Designation: D6968 – 03 (Reapproved 2015)

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 D6968; 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 to be regarded as standard. No other units of measurement are included in this standard.

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]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method
D1945 Test Method for Analysis of Natural Gas by Gas Chromatography
D1946 Practice for Analysis of Reformed Gas by Gas Chromatography
D3609 Practice for Calibration Techniques Using Permeation Tubes
D4626 Practice for Calculation of Gas Chromatographic Response Factors
D5287 Practice for Automatic Sampling of Gaseous Fuels
D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
D5623 Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection
D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection
E840 Practice for Using Flame Photometric Detectors in Gas Chromatography

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[1] This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.06.02 on Analysis of Minor Constituents by Gas Chromatography.

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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.

2.2 *Other References:*

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 D5504 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

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[3] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

[4] Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, http://www.gasprocessors.com.

gas and organic components (Test Methods D1945 and D1946). 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 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*—A30 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