



Designation: D 5504 – 9801

# Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence<sup>1</sup>

This standard is issued under the fixed designation D 5504; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method ~~provides~~ is primarily for the determination of ~~individual~~ speciated volatile sulfur-containing compounds in high methane content gaseous fuels ~~including 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/m<sup>3</sup>, based upon the analysis of a ~~1-cm<sup>3</sup>~~ 1 cc sample.

1.2 This test method does not purport to identify all ~~individual~~ 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 unknown individual~~ method. Thus, unidentified compounds are determined with equal precision to that of ~~known compounds; identified substances.~~ Total sulfur content ~~of samples can be estimated~~ is determined from the total of ~~the individual compounds determined; individually quantified~~ components.

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

1.4 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee ~~D-3~~ D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

Current edition approved ~~May~~ Nov. 10, 1998; 2001. Published ~~March 1999; December 2001. Originally published as D 5504 – 94. Last previous edition D 5504 – 94~~8~~.~~

D 1072 Test Method for Total Sulfur in Fuel Gases<sup>2</sup>

D 1145 Method of Sampling Natural Gas<sup>2</sup>

D 1945 Test Method for Analysis of Natural Gas by Gas Chromatography<sup>2</sup>

~~D-2725 Test Method 3609 Practice for Hydrogen Sulfide in Natural Gas (Methylene Blue Method)<sup>2</sup> Calibration Techniques Using Permeation Tubes<sup>3</sup>~~

~~D-3031 Test 4084 Test Method for Total Sulfur Analysis of Hydrogen Sulfide in Natural Gas by Hydrogeneration Gaseous Fuels (Lead Acetate Reaction Rate Method)<sup>2</sup>~~

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry<sup>2</sup>

D 4626 Practice for Calculation of Gas Chromatographic Response Factors<sup>4</sup>

D 4810 Test Method for Hydrogen Sulfide in Natural Gas Using Length-of-Stain Detector Tubes<sup>2</sup>

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography<sup>5</sup>

### 3. Terminology

3.1 Abbreviations:

3.2 A common abbreviation of hydrocarbon compounds 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<sub>10</sub>; iso-tetradecane = I-C<sub>14</sub>).

3.3 Sulfur compounds are commonly referred to by their initials (chemical or formula), for example, dimethyl sulfide = DMS; carbonyl sulfide = COS.

### 4. Summary of Test Method

~~4.3.1 The analysis of gaseous sulfur compounds is difficult because of challenging due to the reactive nature reactivity of these materials. substances. They pose problems both in sampling are difficult to sample and analysis. A Ideally, analysis is ideally performed on-site to eliminate potential sample deterioration as a factor in analysis. Sampling must be done performed using containers proven to be nonreactive, non-reactive containers, such as Silcosteel<sup>®</sup> lined vessels, Tedlar bags with polypropylene fittings or the equivalent. Tedlar bag samples require protection from light and heat. Laboratory equipment must also be inert and well conditioned or passivated to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis.~~

~~4.2 A 1-cm<sup>3</sup> results.~~

3.2 A one cc (mL) sample of the fuel gas to be analyzed is injected into a gas chromatograph where it is passed eluted through a 60-m, megabore, thick film, methyl silicone liquid phase, open tubular partitioning column or other suitable column, and separated into its individual constituents.

4.3.3 *Sulfur Chemiluminescence Detection*—As sulfur compounds elute from the gas chromatographic column, they are ~~combusted. These~~ 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 ~~detection~~ technique provides a highly sensitive, selective, and linear response to volatile sulfur compounds and may be used ~~simultaneously while the usual 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

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.05.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.02, 11.03.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.01, 05.02.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.01.

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 Other Detectors—This test method~~ Analytical Methods—Gas chromatography (GC) is commonly used in the sulfur chemiluminescent detector, determination of fixed gas and organic composition of natural gas (Test Method D 1945). Other standard ASTM methods are available using for the lead acetate rate analysis of sulfur in fuel gases include Test Methods D 1072 and flame photometric detectors. D 4468 for total sulfur and Test Method D 6228 is the flame photometric detector method. Methods D 4010 and D 4884 for hydrogen sulfide.

## 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.

5.2 Small amounts (for example, 1 to 2 ppm) of sulfur odorant compounds are added to natural gas and LP gases for safety purposes. Some odorant compounds are not absolutely stable and tend to react to form more stable compounds having lower odor thresholds. Sulfur odorant levels are therefore analyzed to help ensure proper safety with fuel gases.

5.3 ~~Current Analytical Methods—~~Gas chromatography (GC) is commonly used to determine the fixed gas and organic component composition of natural gas (Test Method D 1945). Other standard methods for the analysis of sulfur in fuel gases include Test Methods D 1072, D 3031, and D 4468 for total sulfur and Test Method D 2725 for hydrogen sulfide.

## 6. Apparatus

6.1 ~~Chromatograph—~~Any gas chromatograph of standard manufacture, with hardware necessary for interfacing to a chemiluminescence detector and containing all features necessary for the following performance characteristics intended application(s) can be used:

6.1.1 ~~Column Temperature Programmer—~~The chromatograph used. Chromatographic parameters must be capable of linear programmed temperature operation over a range of 30 to 200°C, in programmed rate settings of 0.1 to 30°C/min. The programming rate must be sufficiently reproducible to obtain obtaining retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

6.1.2—

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

6.1.3—

5.1.2 ~~Carrier and Detector Gas Control—~~Constant flow control of carrier and detector gases is critical to for optimum and consistent analytical performance. Control is best provided achieved 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, adjusted. Mass flow controllers, capable of maintaining gas flow constant to  $\pm 1\%$  at the required flow rates necessary for optimal instrument performance can also be used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa (10 psig) 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.

6.1.4— used.

5.1.3 ~~Detector—~~Combustion of the sample can be accomplished—Sulfur compounds are processed using a flame ionization detector (FID), a flameless furnace, heated combustion zone or a combination, similar device. The combusted sample is then products are collected and delivered to the a sulfur chemiluminescence detector (SCD).

6.1.4.3.1 ~~FID—~~The detector must meet or exceed the typical specifications given in Table 1 of Practice E 594 while operating in the normal mode as specified by the manufacturer, within manufacturers specifications. The detector must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. Connection of temperature. The flow path from the injection system through the column to the detector FID must be such that no temperature below remain at or above the column temperature exists, throughout the analysis. The detector design FID must be such to allow for the insertion of the a SCD sampling probe into the flame without interrupting compromising the detection ability of the hydrocarbon response. Initial flow FID to detect hydrocarbons. Flow rates of air and hydrogen or, alternatively of oxygen and air should hydrogen, must be set optimized to the SCD manufactures recommendations. A produce a hydrogen rich flame or combustion zone that is required capable of combusting hydrocarbons. This is necessary to fully combust minimize matrix effects. When performing the hydrocarbons present in the sample. This will afford less sensitivity for the hydrocarbon components and, if simultaneous detection

**TABLE 1 Typical Gas Chromatography Retention Time Comparison of Compounds Using P 4μ Capillary Column (30 m × 0.32 mm)**

Conditions as in Table 2			
Injector, gas sample loop: 150°C	1.0 cm <sup>3</sup>	Compound	Ave. RT min
Compound	Ave. RT min	Compound	Ave. RT min
Injector, splitless:	150°C	?S	100% sample to column
Methane	1.458	?S	16.363
Flame ionization detector: 250°C	H <sub>2</sub> :	200 cm <sup>3</sup> /min	46.423
Ethane	1.730	n-Octane	16.423
	Air:	?S	16.400 cm <sup>3</sup> /min
Ethylene	1.733	?S	16.425
	Air (He):	20 cm <sup>3</sup> /min	
Hydrogen Sulfide	2.053	20 cm <sup>3</sup> /min	
?S		SCD: 16.592	
?S		16.592	
Preoutput at 0-1 V cell pressure at 8.7 torr			
Propylene			
Column Oven: 1.5 min at 30°C			
	2.550		
	15.0°/min to 200°C		
?S			
	hold at 200°		
	16.692		
<u>Gas required</u>			
Carbonyl Sulfide			
Carrier gas (helium): adjust to methane retention time of			
	1.10 min		
	2.10 min		
586			16.983
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
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-Pa (ne)	8.035	?S	18.450
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
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-Trimate	25.134
n-Hexane	11.720	n-Tridecane	25.134
Methyl Sulfide	11.779	MeBzThiophene	25.225
Methyl Ethyl Sulfide	11.779	MeBzThiophene	25.225
MeCyC5	12.457	MeBzThiophene	25.328
MeCyC5	12.457	MeBzThiophene	25.328
Benzene	13.154	MeBzThiophene	25.433
Benzene	13.154	MeBzThiophene	25.433
s-Butanethiol	13.154	MeBzThiophene	25.550

of hydrocarbons is needed, the necessary, a FID should and heated combustion zone can be used in series-w. Zero air is necessary when performing the flameless furnace. Air should be used for makeup gas for a capillary column.

6.1.4.2 *Flameless Furnace*—Sulfur compounds eluting from the FID or the chromatographic column are combusted in a hydrogen-rich flame enclosed by the burner. Combustion occurs within a ceramic chamber heated by an external furnace element. The burner typically consists simultaneous determination of a tower assembly that contains a furnace element, thermocouple, sulfur gases and ceramic combustion tubes. The tower is mounted on a base plate that holds the tower in alignment and provides connections for air and vacuum sensing.

6.1.4.3 *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.

65.1.43.43 *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-producing reaction) from (light emission) produced by the reaction of ozone with an unidentified sulfur compound species produced from the in a combustion zone, flame ionization detector or related device. The chemiluminescent sulfur species is the analyte. A vacuum pump pulls 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 reaction cell at low pressure, where excess ozone is added. Light produced from the subsequent pressure (<20 Torr) reaction is detected with a cell. The ozone reacts to produce blue light (480 nm), oxygen, and other products. A blue sensitive photomultiplier tube and detects the signal emitted light which is then amplified for display or output to a data collection system.

6.1.4.5 As sulfur compounds elute from the gas chromatographic column they are combusted in a hydrogen-rich flame of a flame ionization detector (FID) producing numerous combustion products, one of which is sulfur monoxide (Reaction 1). These combustion products are collected and removed from the flame using a ceramic sampling tube (probe) interface and transferred under a vacuum through a flexible tube to the reaction chamber of the sulfur chemiluminescence detector (SCD). Sulfur monoxide is then sensitively detected by an ozone/sulfur monoxide chemiluminescent reaction to form electronically excited sulfur dioxide, which relaxes with emission of light in the blue and the ultraviolet regions of the spectrum (Reaction 2):



where Hv = chemiluminescent light energy.

6.2

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 shall must provide retention and resolution characteristics such as listed in Table 2 and illustrated in Fig. 1. The column-w must be inert towards sulfur compounds. The column must also demonstrate a sufficiently low liquid phase bleed at high temperature such that no loss of the SCD-sulfur response is not encountered while operating the column at 200°C.

65.3 *Data Acquisition:*

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

65.3.2 *Integrator*—The use of an—An electronic integrating device or computer is recommended; can be used. A dual channel system is useful necessary for simultaneous presentation acquisition of both the FID and SCD signals. The device and software must have the following capabilities:

65.3.2.1 Graphic presentation of the chromatogram.

65.3.2.2 Digital display of chromatographic peak areas.

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

65.3.2.4 Calculation and use of response factors.

65.3.2.5 External standard calculation and data presentation.

## 76. Reagents and Materials

7.1 *Sulfur Compound Standards*—Gaseous permeation tube standards shall be used for all sulfur compounds to be determined.

7.2 Permeation tubes will be weighed to the nearest 0.1 mg on a monthly basis and standard concentration calculated by weight loss and dilution gas flow rate.

7.3 *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 because of instability.

NOTE 1—**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

TABLE 2 ReTypical Gas Chromatographic Openration Tig  
Parame—4u-SPB1ters

Compound	Ave. RT min	Compound	Ave. RT min
Injector, gas sample loop:	150°C	Compound	Ave. 0.5 cc
Methane	1.458	?S	16.363
Injector, splitless:	150°C	?S	100 % sample to column
Ethylene	1.733	n-Octane	16.423
Flame ionization detector (FID):	250°C	n-Octane	16.423
Ethane	1.730	?S	16.425
	H <sub>2</sub> :	?S	16.4200 cm <sup>3</sup> /min
Hydrogen Sulfide	2.053	S	16.592
	Air:	S	16.592400 cm <sup>3</sup> /min
Propylene	2.550	?S	16.692
	Make-up gas (He):	?S	16.6920 cm <sup>3</sup> /min
Carbonyl Sulfide	2.5-86	?-EtThiophene	16.983
Or a Heated combustion zone	800°C	?-EtThiophene	16.983
(HCZ):			
Propane	2.679	?S	17.183
	H <sub>2</sub> :	?S	100 cm <sup>3</sup> /min
Sulfur Dioxide	2.815	?S	40 cm <sup>3</sup> /min
	Air:	?S	40 cm <sup>3</sup> /min
17.319			
i-Butane			
i-BSCD: output at 0-1 V cell			
pressure at 6.0 torr			
4.422			
Column Program: 1.5 min at 30°C			
?S			
	15.0°/min to 200°C		
17.631			
Bu tene-1			
Bu hold at 200°C			
as required			
5.263		?S	17.75
5.263		?S	Carrier gas (helium): adjust to met
n-Butane	5.578	m&p-Xylene	17.788
Carrier: 11 cm <sup>3</sup> /min		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
e-Butene-2	6.409	o-Xylene	18.279
3-Me-Butene-1	7.463	?S	18.450
i-Pentane	8.035	n-None	18.448
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
GP/2,3-DMO4	10.733	n-Undecane	22.033
2-MO5	10.883	?S	22.208
t-Butanethiol	11.278	?S	22.417
3-MO5	11.269	?S	23.046
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

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.

76.1 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

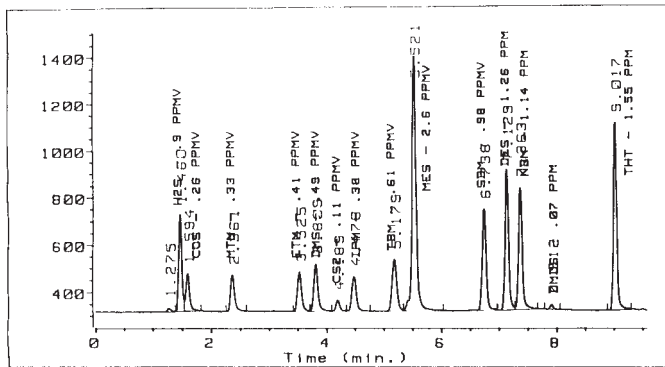


FIG. 1 Standard; Perm Tube Analysis Run

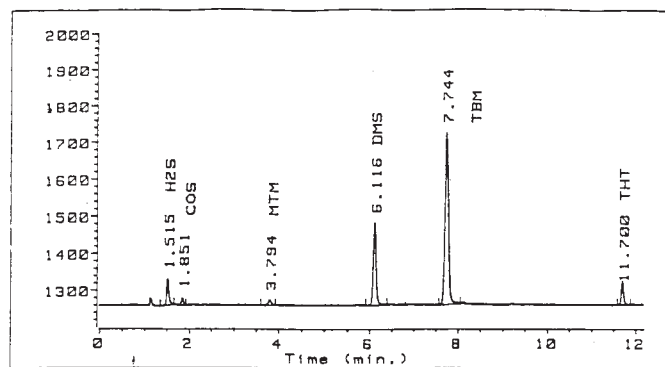


FIG. 2 Natural Gas Analysis-Sulfur Compounds

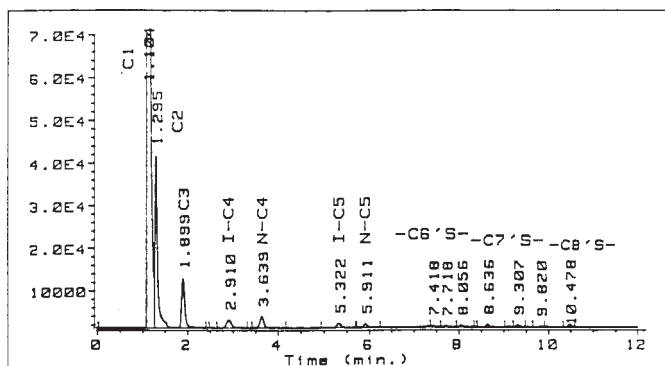


FIG. 3 Natural Gas Analysis-Hydrocarbon Compounds

range of concentration can be generated by varying and accurately measuring the flow rate of diluent gas 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.

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 D 3609. 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 (H<sub>2</sub>S)  
Carbonyl sulfide (COS)  
Methyl mercaptan (CH<sub>3</sub>SH)

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

Ethyl mercaptan (CH<sub>3</sub>CH<sub>2</sub>SH)  
1-propanethiol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH)  
2-propanethiol (CH<sub>3</sub>CHSHCH<sub>3</sub>)  
Dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>)

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

Carbon disulfide (CS<sub>2</sub>)  
Dimethyl disulfide (CH<sub>3</sub>SSCH<sub>3</sub>)  
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 µL 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 (**Warning**—See Note 2). Additional purification is recommended by the use purity. Use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available hydrocarbons is recommended. Gas pressure must be sufficient to ensure a constant carrier gas flow rate (see 6.1.3).

NOTE 2—Warning: Helium and nitrogen can be compressed gases under high pressure:

7.5– 5.1.2).

6.2.8 Hydrogen—Hydrogen of high—High purity (for example, hydrocarbon free) hydrogen is required as fuel for the a flame ionization detector (FID) (**Warning**—See Note 3):

NOTE 3—Warning: Hydrogen is an extremely flammable gas under high pressure:

7.6– detector, a heated combustion zone or a similar device.

6.2.9 Air—High purity (for example, hydrocarbon free) compressed air is required as the oxidant for the a flame ionization detector (FID) (**Warning**—See Note 4).

NOTE 4—Warning: Compressed air can be detector, a heated combustion zone or a similar device.

6.2.10 Oxygen—High purity oxygen supply gas under high pressure and supports combustion.

## **8. Preparation of Apparatus and Calibration**

8.1– 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. Typical Many operating conditions are shown in Table 1. Hydrogen can be used to perform sulfur gas speciation and air flows are critical 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 FID-reducing flame 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 give fulfill the SCD above criteria. Table 1 provides a listing of the retention times of selected sulfur compoundse obtained using the parameters ivn Table 2. Figs. 2 and 3 illustrate typical analyses of a standard mixture and natural gas.

87.2 SCD—Place in service in accordance with the manufacturer’s instructions. When using the FID as the only FID, heated combustion method, the probe placement location is critical zone, and mixed FID/heated combustion zone interface configurations can be successfully applied to maximum sensitivity. During optimization, the analysis of sulfur gases in gaseous samples. For each of these interface configurations, optimization of the oxidant/fuel ratio is critical to provide for ensuring complete combustion of the hydrocarabon components. Too rich hydrocarbon components in a sample. A flame can produce or combustion zone that is too hydrogen rich will result in incomplete combustion as seen by and will produce a small methane peak before elution of H<sub>2</sub>S

(see Fig. (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 seen analyzed by varying the 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 measuring response. If response stays reproducibility. Response that remains the same or decreases with increasing sample size, the burner efficiency is indicates questionable (s interface efficiency (Figs. 5 and 6). Samples with high hydrocarbon interference will require dual combustion using 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.

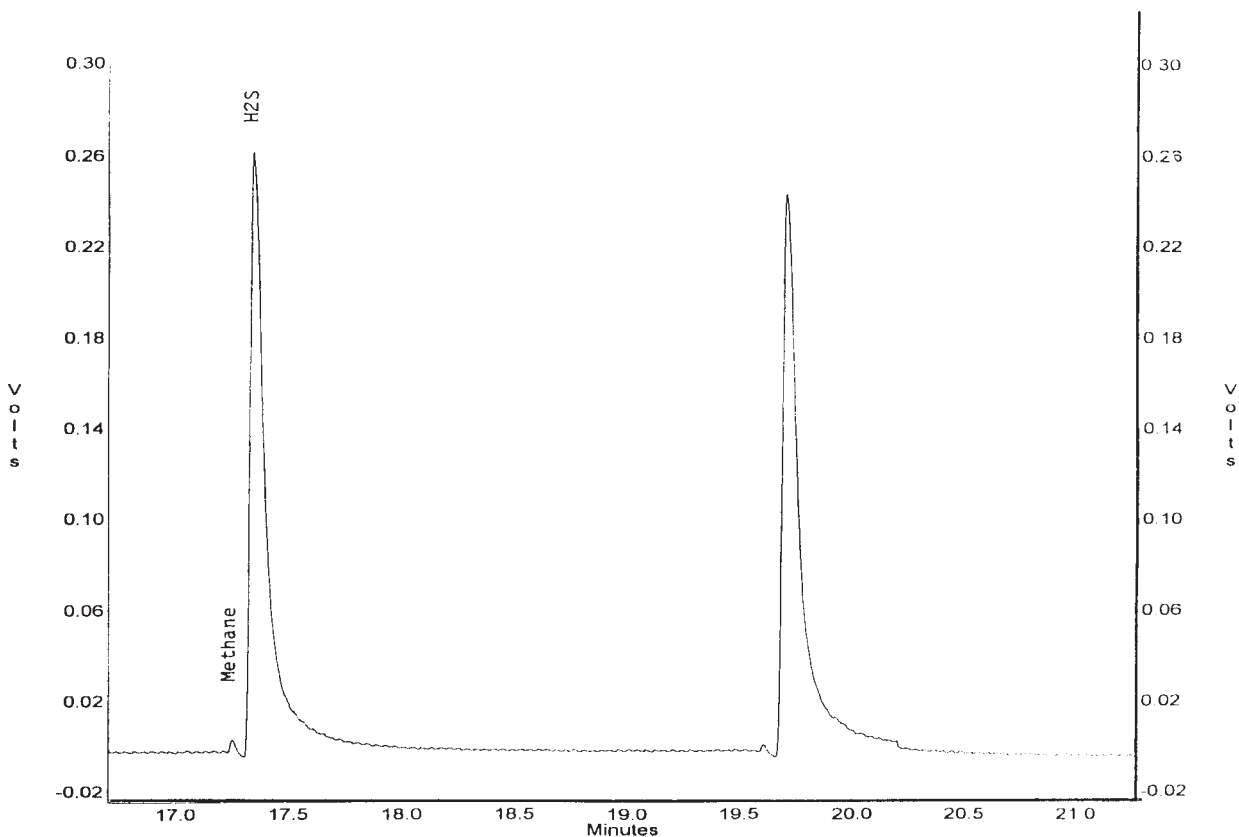
**7.2.3 Mixed FID Heated Combustion Zone Systems**—Combining a FID and flameless furnace a heated combustion zone in series. S can afford the simultaneous detection of hydrocarbons with the FID and sulfur detection with the SCD is afforded in gases. Samples demonstrating high hydrocarbon interference can frequently be analyzed using this configuration. After sufficient equilibration time (usually overnight), adjust the detector output signal configuration.

## 8. Calibration

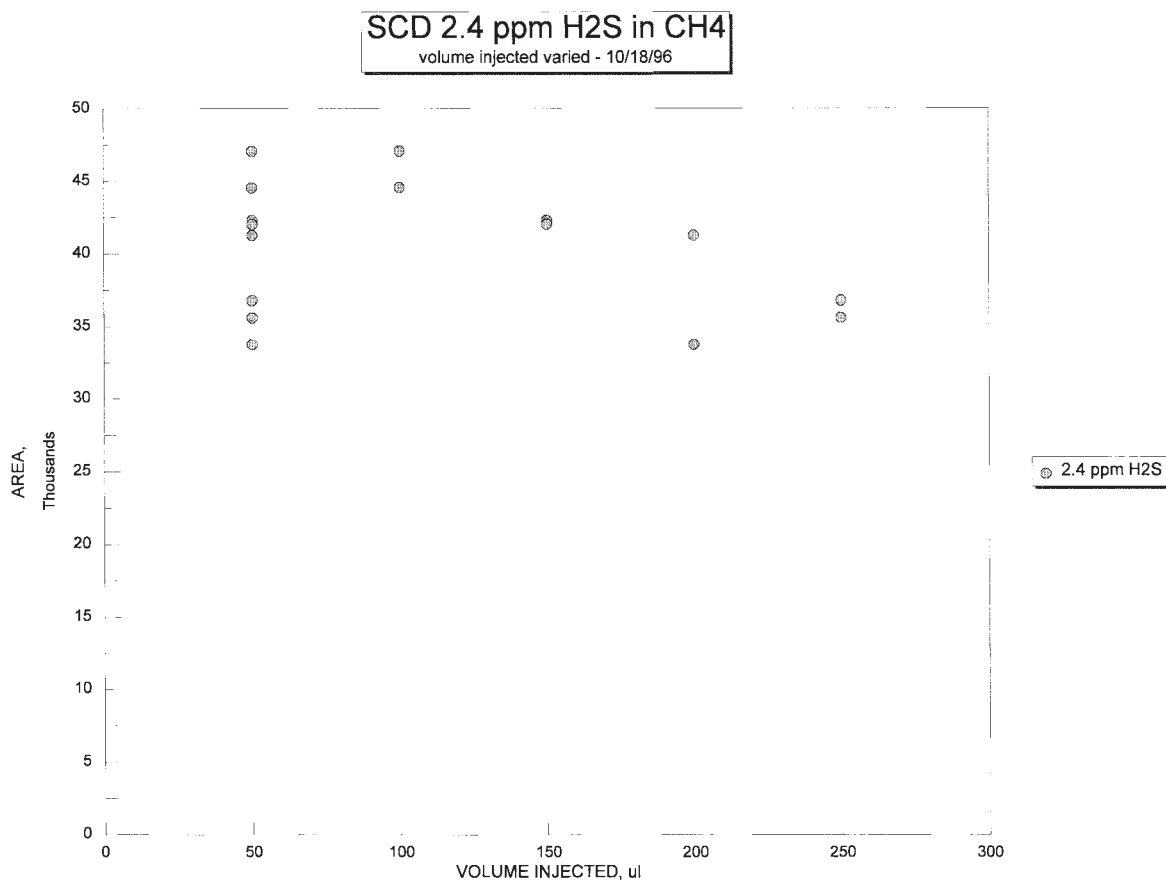
**8.1 Sample Introduction**—Using passivated or integrator input signal inert equipment, transfer an aliquot of calibration standard to approximately zero. Monitor the signal for several minutes GC sample loop. The aliquot must be of sufficient size to verify compliance with the specified signal noise completely flush and drift.

**8.2.1 Sample Injection**—Inject 1.0 cm<sup>3</sup> from fill the sample loop. Generally, a sample loop 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.



**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**

8.2.1 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 interest.

8.2.2 *Detector Response Calibration—Analyze 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 gas and obtain 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:

$$F_n = (C_n/A_n) \tag{1}$$

$$F_n = (C_n/A_n) \tag{1}$$

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 10% 5% of  $F_n$  for dimethyl 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.

## 9. Procedure

9.1 Many operating conditions can be used to perform sulfur gas speciation and quantitation. Minimum criteria for acceptable operating conditions are as stated in 7.1. In addition, it is advisable and required for regulatory purposes to establish the limit of detection (LOD) for a SCD system.

SCD 2.4 ppm H<sub>2</sub>S in CH<sub>4</sub>  
 volume injected varied - 10/18/96

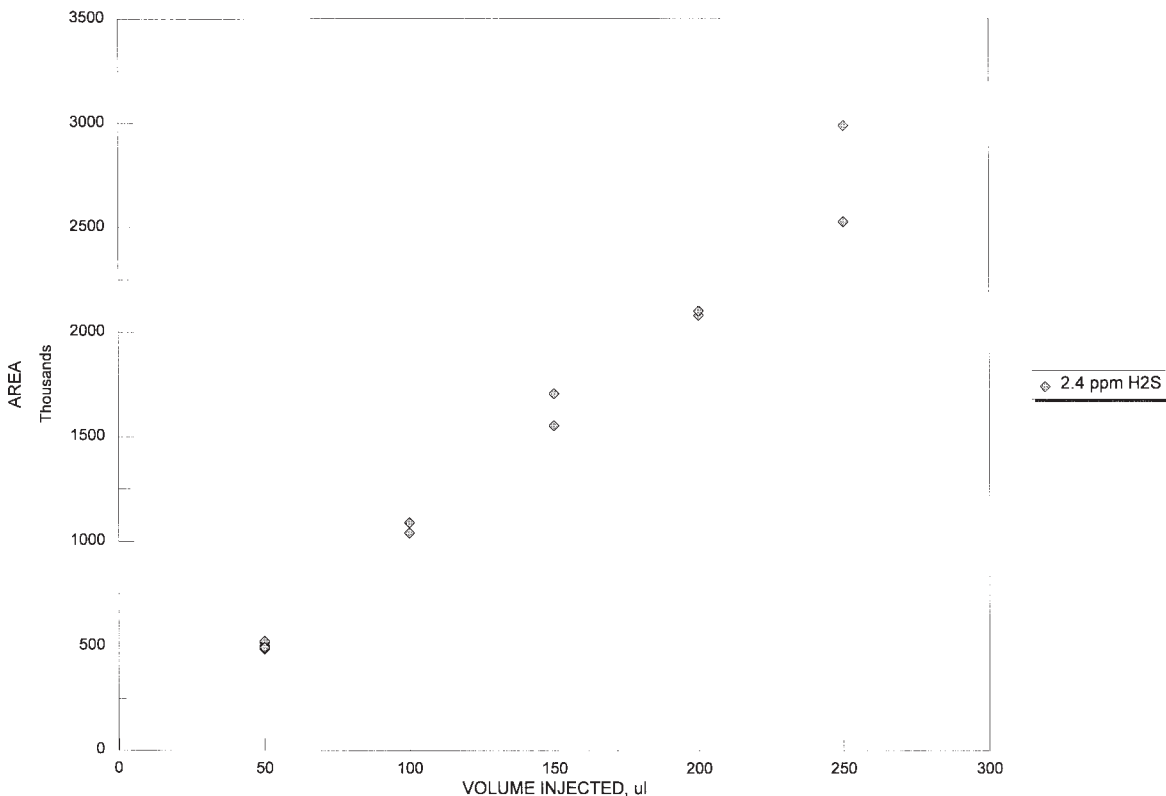


FIG. 6 Example of Typical Response Curve with Varying Sample Size

TABLE 3 Sulfur Gas Standard

Compound	Mol. Wt.	Density	BP°C	%S	(Conversion) Mg/M3 per PPMV
Hydrogen sulfide (H <sub>2</sub> S)	34.08	1.1857	—	94.08	1.39
Carbonyl sulfide (COS)	60.08	1.24	—	53.37	2.46
Methanethiol (MeSH)	48.110	0.8665	6.2	66.65	1.97
Ethanethiol (EtSH)	62.134	0.8391	35.0	51.61	2.54
Dimethylsulfide (DMS)	62.134	0.8483	37.3	51.61	2.54
Carbon disulfide (CS <sub>2</sub> )	76.14	—	—	84.23	3.11
2-Propanethiol (iPrSH)	76.160	0.8143	52.6	42.10	3.11
t-Butanethiol (tBSH)	64.220	0.8002	65.0	49.93	2.62
1-Propanethiol (nPrSH)	76.160	0.8415	67.0	42.10	3.11
Methylethylsulfide (MES)	76.160	0.8422	67.0	42.10	3.11
Thiophene (TP)	84.14	1.07	84.16	38.03	3.44
s-Butanethiol (s-BuSH)	90.186	0.8299	85.0	35.56	3.69
i-Butanethiol (i-BuSH)	90.186	0.8343	88.7	35.56	3.69
Diethylsulfide (DES)	90.190	0.8362	92.0	35.55	3.69
n-Butanethiol (n-BuSH)	90.186	0.8416	98.5	35.56	3.69
Dimethyldisulfide (DMDS)	94.200	1.0625	109.7	68.08	3.85
Diethyldisulfide (DEDS)	122.252	0.9931	154.0	52.46	5.00

9.2 Sampling and Preparation of Sample Aliquots:

9.1.1 Gas Samples—Appropriate sampling procedures are critical for meaningful sulfur determination and must be supplied tailored to the particular sample source.

9.2.1 Samples—Samples are delivered to the laboratory in specially conditioned high-pressure sample containers or in Tedlar bags with polypropylene fittings or other inert fittings at atmospheric pressure. Such bags for H<sub>2</sub>S analysis pressure, protected from heat and light. Samples normally must be analyzed within 24 h of sampling.

9.2 Table 1 lists sampling. Alternatively, samples are delivered to the laboratory in Silcosteel lined vessels or other passivated/lined vessel demonstrated to not degrade sulfur gas chromatograph operating parameters. Table 2 provides a partial listing samples over 24 h. As part of the retention times of light a QA/QC program, passivated or lined vessels should periodically

**TABLE 4 Calibration Table**

SIEVERS 8 PTUBES NEW DET—MEGABORE/20PSIG He 5/6/91  
 SPLITLESS Calibration file: DATA:SVPT.Q Last Update: 24 Jul 91  
 5:37 pm Reference Peak Window: 5.00 % of Retention Time Non-  
 Reference Peak Window: 5.00 % of Retention Time Sample Amount:  
 0.000 Uncalibrated Peak RF: 60.00e-6 Multiplier: 1.000

Ret Time	Ph#	Signal Descr	Amt PPMV	cvl RespFact	Pk-Type Partial Name
1.461	1	GC Signal 1	0.9100	1 59.60e-6	1 H2S
1.595	2	GC Signal 1	0.2610	1 36.92e-6	1 COS
2.861	3	GC Signal 1	0.3570	1 50.11e-6	1 MTM
3.529	4	GC Signal 1	0.4150	1 50.28e-6	1 ETM
3.809	5	GC Signal 1	0.4943	1 49.02e-6	1 DMS
4.185	6	GC Signal 1	0.2289	1 0001001	1 CS2
4.481	7	GC Signal 1	0.3904	1 50.04e-6	1 1PM
5.179	8	GC Signal 1	0.6140	1 49.99e-6	1 TBM
5.521	9	GC Signal 1	2.600	1 50.00e-6	1 MES
6.738	10	GC Signal 1	0.9870	1 49.99e-6	1 SBM
7.129	11	GC Signal 1	1.225	1 48.81e-6	1 DES
7.868	12	GC Signal 1	1.135	1 49.99e-6	1 NBM
7.912	13	GC Signal 1	0.07660	1 0.0001000	1 DMDS
9.017	14	GC Signal 1	1.558	1 49.99e-6	1 THT

be examined for continued sulfur compounds. Figs. 1 gas stability and 2 acceptable sample carryover characteristics. Passivated or lined vessels may allow for reliable sample analysis after 24 h. In such cases, analysis is recommended within 7 days of a standard mixture and natural gas collection.

9.3 *External Standard Calibration*—Procedures delineated in 8.2 validate the use of a single-point calibration. At least once a day or as frequently as deemed expedient, day, analyze the calibration standard mix and determine standard response factors (see 10.1) factors. Typically, standards are analyzed until three (3) consecutive trials yield a maximum range of 5 %.

9.4 *Blank Analysis*—Confirmation of a lack of carry-over or contamination is recommended and may be required for certain applications. This is accomplished through analysis of a nitrogen or zero air blank. Observation of excessive amounts of high molecular weight volatile sulfur compounds is typical of injection valve deterioration.

9.5 *Sample Analysis*—Purge the lines from the—The analysis of each sample container through the sample loop in the gas chromatograph. Inject duplicate is strongly suggested and may be required for certain applications. Duplicate sample analysis will verify adequate SCD system conditioning and performance. Duplicate sample response for components present at or greater than 1-ee with a gas sampling valve as ppm (v/v) concentration in 8.2.1. If either analysis should generally be within ten (10) percent of the sample size exceeds initial analysis to verify acceptable system performance. When the linear range determined amount of any sulfur component exceeds the detector calibration range established under 8.2.2 a split injection should be used. Alternatively, samples may be diluted up to 1:10 using an air-tight or ground glass syringe and UHP nitrogen or zero air as the diluant. Retention times for peaks in sample chromatogram are compared to those of peaks in the standard chromatograms to identify sulfur compounds. Compounds for which a standard is not available are conveniently quantified using the response factor from one of the calibrants. Run the analysis per the conditions specified in Table 1, or using other conditions satisfying the chromatographic performance criteria in 7.1. Obtain the chromatographic data via a potentiometric record (graphic), digital integrator, or computer-based chromatographic data system. Examine the graphic display or digital data for any errors (for example, over-range component data).

9.6 *Quality Assurance*—The following quality assurance (QA) procedures are suggested and may be required in certain applications. These QA procedures will identify inaccuracy due to a compromised flame ionization detector or heated combustion zone or other SCD system component.

9.6.1 *Spiked Samples*—A spiked sample is analyzed each day as part of a QA/QC program. Spikes are prepared by quantitative addition of a mixed component calibration gas to a known volume of sample gas. Typically, 20 or 50 mL of a mixed component standard is added to a sample to give a final volume of 100 mL. Acceptable recoveries for components present at the greater of 5 ppmv or 5 % of the total volatile sulfur should fall within 10 % of the theoretical amounts to verify nominal system performance. Unacceptable recoveries indicate matrix interference or system malfunction. In many instances, when unacceptable recoveries are obtained, samples can be analyzed by dilution or other mitigation efforts.

9.6.2 *Calibration Standard Reanalysis*—A standard is reanalyzed after samples every day as part of a QA/QC program. All components should be within 10 % of the theoretical amounts based on the original standards. Unacceptable results typically are indicative of SCD combustion zone failure.

## 10. Calculations

10.1 Determine the chromatographic peak area for components and use the response factors obtained from the calibration run to calculate amounts of sulfurs present.

Example:

Assume 1.0 ppmv of dimethyl sulfide, DMS, injected into a ~~1.0-cm<sup>3</sup>~~ 1.0 cc sample loop with no split.

1 ppmv DMS = 2.54 mg/M<sup>3</sup> (Table 3)

2540 pg × 51.61 % S = 1310 picog S/peak

If area is found to be 15 850 counts—

response factor picograms (S/peak) is 1310/15 850 =  $8.27 \times 10^{-2}$  (in terms of picograms sulfur per peak) or

response factor (ppmv DMS sample) = 1.0/15 850 =  $63 \times 10^{-6}$  (in terms of ppmv of sulfur compound in sample)

NOTE 52—Since detector response is proportional to weight sulfur, all mono sulfur compounds (COS, H<sub>2</sub>S, DMS, etc.) will have approximately the same response factor for picograms S or ppmv (see 8.2.2).

Alternatively, concentration of volatile sulfur compounds is calculated in ppm (v/v) by the following:

$$\text{Analyte concentration, ppm} = \frac{\text{pk}_{\text{samp}}}{\text{pk}_{\text{std}}} \times \text{Std} \quad (2)$$

where:

analyte concentration = concentration of individual sulfur compounds or SO<sub>2</sub>,

pk<sub>samp</sub> = peak area in the sample,

pk<sub>std</sub> = peak area in the standard, and

Std = concentration of analyte in the standard, ppm.

Peak heights can be substituted for peak areas.

Total volatile sulfur is the sum of all identified and unidentified sulfur compounds.

10.2 Recoveries for the total volatile sulfur or each component in spiked samples are calculated by the following:

$$\text{Recovery (\%)} = \frac{\text{SM}}{(\text{SA}) (\text{DF}_1) + (\text{SS}) (\text{DF}_2)} \times 100 \quad (3)$$

where:

SM = measure spiked sample concentration in ppm (v/v),

SA = the average sample concentration from duplicate analysis of the sample in ppm (v/v),

SS = Concentration of the analyte used to spike the sample in ppmv,

DF<sub>1</sub> = dilution factor for the sample, and

DF<sub>2</sub> = dilution factor for the standard.

Recoveries are only calculated for components in the standard used to spike the sample. The total recovery for the spike is calculated according to the above equation using only components in the standard used to perform the spike.

10.3 Recoveries for post sample reanalyzed standards are calculated by the following:

$$\text{QA\QC Recovery (\%)} = \frac{\text{Calibration Value} - \text{Measured Value}}{\text{Calibration Value}} \times 100 \quad (4)$$

## 11. Report

11.1 Report the identification and concentration of each individual sulfur compound. The sum of all sulfur components detected to the nearest picogram, calculated as sulfur (pg S) can be used to calculate the total sulfur. Alternatively, the results may be reported in ppm (v/v) when required by using the alternative calculations contained in 10.1.

## 12. Precision and Bias

12.1 *Precision*—The precision of this test method as determined by the statistical examination of the inter-laboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values by only one case in twenty. (Experimental results to be determined.)

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only one case in twenty. (Experimental results to be determined.)

12.2 *Bias*—The procedure in Test Method D 5504 for the analysis of sulfur compounds in petroleum and petroleum products by gas chromatography has no bias.

## 13. Keywords

13.1 chemiluminescence detection; gas chromatography; sulfur compounds

**APPENDIXES**

**(Nonmandatory Information)**

**X1. PROTOCOL FOR COMPRESSED GAS CALIBRATION STANDARDS**

This protocol was developed to assist compressed gas sulfur standard users. It can provide calibration gas traceability to a NIST, NMI, or similar standard reference material. This protocol requires the determination of the speciated and total sulfur using a NIST or 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.

X1.1 A standard is analyzed according to Test Method D 5504. 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 one percent. An average area for each component and the total sulfur area is calculated using all consecutive analyses.

X1.2 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 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:

X1.3 The values for individual sulfur components and the total sulfur amount are calculated according to the formula:

$$\text{Sulfur calculated concentration} = \frac{\text{Average area as calculated in step 1}}{\text{Average area as calculated in step 2}} \times \text{H}_2\text{S Std.Conc.} \quad (\text{X1.1})$$

X1.4 The analysis for total volatile sulfur and individual components calculated as hydrogen sulfide (X1.1-X1.3) 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 volatile 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.

X1.5 The values for total volatile sulfur and individual components are reported on the certificate of analysis as follows:

X1.5.1 The values for the total volatile sulfur and individual components from both the first and second analysis in X1.4, along with the date of analyses.

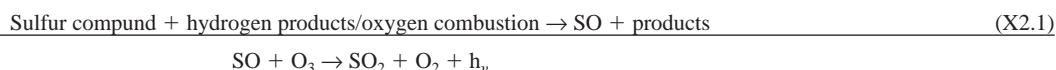
X1.5.1.1 The cylinder number, concentration and NIST or NMI SRM/NTRM batch ID from the NIST reference standard used in the standard analysis.

X1.5.1.2 The total sulfur reported must include all components including any unknowns. The total of the unknowns shall also be reported in ppm.

**X2. CHEMILUMINESCENCE REACTION MODELS**

Gas chromatography with sulfur chemiluminescence detection is a powerful means to separate and measure sulfur compounds in complex samples including natural gas, refinery fuel gas, landfill gas and other gaseous fuels (1-3).<sup>6</sup> Two mechanisms have been proposed as the basis for SCD operation.

X2.1 Model 1—One chemical reaction proposed as the basis for SCD operation is shown below (4-9) some background references on sulfur chemistry and chemiluminescence are also given (10-14):



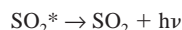
where:

$h_\nu \equiv$  light energy at 300-400 nm.

According to this mechanism, sulfur monoxide and the other combustion products are transferred to a reaction cell. Ozone produced in an ozonator is added to the reaction cell where it reacts with sulfur monoxide. The emitted light is measured using a photomultiplier tube. A vacuum maintains the reaction cell at or below 10 mm of pressure. This prevents the loss of sulfur monoxide and minimizes loss of response due to collisional quenching.

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

X2.2 Model 2—A second reaction mechanism proposed as the basis for SCD operation is depicted below (13-15):



According to this mechanism, sulfur compounds are combusted to  $\text{SO}_2$ . Sulfur dioxide is reduced, in the presence of excess hydrogen to  $\text{H}_2\text{S}$ . Hydrogen sulfide is transferred to a reaction cell. Ozone produced in an ozonator is added to the reaction cell where it reacts with hydrogen sulfide to create excited state sulfur dioxide. Relaxation of sulfur dioxide to the ground state releases a photon. The emitted light is measured using a photomultiplier tube. A vacuum maintains the reaction cell at or below 10 mm of pressure. This minimizes the loss of response due to collisional quenching of excited state sulfur dioxide.

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