePentadiene	10.525	?S	21.808
CP/2,3-DMO4	10.733	n-Undecane	22.033
2-MO5	10.883	?S	22.208
3-MO5	11.269	?S	23.046
t-Butanethiol	11.278	?S	22.417
Hexene-1	11.392	n-Dodecane	23.631
n-Propanethiol	11.625	Benzothiophene	23.717
n-Hexane	11.720	n-Tridecane	25.134
MethylEthylSulfide	11.779	MeBzThiophene	25.225
MeCyC5	12.457	MeBzThiophene	25.328
Benzene	13.154	MeBzThiophene	25.433
s-Butanethiol	13.154	MeBzThiophene	25.550

TABLE 2 Typical Gas Chromatographic Operating Parameters

Injector, gas sample loop:	150°C	0.5 cc
Injector, splitless:	150°C	100 % sample to column
Flame ionization detector (FID):	250°C	
	H2:	200 cm ³ /min
	Air:	400 cm ³ /min
	Make-up gas (He):	20 cm ³ /min
Or a Heated combustion zone (HCZ):	800°C	
	H2:	100 cm ³ /min
	Air:	40 cm ³ /min
SCD: output at 0–1 V cell pressure at 6.0 torr		
Column Program: 1.5 min at 30°C		
	15.0°/min to 200°C	
	hold at 200°C as required	
Carrier gas (helium): adjust to methane retention time of 1.10 min		
Carrier: 11 cm ³ /min		

passing over the tubes. These calibration gases are used to calibrate the GC/SCD system.

6.1.1.1 Permeation System Temperature Control—Permeation devices are maintained at the calibration temperature within 0.1°C.

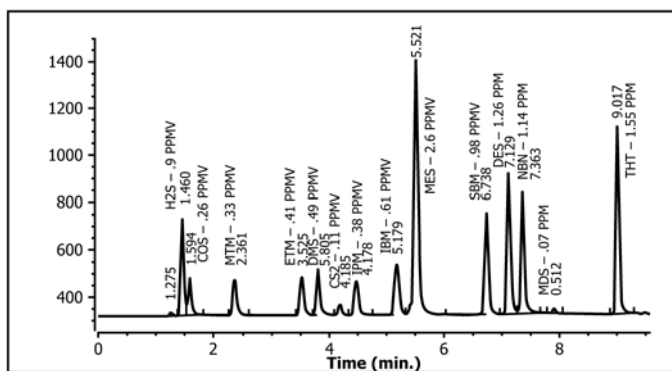


FIG. 1 Standard: Perm Tube Analysis Run

6.1.1.2 *Permeation System Flow Control*—The permeation flow system measures diluent gas flow over the permeation tubes within ± 2 percent.

6.1.1.3 Permeation tubes are inspected and weighed to the nearest 0.01 mg on at least a monthly basis using a balance calibrated against NIST traceable “S” class weights or the equivalent. Analyte concentration is calculated by weight loss and dilution gas flow rate as per Practice D3609. These devices are discarded when the liquid contents are reduced to less than ten (10) percent of the initial volume or when the permeation surface is unusually discolored or otherwise compromised.

6.2 *Compressed Gas Standards*—Alternatively, blended gaseous sulfur standards in nitrogen, helium or methane base gas may be used. Care must be exercised in the use of 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 NMi reference material.

6.2.1 Compressed gas standard regulators must be appropriate for the delivery of sulfur gases and attached fittings must be passivated or inert to sulfur gases.

6.2.2 The following sulfur compounds are recommended for inclusion in a compressed gas standard.

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

6.2.3 The following substances can also be included in a compressed gas standard.

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

6.2.4 The following compounds are not recommended for inclusion in mixed component standards due to their potential for promoting degradation.

Carbon disulfide (CS₂)
 Dimethyl disulfide (CH₃SSCH₃)
 Other disulfides

6.2.5 All multicomponent compressed gas standards must be re-certified as recommended by the manufacturer or as needed to insure accuracy.

6.2.6 For the analysis of complex samples, such as refinery fuel and related fuel type gases, the SCD system must demonstrate the capability of eluting common relatively high molecular weight volatile sulfur compounds including di-n-propyl sulfide (propyl sulfide). A retention time standard for demonstrating this capability can be prepared from the compound (ACS Grade) at approximately 160 ppmv concentration by addition of a 1 μ L aliquot of the liquid to a 10 L Tedlar bag filled with UHP nitrogen or helium.

6.2.7 *Carrier Gas*—Helium or nitrogen of high purity. Use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons is recommended. Gas pressure must be sufficient to ensure a constant carrier flow rate (see 5.1.2).

6.2.8 *Hydrogen*—High purity hydrogen is required as fuel for a flame ionization detector, a heated combustion zone or a similar device.

6.2.9 *Air*—High purity air is required as oxidant for a flame ionization detector, a heated combustion zone or a similar device.

6.2.10 *Oxygen*—High purity oxygen supply gas to the SCD ozone generator may be used for maximum detector sensitivity.

7. Equipment Preparation

7.1 *Chromatograph*—Place in service in accordance with the manufacturer’s instructions. Many operating conditions can be used to perform sulfur gas speciation and quantitation. Typical, minimal performance criteria for chromatographic conditions are:

7.1.1 The conditions must separate all volatile sulfur compounds required for calibration.

7.1.2 Chromatographic conditions must elute all sulfur species of interest.

7.1.3 The injection system must transfer without loss or absorption all sulfur compounds of interest to the GC column without reaction between sulfur species or excessive carryover between samples.

7.1.4 The operating conditions presented in Table 1 have been successfully used to fulfill the above criteria. Table 1 provides a listing of the retention times of selected sulfur compounds obtained using the parameters in Table 2. Figs. 2 and 3 illustrate typical analyses of a standard mixture and natural gas.

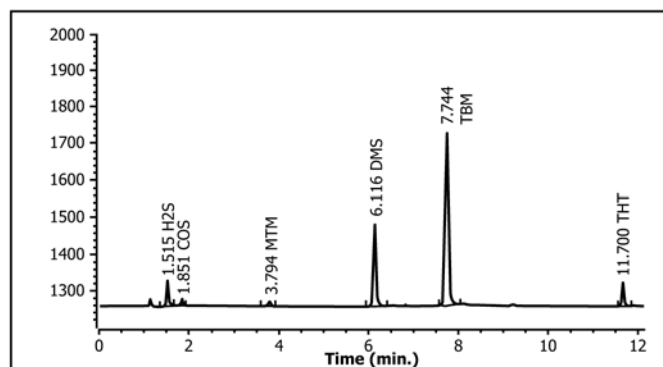


FIG. 2 Natural Gas Analysis-Sulfur Compounds

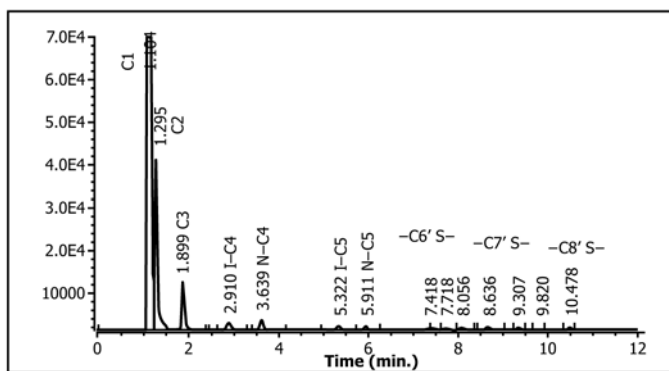


FIG. 3 Natural Gas Analysis-Hydrocarbon Compounds

7.2 SCD—Place in service in accordance with the manufacturer’s instructions. FID, heated combustion zone, and mixed FID/heated combustion zone interface configurations can be successfully applied to the analysis of sulfur gases in gaseous samples. For each of these interface configurations, optimization of the oxidant/fuel ratio is critical for ensuring complete combustion of hydrocarbon components in a sample. A flame or combustion zone that is too hydrogen rich will result in incomplete combustion and will produce a methane peak before elution of H₂S (Fig. 4). Matrix interference is occasionally observed when changing sample size. Matrix interference is also indicated by recoveries less than 90 % or greater than 110 % for samples spiked with calibration gas or samples diluted with air. When matrix interference is indicated, samples

may be analyzed by dilution or application of other mitigation efforts provided a spiked sample performed using the mitigation procedure results in recoveries within 10 % of theoretical results. Operational features specific to the interface configuration employed are described in the following.

7.2.1 FID Interface—Placed into service as per the SCD manufacturers instructions. For this interface, probe placement is critical for optimal sensitivity and reproducibility. Response that remains the same or decreases with increasing sample size, indicates questionable interface efficiency (Figs. 5 and 6).

7.2.2 Flameless Interface or Other Heated Combustion Zone—Placed into service as per manufacturers instructions. The typical flameless/combustion zone interface contains ceramic tubes in its construction. The performance of these tubes is critical to performance of the SCD system. Compromised ceramic tubes are susceptible to matrix effects. Compromised tubes may allow for reproducible duplicate sample analysis but will fail QA procedures such as matrix dilution and spike analyses. Poorly functioning tubes can also result in severe instrument drift, loss of equimolar response and general response instability. Compromised tubes must be replaced to restore nominal instrument function.

7.2.3 Mixed FID Heated Combustion Zone Systems—Combining a FID and a heated combustion zone in series can afford the simultaneous detection of hydrocarbons and sulfur gases. Samples demonstrating high hydrocarbon interference can frequently be analyzed using this configuration.

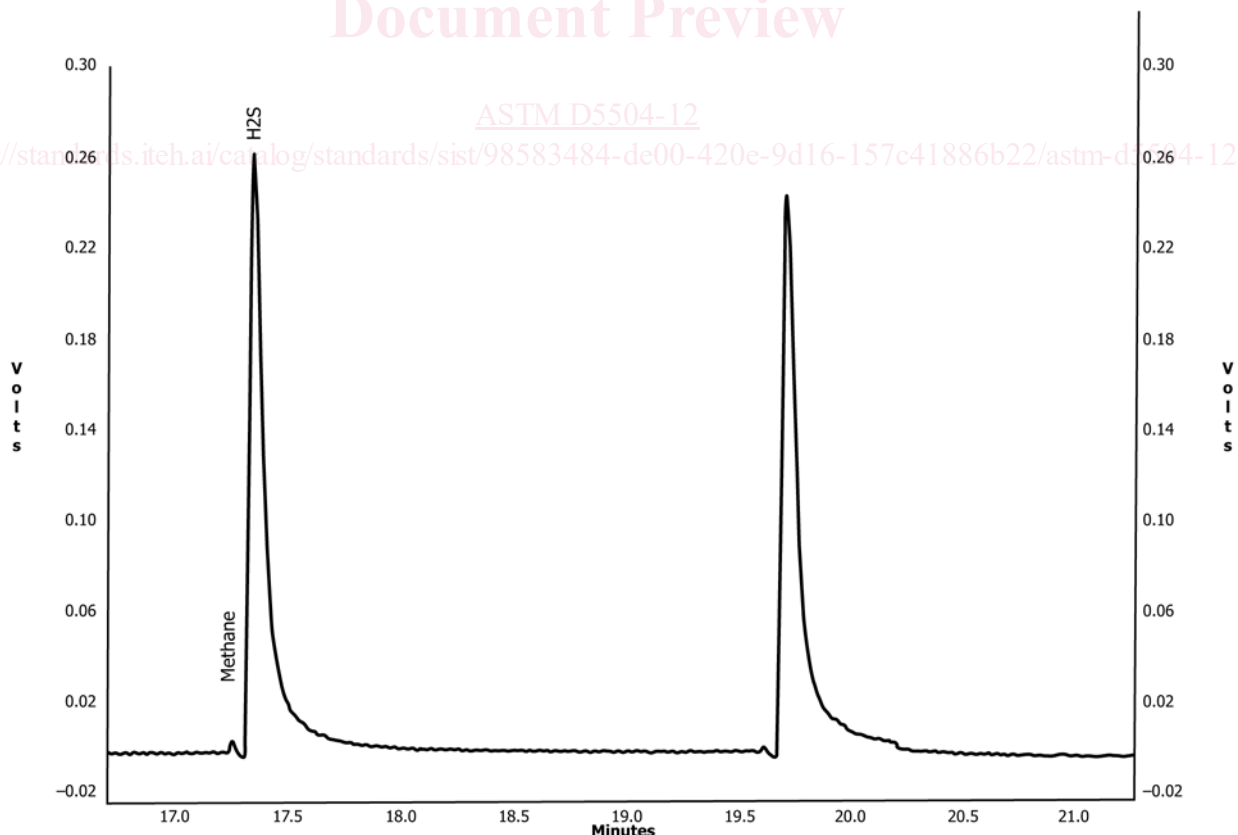


FIG. 4 Too Rich of a Combustion Flame Will Cause Methane Breakthrough

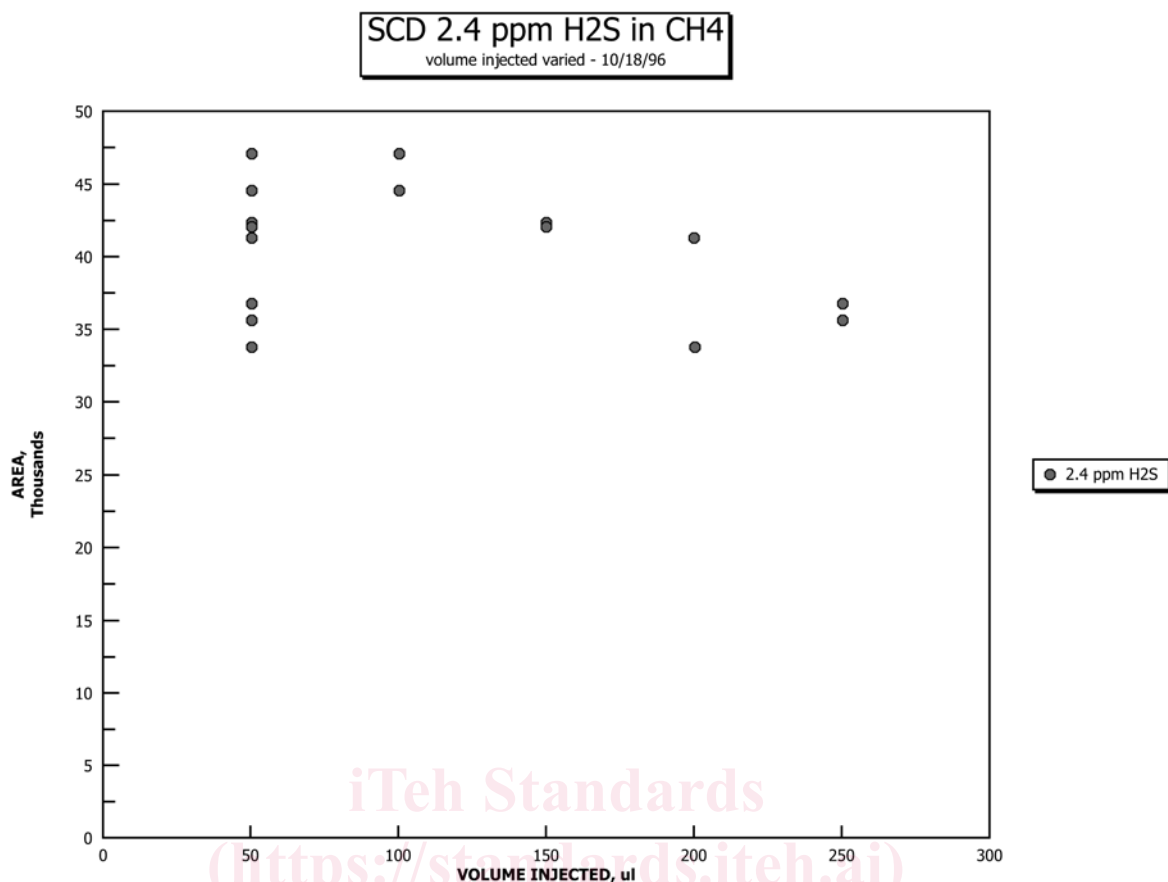


FIG. 5 Example of Matrix Interference. Changing the Sample Size Should Give a Change in Response

8. Calibration

8.1.1 *Sample Introduction*—Using passivated or inert equipment, transfer an aliquot of calibration standard to the GC sample loop. The aliquot must be of sufficient size to completely flush and fill the sample loop. Generally, a sample size 10 times the volume of the sample loop and inlet line is sufficient. Inject the sample in the sample loop into the GC column and start the chromatographic program. Appropriate analyte concentrations should be selected for calibration.

8.2 *SCD Calibration*—Monthly or whenever maintenance is performed, a three-point calibration curve forced through zero and prepared for each analyte of interest is suggested and may be required for certain applications. Linearity confirmation is consistent with acceptable SCD performance.

8.2.1 When needed, linearity can be established according to the following procedure. For each concentration of analyte, the standard is analyzed until three (3) consecutive trials yield a maximum range of 5%. The average area for each point is calculated. A linear regression is performed for each component using the average area. For each calibration point, the determined concentration is calculated from the average areas. Linearity is confirmed when the determined amount is within 5% of the actual amount of the analyte.

8.2.2 Establishment of linearity validates use of daily single-point calibration. When linearity cannot be established,

a daily three-point calibration curve with end points bracketing anticipated analyte concentrations is suggested.

8.2.3 Typically daily, standards are analyzed until three (3) consecutive trials yield a maximum range of 5%.

8.2.4 The SCD is an equimolar detector; therefore, response factors for all calibration components should be within 5% of the response factor for hydrogen sulfide. Failure to satisfy this criteria indicates either calibration standard degradation or failure of the SCD heated combustion zone, flame ionization detector (FID), or related device.

8.2.5 Calculate the relative response factor for each sulfur compound:

$$F_n = (C_n/A_n) \quad (1)$$

where:

F_n = response factor of compound,

C_n = concentration of the sulfur compound in the mixture, and

A_n = peak area of the sulfur compound in the mixture.

The response factor (F_n) of each single sulfur compound should be within 5% of F_n for hydrogen sulfide. Fig. 1 provides an example of a typical chromatogram and Table 4 shows the data and calibration report. Table 3 contains information useful for calibration calculations.