Designation: D 6968 – 03

Standard Test Method for Simultaneous Measurement of Sulfur Compounds and Minor Hydrocarbons in Natural Gas and Gaseous Fuels by Gas Chromatography and Atomic Emission Detection[1]

This standard is issued under the fixed designation D 6968; 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 for the determination of volatile sulfur-containing compounds and minor hydrocarbons in gaseous fuels including components with higher molar mass than that of propane in a high methane gas, by gas chromatography (GC) and atomic emission detection (AED). Hydrocarbons include individual aliphatic components from C_4 to C_6, aromatic components and groups of hydrocarbons classified according to carbon numbers up to C_{12} at least, such as C_6-C_7, C_7-C_8, C_8-C_9 and C_9-C_{10}, etc. The detection range for sulfur and carbon containing compounds is approximately 20 to 100 000 picograms (pg). This is roughly equivalent to 0.04 to 200 mg/m^3 sulfur or carbon based upon the analysis of a 0.25 mL sample.

1.2 This test method describes a GC-AED method employing a specific capillary GC column as an illustration for natural gas and other gaseous fuel containing low percentages of ethane and propane. Alternative GC columns and instrument parameters may be used in this analysis optimized for different types of gaseous fuel, provided that appropriate separation of the compounds of interest can be achieved.

1.3 This test method does not intend to identify all individual sulfur species. Unknown sulfur compounds are measured as mono-sulfur containing compounds. Total sulfur content of a sample can be found by summing up sulfur content present in all sulfur species.

1.4 This method is not a Detailed Hydrocarbon Analysis (DHA) method and does not intend to identify all individual hydrocarbon species. Aliphatic hydrocarbon components lighter than *n*-hexane, benzene, toluene, ethyl benzene, *m*,*p*-xylenes and *o*-xylene (BTEX) are generally separated and identified individually. Higher molar mass hydrocarbons are determined as groups based on carbon number, excluding BTEX. The total carbon content of propane and higher molar mass components in a sample can be found by summing up carbon content present in all species containing carbon.

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

1.6 *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:* [2]

D 1265 Practice for Sampling Liquefied Petroleum Gas (Manual Method)

D 1945 Test Method for Analysis of Natural Gas by Gas Chromatography

D 3609 Practice for Calibration Techniques Using Permeation Tubes

D 4626 Practice for Calculation of Gas Chromatographic Response Factors

D 5287 Test Method of Automatic Sampling of Gaseous Fuels

D 5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

D 5623 Test Method for Sulfur Compound in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection

D 6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection

E 840 Practice for Using Atomic Emission Detectors in Gas Chromatography

2.2 *Other References:*

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

ISO 19739 Natural Gas—Determination of Sulfur Compounds by Gas chromatography[3]

GPA 2199 Determination—Specific Sulfur Compounds[4]

"Improved Measurement of Sulfur and Nitrogen Compounds in Refinery Liquids Using Gas Chromatography—Atomic Emission Detection," *Journal of Chromatographic Science*, 36, No 9, September, 1998, p. 435.

3. Terminology

3.1 *Abbreviations*:

3.1.1 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 butane = *n*-C_4; *Iso*-pentane = *i*-C_5, aliphatic hydrocarbons heavier than *n*-heptane but not heavier than *n*-octane = C_7-C_8).

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

4. Summary of Test Method

4.1 The sampling and analysis of gaseous sulfur compounds is challenging due to the reactivity of these compounds. Samples should be collected and stored in containers that are non-reactive to sulfur compounds, such as thin silica-lined stainless steel vessels and Tedlar® bags with polypropylene fittings or the equivalent. Sample containers should be filled and purged at least three times to ensure representative sampling. Laboratory equipment must also be inert, well conditioned and passivated with a gas containing the sulfur compounds of interest to ensure reliable results. Frequent calibration using stable standards is required. Samples should be analyzed as quickly as possible not beyond the proven storage time after collection to minimize sample deterioration. If the stability of analyzed sulfur components is experimentally proven, the time between collection and analysis may be lengthened.

4.2 A 0.25 mL sample of the fuel gas is injected into a gas chromatograph where it is passed through a 30 meter, 0.32 mm I.D., thick film, methyl silicone liquid phase, open tubular partitioning column, or a column capable of separating the same target sulfur and hydrocarbon components. A wider bore (0.53 mm I.D.) column may be used for better compound separation and/or for lower detection limits using a larger injection volume.

4.3 *Atomic Emission Detectors*—All sulfur and carbon compounds can be detected by this technique. GC-AED has recently been developed for analysis of many elements, including sulfur and carbon. The AED uses a microwave induced helium plasma to disassociate molecules and atomize/excite elements at high temperature (~5000°C). The characteristic emission lines from specific excited atoms are detected by a Photo Diode Array detector (PDA). Sulfur emission is measured at 181 nm. Carbon emission (193 and 179 nm) can be monitored simultaneously. The amount of light emitted at each wavelength is proportional to the concentration of sulfur or carbon. Carbon and hydrogen emission can also be measured at 498 and 486 nm, respectively, in a separate run using the same GC procedure for additional elemental information. However, hydrogen response is not linear and a quadratic calibration curve must be constructed for hydrogen measurement. GC-AED offers a very high degree of selectivity and a wide dynamic range for detection of various types of compound. The AED, just like the Sulfur Chemiluminescence Detector (SCD) employed in Test Method D 5504 for sulfur analysis, has the advantage over other types of detector in that the elemental response is generally independent of the structure of the associated molecule containing the element of interest. It offers the potential of using a single standard to calibrate the instrument for determination of all sulfur and hydrocarbon components, diminishing the need of multiple standards that may not be commercially available or that are prohibitively expensive to prepare. The real-time simultaneous measurement of carbon and sulfur content by AED provides the elemental ratio of carbon to sulfur for each sulfur compound, which along with retention time can be used to confirm the identity of sulfur compounds. The elemental ratio of carbon to hydrogen can be used to differentiate aromatic compounds from aliphatic compounds for identification and confirmation as well.

4.4 *Other Detectors*—This test method is written primarily for the atomic emission detector. The same GC method can be employed with other detectors provided they have sufficient sensitivity and response to all sulfur and hydrocarbon compounds of interest in the required measurement range. A FID-SCD combination detector may satisfy these criteria.

5. Significance and Use

5.1 Gaseous fuels, such as natural gas, petroleum gases and bio-gases, contain varying amounts and types of sulfur compounds. They are generally odorous, corrosive to equipment, and can inhibit or destroy catalysts employed in gas processing. Their accurate measurement is essential to gas processing, operation and utilization, and may be of regulatory interest.

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

5.3 This method offers a technique to determine individual sulfur species in gaseous fuel and the total sulfur content by calculation.

5.4 Gas chromatography is commonly and extensively used to determine all components in gaseous fuels including fixed gas and organic components (Test Methods D 1945 and D 1946). Major components measured are often used for the determination of gas property, such as heating value and relative density. Higher molar mass hydrocarbons are of

[3] Available from International Organization for Standardization (ISO), 1 rue de Varembé, Case postale 56, CH-1211, Geneva 20, Switzerland.

[4] Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145.

interest even when present in small amounts because their larger impact on heating value, hydrocarbon dew point and gas quality relating to gas operation, gas utilization and environmental impacts.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph of standard manufacture with hardware and software necessary for interfacing to an atomic emission detector and for the intended application and performance.

6.1.1 *Sample Inlet System*—Gas samples are introduced to the GC using an automated or manually operated non-reactive stainless steel gas sampling valve heated continuously at a temperature significantly (~10°C) above the temperature at which the gas was sampled to avoid sample condensation and discrimination. Inert tubing made of non-permeable, non-sorbing and non-reactive materials, as short as possible and heat traced at the same temperature, should be employed for transferring the sample from a sample container to the gas sampling valve and to the GC inlet system. Silica-coated 316 stainless steel (s.s.) tubing is often employed. A fixed volume, 0.25 mL, sampling loop made of the same non-reactive materials is used to avoid possible decomposition or absorption of reactive species. Other size fixed-volume sampling loops may be used for different concentration ranges. An on-column or a split/splitless injection system operated at the splitless mode or at the split mode with a low split ratio may be used with capillary columns. One should avoid using a split liner with a split ratio set to zero as a means of achieving splitless injection. A one-meter section of deactivated pre-column attached to the front of the analytical column is recommended. The inlet system must be well conditioned and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds, such as *tert*-butyl mercaptan.

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

6.1.3 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range of 30 to 250°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.

6.1.4 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical for optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. The gas flow rate is measured by any appropriate means and the required gas flow indicated by the use of a pressure gauge. Mass flow controllers, capable of maintaining gas flow constant to ± 1 % at the required flow rates 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) is satisfactory.

6.1.5 *Detector*—An atomic emission detector calibrated in the carbon and sulfur specific mode is used in this method. Other detectors capable of simultaneous measurement of sulfur and carbon as stated in 4.4 are not covered in this test method. The detector is set according to the manufacturer's specifications and tuned to the optimal sensitivity and selectivity for the application.

6.1.5.1 When sulfur and hydrocarbon compounds are decomposed in the high temperature AED zone they quantitatively produce excited state atomic sulfur and carbon species. A diode array detector detects the light emitted from these species as they relax to ground states. Carbon containing components are simultaneously detected at 179 and 193 nm wavelength for different sensitivity measurements extending the linear concentration range. Sulfur species are detected at 181 nm with a high selectivity. The selectivity is normally better than 3×10^4, by mass of sulfur to mass of carbon. The detector response is linear with respect to sulfur and carbon concentrations. The dynamic range of this linear relationship is better than 1×10^4.

6.2 *Column*—A 30 m by 0.32 mm ID fused silica open tubular column containing a 4 µm film thickness of bonded methyl silicone liquid phase is used. The column shall provide adequate retention and resolution characteristics under the experimental conditions described in 7.3. Other columns that can provide equivalent or desirable separation can be employed as well. For example, a 60 m by 0.53 mm ID column with a 5 µm film thickness of bonded methyl silicone liquid phase can be used with a larger sample volume injection for better resolution and a lower detection limit when needed.

6.3 *Data Acquisition*:

6.3.1 The SRF should not exceed 10 % difference for all sulfur components. The CRF should not exceed 10 % difference for all hydrocarbon components as well. A multiple component calibration standard or a control standard or sample should be used daily to verify this. The day-to-day variation of F_n should not be greater than 5 %. The detector should be maintained, flow rates readjusted to optimize the detector performance, and the detector should be fully recalibrated for optimal sensitivity and linearity if F_n exceeds this limitation. The device and software must have the following capabilities:

6.3.1.1 Graphic presentation of the chromatogram and AED spectra,

6.3.1.2 Digital display of chromatographic peak areas,

6.3.1.3 Identification of peaks by retention time or relative retention time, or both,

6.3.1.4 Calculation and use of response factors,

6.3.1.5 External standard calculation and data presentation, and

6.3.1.6 Instrument control for AED operation, such as reagent gas and venting control.

7. Reagents and Materials

7.1 *Compressed Cylinder Gas Standards*—Gas standards should be stable, of high purity, and of the highest available accuracy. Blended gaseous sulfur and hydrocarbon standards may be used if a means to ensure accuracy and stability of the mixture is available. Gas standards can be a source of error if their stability during storage cannot be guaranteed.

7.1.1 *Compressed Cylinder Gas Standards*—Compressed gas 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 standard cited in Test Method D 5504 can be used to ensure the quality of standards and to establish traceability to a NIST or Nmi standard reference material.

7.1.2 *Compressed Gas Standard Delivery System*—Pressure regulators, gas lines and fittings must be inert, appropriate for the delivery of sulfur gases and well passivated.

NOTE 1—**Warning:** Sulfur and hydrocarbon compounds may be flammable. Sulfur and aromatic compounds may be harmful if ingested or inhaled.

7.2 *Sulfur Permeation Tube Standards*—Gaseous standards generated from individual or a combination of certified permeation tubes at a constant temperature and flow rate can be used for all calibrations. The standard concentration is calculated by mass loss and dilution gas flow rate. Impurities permeated from each tube must be detected, measured and accounted for in the mass loss, if they are present above a level of 0.1 % of the permeated sulfur species. Practice D 3609 for calibration techniques using permeation tubes should be enforced.

7.3 *Carrier Gas*—Helium of high purity (99.999 % minimum 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 6.1.4).

NOTE 2—**Warning:** Helium and nitrogen employed are compressed gases under high pressure.

7.4 *Hydrogen*—Hydrogen of high purity (99.999 % minimum purity) is used as fuel for the atomic emission detector (AED) (**Warning**—See Note 3).

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

7.5 *Oxygen*—High purity (99.999 % minimum purity) compressed oxygen is used as the oxidant for the atomic emission detector (AED) (**Warning**—See Note 4).

NOTE 4—**Warning:** Compressed oxygen is a gas under high pressure that supports combustion.

8. Preparation of Apparatus and Calibration

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

8.2 *Atomic Emission Detector*—Place the detector in service according to the manufacturer's instructions. Hydrogen, oxygen and He make-up gas flows are critical and must be properly adjusted according to manufacturer's instructions. The AED plasma source should be maintained and monitored to give consistent and optimum sensitivity. The flow rate may be fine-tuned to achieve equimolar responses for both carbon and sulfur channels. Multiple standards containing different types of sulfur and hydrocarbon compounds may be used to verify equimolar responses. Suggested sulfur compounds include H_2S, COS, IPM, DMS, DMDS, Thiophene and Thiophane. Suggested hydrocarbon compounds include *n*-butane, *n*-pentane, *n*-hexane, benzene and toluene.

TABLE 1 Gas Chromatographic Operating Parameters

Gas Sample Loop	0.25 mL at 125°C
Injection Type	On-column
Carrier Gas	He at 2.4 mL/min.
Column Oven	32°C Hold 4.0 min., 12°C/min. to 225°C, Hold 6 min., or as needed
Detector	Reagent and makeup gas flow as recommended by the AED manufacturer, detector vent on from 0.1 min to 0.1 min before H_2S elutes.

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

$$C_n = (P_s/P_o) \times C_{no} \quad (1)$$

where:

C_n = calculated concentration of a sulfur or hydrocarbon compound on mole or volume basis,
P_s = sampling pressure as absolute,
P_o = laboratory ambient pressure as absolute, and
C_{no} = concentration of the specific sulfur or hydrocarbon compound in the calibration standard.

8.2.2 *Detector Response Calibration*—Analyze calibration gases and obtain the chromatograms and peak areas. Determine the linear range of detector response toward sulfur and carbon using sample injection techniques illustrated in 8.2.1. A linear standard curve is constructed with the linear correlation factor calculated. Calculate the relative sulfur or carbon response factor of each compound at ambient pressure by:

$$F_n = (C_n/A_n) \times L_n \quad (2)$$

where:

F_n = response factor of a compound based on sulfur (Sulfur Response Factor) or carbon (Carbon Response Factor) measurement,
C_n = concentration of the compound in the sampled gas on mole or volume basis,
A_n = peak area of the compound measured, and
L_n = moles of sulfur or carbon in the compound.

Example:

Assume 1.0 ppmv of dimethyl sulfide (DMS) injected onto GC with a 0.25 mL fixed sample loop. The peak areas of its carbon and sulfur responses are 2000 and 500 counts.

1 ppmv DMS = 2 ppmv Carbon = 1 ppmv Sulfur
Carbon Response Factor (CRF) = 2 ppmv Carbon /2000 = 0.001 ppmv Carbon
Sulfur Response Factor (SRF) = 1 ppmv Sulfur /500 = 0.002 ppmv Sulfur

The SRF should not exceed 10 % difference for all sulfur components. The CRF should not exceed 10 % difference for all hydrocarbon components as well. A multiple component calibration standard or a control standard or sample should be used daily to verify this. The day-to-day variation of F_n should not be greater than 5 %. The detector should be maintained,

flow rates readjusted to optimize the detector performance, and the detector should be fully recalibrated for optimal sensitivity and linearity if F_n exceeds this limitation.

8.2.3 *Interferences*—Spectral interference must be minimized for reliable quantitation. Optimizing detector reagent and make-up gas flows, reducing sample injection volume and venting light components, such as methane and ethane, before they enter the detector are acceptable and sometimes necessary ways to improve the performance. A high concentration hydrocarbon component may interfere with the measurement of a closely eluted sulfur compound if their chromatographic separation is not adequate and the selectivity of sulfur measurement over carbon ($> 3\times10^4$) is insufficient. For example, a large amount of propane present in a gaseous fuel sample can interfere with the measurement of carbonyl sulfide when a methyl silicone column is used. The measurement of H_2S may be affected by the presence of a large amount of ethane in gas samples. Different GC column may be employed for better separation of propane and COS or ethane and H_2S. Tests can be conducted to verify possible interferences.

8.2.3.1 *Standard Addition*—Standard addition methods can be employed to identify interferences. Standard addition can be done by simultaneous injection of a gas standard with the sample gas using a 10-port injection valve or by analysis of a sample spiked with a known volume of a standard gas. This standard gas should contain those possible interfered components. RTs and recoveries of spiked components are used to verify possible interferences. Acceptable recoveries for components present at concentrations that fall within the mid range of the linear calibration curve should be better than 90 %. Unacceptable lower or higher recoveries indicate matrix interference or other analysis problems.

8.2.3.2 *Matrix Dilution*—Sample gas can be diluted with a pure inert gas and analyzed to detect and sometimes reduce possible interferences.

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

9. Procedure

9.1 *Sampling and Preparation of Sample Aliquots*:

9.1.1 *Gas Samples*—Samples should be supplied to the laboratory in specially conditioned high-pressure sample containers or in Tedlar bags at atmospheric pressure. The sample must be analyzed as soon as possible within 1 to 7 days of sampling depending on the type of storage container.

9.2 *Instrument Setup*—Set up the GC-AED according to the chromatograph operating parameters listed in Table 1.

9.3 *Instrument Performance Check*—Analyze selected control standards or samples, in duplicate if necessary, to verify the chromatographic performance (see 8.3), retention times (Table 1), and response factors (see 8.2.2). Components present in controls must be identified correctly based on RTs. The day to day variation of response factors should not exceed 10 %. System maintenance and recalibration are required if these criteria cannot be met.

9.4 *External Standard Calibration*—At least twice a day or as frequently as necessary, analyze the calibration standard mix to verify the calibration curve determined in 8.2.1 and 8.2.2. and determine the standard response factors for the sample analysis. The difference of response factors found at the beginning and the end of each run or series of runs within 24-h period should not exceed 5 %.

9.5 *Sample Analysis*—Evacuate and purge the lines from the sample container through the sample loop in the gas chromatograph. Inject 0.25 mL with a gas-sampling valve as in 8.2.1. If the sample size exceeds the linear range of the detector, reduce the sample size using a smaller loop or lower sampling pressure. Alternatively, a diluted sample may be used. Run the analysis per the conditions specified in Table 1. Obtain the chromatographic data via a computer-based chromatographic data system. Examine the graphic display for any errors (for example, over-range component data), and repeat the injection and analysis if necessary. The difference between corresponding peak areas of repeated runs should not exceed 5 % for compounds present at concentrations equal to or higher than 50 times of their corresponding detection limits. Standard addition and matrix dilution should be carried out to identify possible interferences and improve qualitative and quantitative determination.

9.6 *Compound Identification*—Sulfur and hydrocarbon compounds are identified by their retention times established during calibration. The carbon and sulfur determined in each compound are used to confirm the identification based on the sulfur/carbon ratio. The amounts of carbon and hydrogen determined at 498 and 486 nm in separate runs can be used for further confirmation of the identity of aromatic hydrocarbons and other unsaturated hydrocarbons based on the carbon/hydrogen ratio. All compounds without matching standards are identified as unknowns. Hydrocarbon groups are classified according to carbon numbers using *n*-alkanes as references. A hydrocarbon group of C_n-C_{n+1} consists of all compounds eluted between nC_n and nC_{n+1} peaks including nC_n and nC_{n+1}.

10. Calculations

10.1 Determine the chromatographic peak area of each component and use the response factor (Eq 2) obtained from the calibration run to calculate the amount of each sulfur or hydrocarbon compound present corrected for injection pressure. The amount of each unknown compound is calculated using the response factor of the closest adjacent calibration compound and reported as the amount of sulfur or carbon.

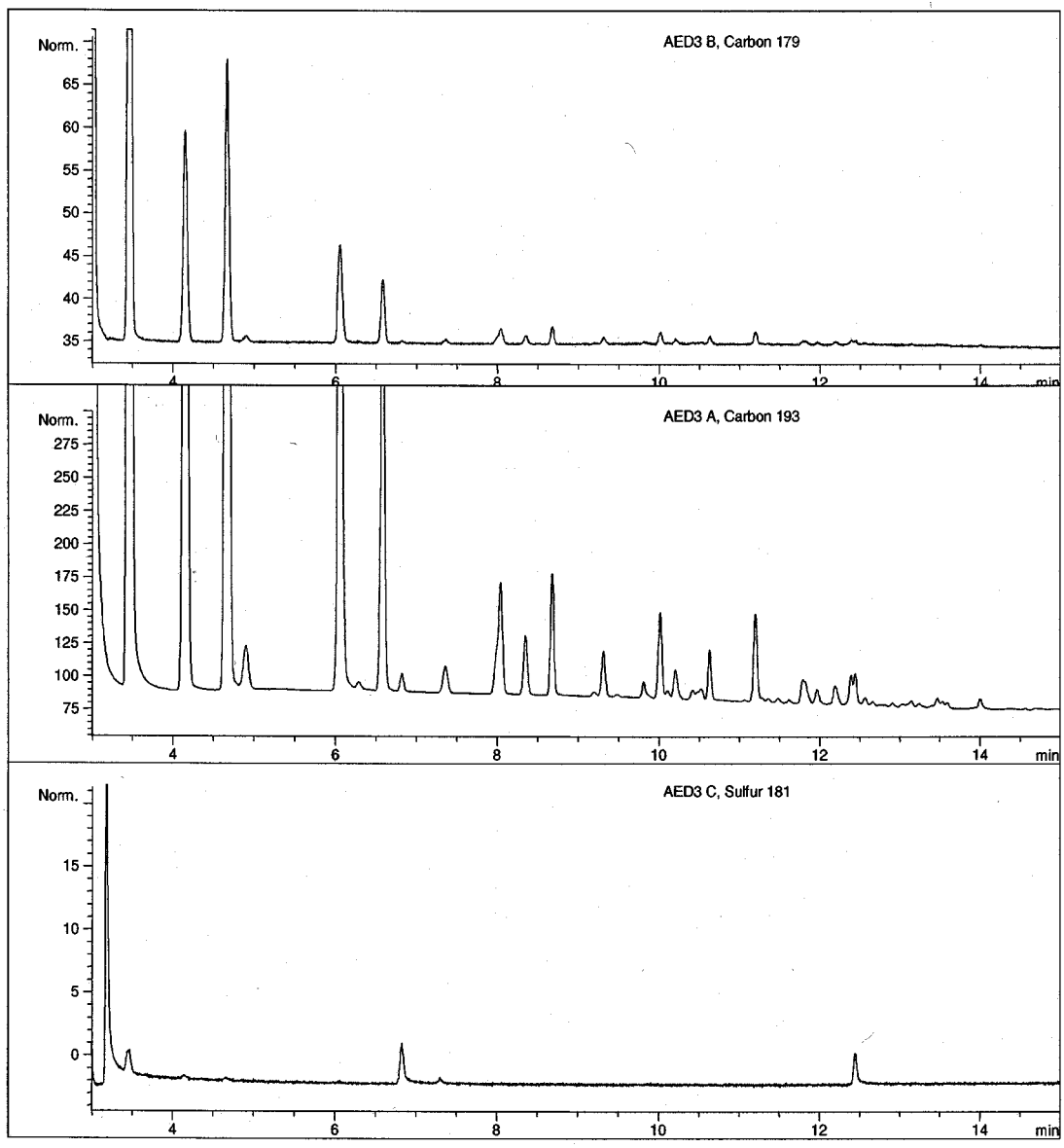

FIG. 1 Chromatograms (C-179, C-193, S-181) of a Composite Natural Gas containing H_2S, COS, DMS and THT

TABLE 2 Retention Times of Various Hydrocarbon and Sulfur Components

RT (min)	Compound	RT (min)	Compound	RT (min)	Compound
3.23	H_2S	7.60	IprSH	12.66	*n*-Octane
3.43	COS	8.03	2-Methylpentane	12.81	THT
3.50	Propane	8.43	TBM	13.43	Ethylbenzene
4.04	*i*-Butane	8.63	NPrSH	13.55	MEDS
4.53	*n*-Butane	8.75	*n*-Hexane	13.66	*m,p*-Xylenes
4.67	MeSH	8.87	MES	14.29	*o*-Xylene
4.72	2,2-Dimethylpropane	9.00	Thiophene	14.42	*n*-Nonane
5.92	*i*-Pentane	10.06	Benzene	15.98	*n*-Decane
6.30	EtSH	10.22	Cyclohexane	17.40	*n*-Undecane
6.47	*n*-Pentane	10.45	DES	18.73	*n*-Dodecane
6.77	DMS	10.85	*n*-Heptane	20.03	*n*-Tridecane
7.23	CS_2	11.45	DMDS	21.23	*n*-Tetradecane
7.27	2,2-Dimethylbutane	11.76	Toluene	22.67	*n*-Pentadecane

$$C_n = (A_n \times P_o/P_n) \times F_n/L_n \quad (3)$$

where:

C_n = concentration of the compound or the compound group in the gas on mole or volume basis (ppmv),
A_n = peak area of the compound or the compound group measured,
F_n = response factor of the compound or an adjacent compound based on carbon or sulfur detection (ppmv/unit area),
P_o = laboratory ambient pressure,
P_n = sampling pressure,
L_n = moles of sulfur or carbon in the compound,
L_n = 1 for all unknown sulfur compounds reported as mono-sulfur compounds, and

L_n = carbon number (x) for the hydrocarbon group of C_x-C_{x+1} reported as C_x.

10.2 Total sulfur can be calculated by summing up sulfur content present in all sulfur species.

$$S_{total} = \sum(L_n \times C_n) \quad (4)$$

where:

C_n = concentration of the sulfur compound on mole or volume basis (ppmv), and

L_n = moles of sulfur in the compound.

10.3 Total carbon of propane and heavier components in a sample can be calculated by summing up carbon content present in all carbon species.

$$C_{total} = \sum(L_n \times C_n) \quad (5)$$

where:

C_n = concentration of the carbon compound on mole or volume basis (ppmv), and

L_n = moles of carbon in the compound.

10.4 *Unit Conversion*:

$C_n(mg/m^3) = C_n(ppmv) \times$ relative molecular mass of the compound/ molar volume in liter

$S_{total}(mg/m^3) = S_{total}(ppmv) \times$ relative atomic mass of sulfur/ molar volume in liter

$C_{total}(mg/m^3) = C_{total}(ppmv) \times$ relative atomic mass of carbon/ molar volume in liter

11. Report

11.1 Report the identification and concentration of each individual sulfur, C_5-C_6 hydrocarbon and aromatic compounds (benzene, toluene, ethylbenzene and xylenes), and groups of C_6+ hydrocarbon, C_n-C_{n+1}, such as C_6-C_7, C_7-C_8, C_8-C_9, and C_9-C_{10}, etc., in ppmv. Report the sum of all sulfur components detected to the nearest ppmv or mg/M^3 as total sulfur.

12. Precision and Bias

12.1 *Precision*—This standard has not yet undergone an interlaboratory study to substantiate the listed precision data. The precision of this test method is determined based on a sulfur standard methane mix containing COS, DMS and THT, which is stable during the testing period, and a natural gas standard containing alkanes from C_1-C_6 and benzene. The statistical examination of the laboratory test results is as follows:

12.1.1 *Repeatability (Single Operator and Apparatus)*—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.

Compound	ppmv	Repeatability
COS	3.00	± 0.23
DMS	4.00	± 0.30
THT	6.00	± 0.29
n-Pentane	1000	± 38
n-Hexane	530	± 36
Benzene	530	± 53

12.1.2 *Reproducibility (Different Operators, Apparatus and Laboratories)*—No hydrocarbon reproducibility data is accessible at this time. Sulfur reference samples stable over a long testing period, which are required for this determination, are not available at this time, reproducibilty cannot be determined.

12.2 *Bias*—Bias of hydrocarbon measurement is not determined yet. Since there is no accepted sulfur reference material for determining the bias of sulfur measurement, no statement on this can be made.

13. Keywords

13.1 atomic emission detection; extended gas analysis; gas chromatography; hydrocarbons; odorants; sulfur compounds; total sulfur