Designation: D 5504 – 98

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

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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method provides for the determination of individual volatile sulfur-containing compounds in gaseous fuels including natural 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 1000 mg/m^3, based upon the analysis of a 1-cm^3 sample.

1.2 The test method does not purport to identify all individual sulfur species. The detector response to sulfur is equimolar for all sulfur compounds within the scope (1.1) of this test method; thus unknown individual compounds are determined with equal precision to that of known compounds. Total sulfur content of samples can be estimated from the total of the individual compounds determined.

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:*

D 1072 Test Method for Total Sulfur in Fuel Gases[2]

D 1145 Method of Sampling Natural Gas[2]

D 1945 Test Method for Analysis of Natural Gas by Gas Chromatography[2]

D 2725 Test Method for Hydrogen Sulfide in Natural Gas (Methylene Blue Method)[2]

D 3031 Test Method for Total Sulfur in Natural Gas by Hydrogeneration[2]

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry[2]

D 4626 Practice for Calculation of Gas Chromatographic Response Factors[3]

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography[4]

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_{10}; iso-tetradecane = I-C_{14}).

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

4.1 The analysis of gaseous sulfur compounds is difficult because of the reactive nature of these materials. They pose problems both in sampling and analysis. Analysis is ideally performed on-site to eliminate potential sample deterioration. Sampling must be done using containers proven to be nonreactive, such as Tedlar bags. Laboratory equipment must also be inert and well conditioned to ensure reliable results. Frequent calibration using stable standards is required in sulfur analysis.

4.2 A 1-cm^3 sample of the fuel gas to be analyzed is injected into a gas chromatograph where it is passed through a 60-m, megabore, thick film, methyl silicone liquid phase, open tubular partitioning column, and separated into its individual constituents.

4.3 *Sulfur Chemiluminescence Detection*—As sulfur compounds elute from the gas chromatographic column, they are combusted. These combustion 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 fixed gas and hydrocarbon determinations are being made.

4.4 *Other Detectors*—This test method is written for the sulfur chemiluminescent detector. Other methods are available

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[1] This test method is under the jurisdiction of ASTM Committee D-3 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] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

using the lead acetate rate of stain and flame photometric detectors. Test Method D 6228 is the flame photometric detector method.

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 that has the following performance characteristics can be used:

6.1.1 *Column Temperature Programmer*—The chromatograph 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 retention time repeatability of 0.05 min (3 s) throughout the scope of this analysis.

6.1.2 *Sample Inlet System*—The sample inlet system must be capable of operating continuously at a temperature up to the maximum column temperature used. A splitting injector is recommended, capable of splitless or accurate split control in the range of 10:1 to 50:1. An automated gas sampling valve is also recommended. The inlet system must be well conditioned and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds.

6.1.3 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical to optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. The gas flow rate is measured by any appropriate means and the required gas flow indicated by the use of a pressure gage. Mass flow controllers, capable of maintaining gas flow constant to ± 1 % at the required flow rates 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 *Detector*—Combustion of the sample can be accomplished using a flame ionization detector (FID), a flameless furnace, or a combination. The combusted sample is then delivered to the sulfur chemiluminescence detector (SCD).

6.1.4.1 *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. The detector must be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. Connection of the column to the detector must be such that no temperature below the column temperature exists. The detector design must be such to allow the insertion of the SCD sampling probe into the flame without interrupting the detection of the hydrocarbon response. Initial flow rates of hydrogen and air should be set to the SCD manufactures recommendations. A hydrogen rich flame is required to fully combust the hydrocarbons present in the sample. This will afford less sensitivity for the hydrocarbon components and, if simultaneous detection is needed, the FID should be used in series with the flameless furnace. Air should be used for makeup gas for a capillary column.

TABLE 1 Typical Gas Chromatographic Operating Parameters

Injector, gas sample loop: 150°C	1.0 cm^3	
Injector, splitless:	150°C	100 % sample to column
Flame ionization detector: 250°C	H2:	200 cm^3/min
	Air:	400 cm^3/min
	Air (He):	20 cm^3/min
SCD: output at 0–1 V cell pressure at 8.7 torr		
Column Oven: 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 14.5 kPa (20 psig) or approximately 11 cm^3/min		

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 of a tower assembly that contains a furnace element, thermocouple, 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 *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.

6.1.4.4 Operation of the SCD is based on the chemiluminescence (light-producing reaction) from the reaction of ozone with a sulfur compound produced from the combustion of the analyte. A vacuum pump pulls the combustion products into a reaction cell at low pressure, where excess ozone is added. Light produced from the subsequent reaction is detected with a blue sensitive photomultiplier tube and the signal is amplified for display or output to a data 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).

$$\text{Sulfur compound} + \text{hydrogen/air flame} \rightarrow SO + \text{products} \tag{1}$$

$$SO + O_3 \rightarrow SO_2 + O_2 + Hv \tag{2}$$

where Hv = chemiluminescent light energy.

6.2 *Column*—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 column shall provide retention and resolution characteristics as listed in Table 2 and illustrated in Fig. 1. The column will also demonstrate a sufficiently low liquid phase bleed at high temperature such that no loss of the SCD sulfur response is encountered while operating the column at 200°C.

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. A dual channel system is useful for simultaneous presentation of both the FID and SCD signals. The device and software must have the following capabilities:

TABLE 2 Retention Time—4u SPB1

Conditions as in Table 1

Compound	Ave. RT min	Compound	Ave. RT min
Methane	1.458	?S	16.363
Ethylene	1.733	*n*-Octane	16.423
Ethane	1.730	?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	5.578	*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	?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
CP/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

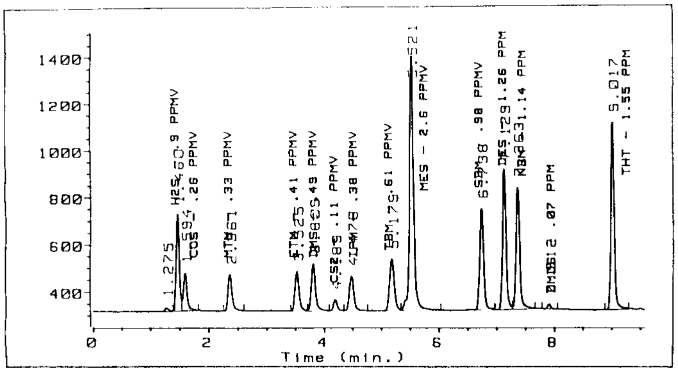

FIG. 1 Standard Perm Tube Analysis Run

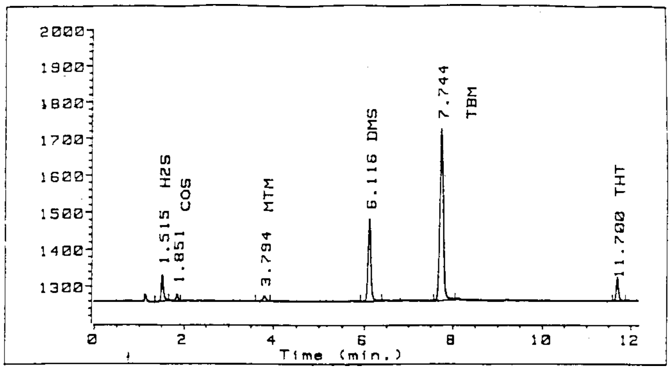

FIG. 2 Natural Gas Analysis-Sulfur Compounds

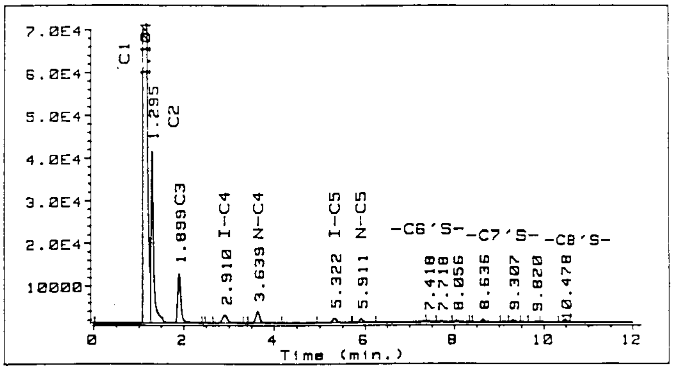

FIG. 3 Natural Gas Analysis-Hydrocarbon Compounds

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.

6.3.2.4 Calculation and use of response factors.

6.3.2.5 External standard calculation and data presentation.

7. 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 may be flammable and harmful or fatal if ingested or inhaled.

7.4 *Carrier Gas*—Helium or nitrogen of high purity (**Warning**—See Note 2). 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 6.1.3).

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

7.5 *Hydrogen*—Hydrogen of high purity (for example, hydrocarbon free) is used as fuel for the flame ionization detector (FID) (**Warning**—See Note 3).

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

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

NOTE 4—**Warning:** Compressed air can be a gas under high pressure and 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. Hydrogen and air flows are critical for the FID reducing flame to give the SCD optimum sensitivity.

8.2 *SCD*—Place in service in accordance with the manufacturer's instructions. When using the FID as the only combustion method, the probe placement location is critical to maximum sensitivity. During optiminization, the oxidant/fuel ratio is critical to provide complete combustion of the hydrocarabon components. Too rich a flame can produce incomplete combustion as seen by a small methane peak before H_2S (see Fig. 4). Matrix interference can be seen by varying the sample size and measuring response. If response stays the same or decreases with increasing sample size, the burner efficiency is questionable (see Figs. 5 and 6). Samples with high hydrocarbon interference will require dual combustion using the FID and flameless furnace in series. Simultaneous detection of hydrocarbons with the FID and sulfur detection with the SCD is afforded in this configuration. After sufficient equilibration time (usually overnight), adjust the detector output signal or integrator input signal to approximately zero. Monitor the signal for several minutes to verify compliance with the specified signal noise and drift.

8.2.1 *Sample Injection*—Inject 1.0 cm^3 from a sample loop of the calibration standard gas mix that covers the concentrations of interest.

8.2.2 *Detector Response Calibration*—Analyze the calibration gas and obtain the chromatograms. Calculate the relative response factor for each sulfur compound:

$$F_n = (C_n/A_n \qquad (3)$$

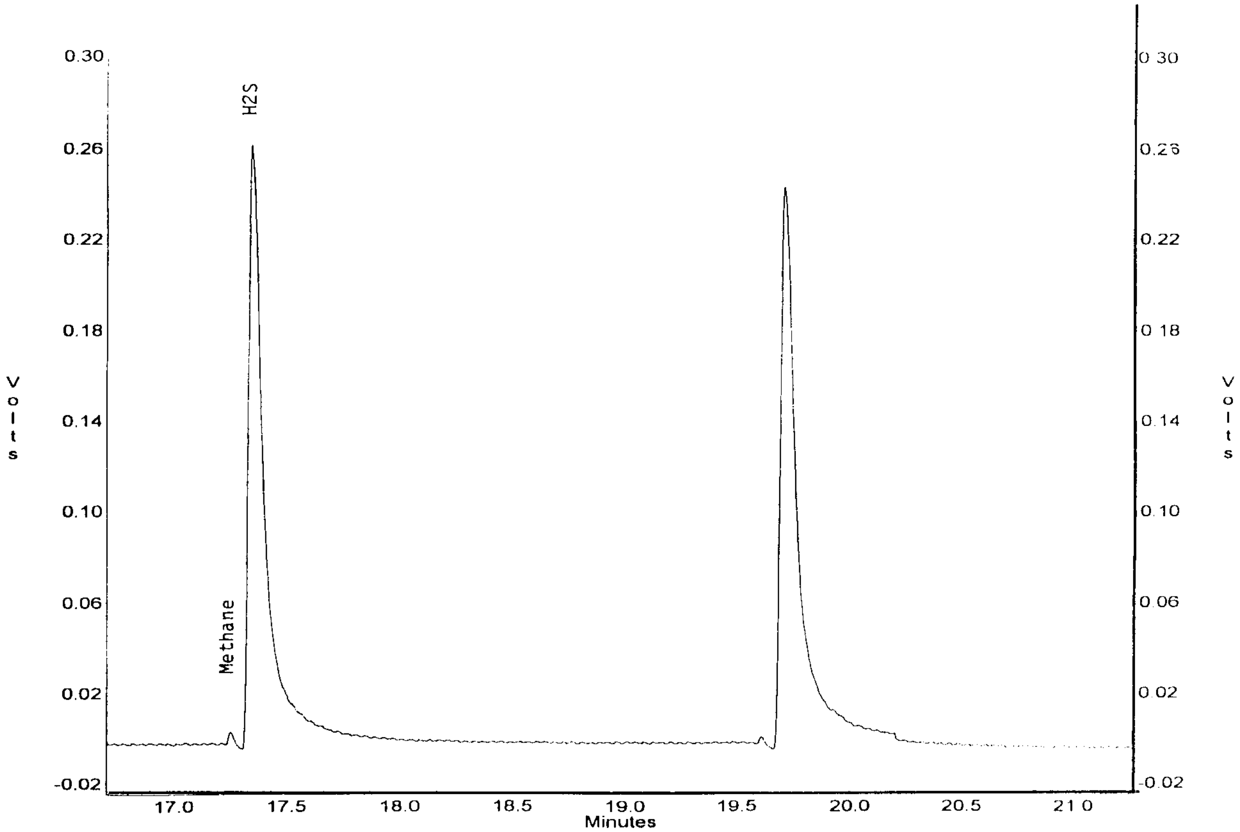

FIG. 4 Too Rich of a Combustion Flame Will Cause Methane Breakthrough

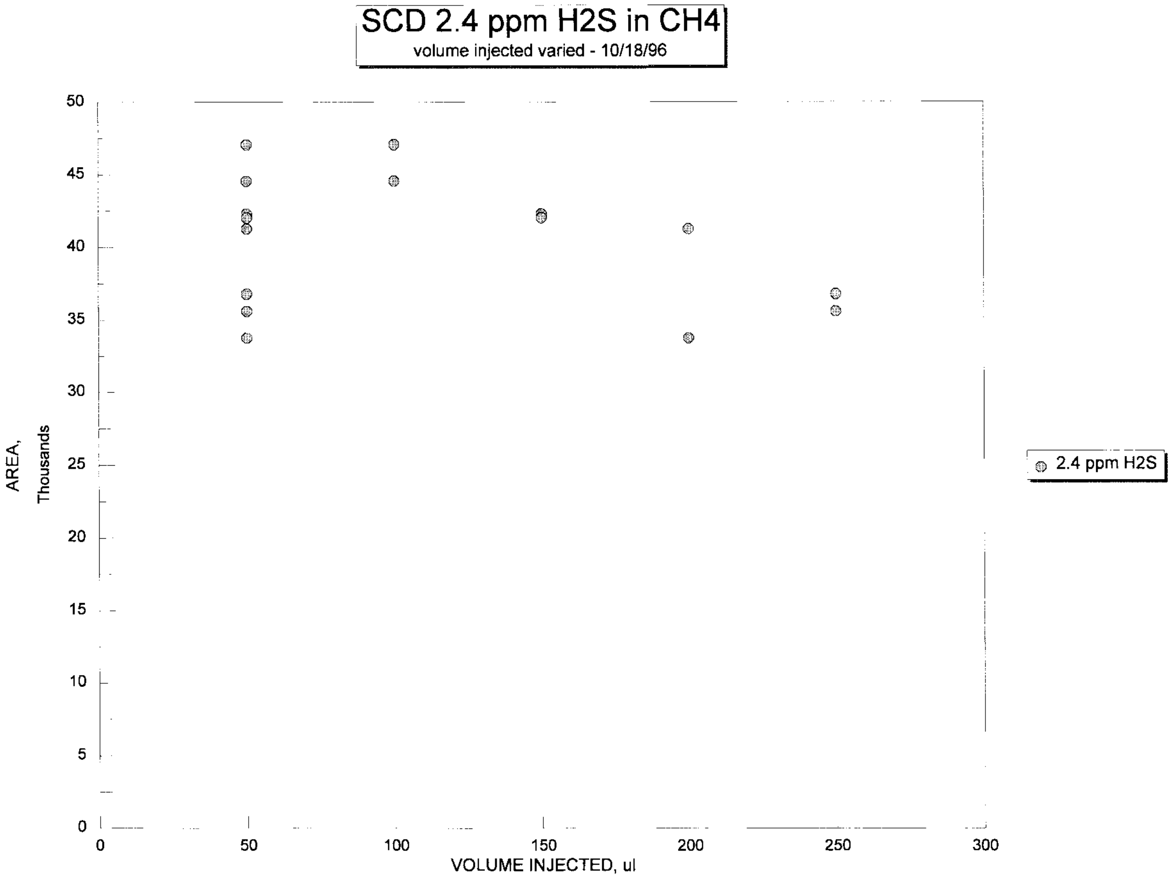

FIG. 5 Example of Matrix Interference. Changing the Sample Size Should Give a Change in Response

where:

F_n = response factor of compound.
C_n = concentration of the sulfur compound in the mixture.
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 % of F_n for dimethyl 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 *Sampling and Preparation of Sample Aliquots*:

9.1.1 *Gas Samples*—Samples will be supplied to the laboratory in specially conditioned high-pressure sample containers or in Tedlar bags at atmospheric pressure. Such bags for H_2S analysis must be run within 24 h of sampling.

9.2 Table 1 lists the gas chromatograph operating parameters. Table 2 provides a partial listing of the retention times of light sulfur compounds. Figs. 1 and 2 illustrate typical analyses of a standard mixture and natural gas.

9.3 *External Standard Calibration*—At least once a day or as frequently as deemed expedient, analyze the calibration standard mix and determine standard response factors (see 10.1).

9.4 *Sample Analysis*—Purge the lines from the sample container through the sample loop in the gas chromatograph. Inject 1 cc with a gas sampling valve as in 8.2.1. If the sample size exceeds the linear range of the detector a split injection should be used. Run the analysis per the conditions specified in Table 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).

10. Calculation

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^3 sample loop with no split.

1 ppmv DMS = 2.54 mg/M^3 (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 = 8.27×10^{-2} (in terms of picograms sulfur per peak) or

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

NOTE 5—Since detector response is proportional to weight sulfur, all mono sulfur compounds (COS, H2S, DMS, etc.) will have approximately the same response factor for picograms S or ppmv (see 8.2.2).

11. Report

11.1 Report the identification and concentration of each individual sulfur compound. The sum of all sulfur components

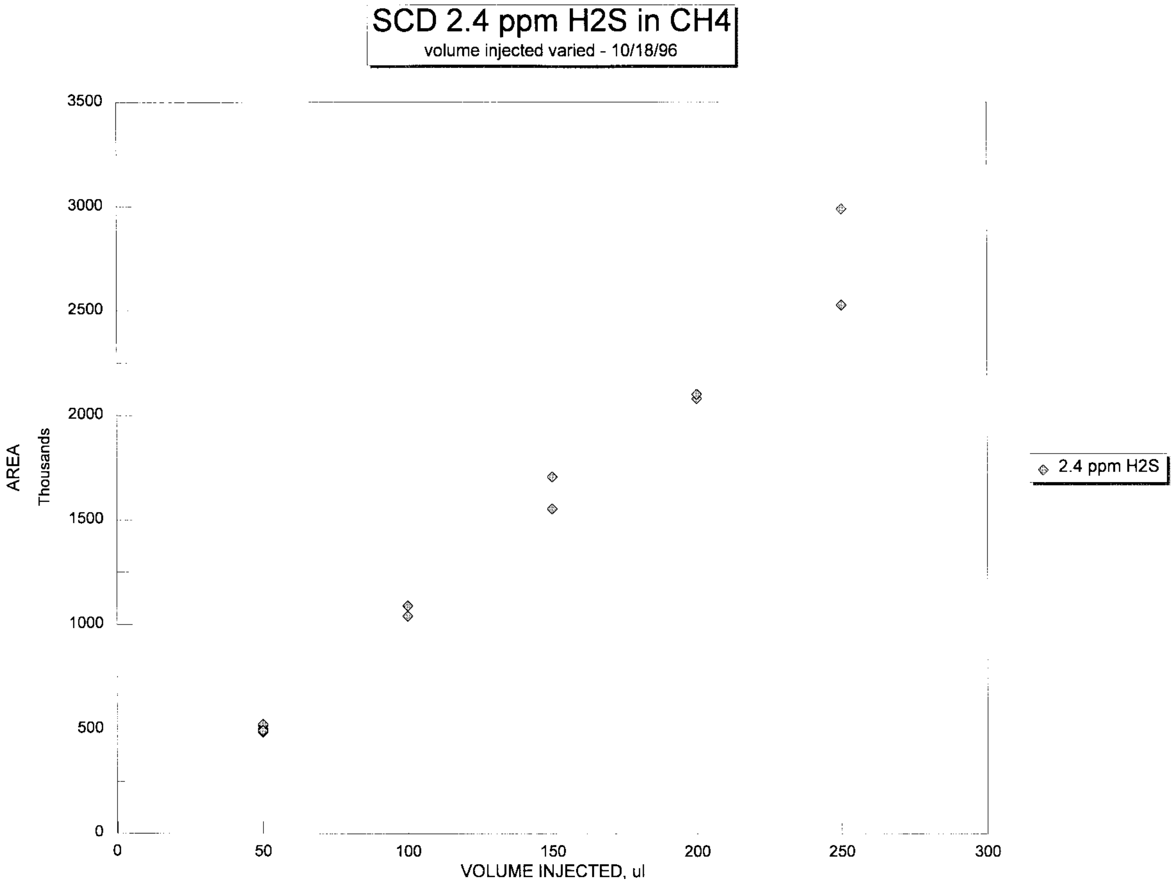

FIG. 6 Example of Typical Response Curve with Varying Sample Size

TABLE 3 Sulfur Gas Standard

Compound	Mol. Wt.	Density	BP°C	%S	(Conversion) Mg/M3 per PPMV
Hydrogen sulfide (H_2S)	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_2)	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

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

detected to the nearest picogram, calculated as sulfur (pg S) can be used to calculate the total sulfur.

12. Precision and Bias

12.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory 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

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