Designation: ~~D5623 – 94 (Reapproved 2014)~~ D5623 – 19

Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection[1]

This standard is issued under the fixed designation D5623; 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~~ Scope*

1.1 This test method covers the determination of volatile sulfur-containing compounds in light petroleum liquids. This test method is applicable to distillates, gasoline motor fuels (including those containing oxygenates) and other petroleum liquids with a final boiling point of approximately ~~230°C (450°F)~~230 °C (450 °F) or lower at atmospheric pressure. The applicable concentration range will vary to some extent depending on the nature of the sample and the instrumentation used; however, in most cases, the test method is applicable to the determination of individual sulfur species at levels of ~~0.1~~0.1 mg/kg to ~~100~~ 100 mg ~~mg/kg.~~/kg.

1.2 The test method does not purport to identify all individual sulfur components. Detector response to sulfur is linear and essentially equimolar for all sulfur compounds within the scope (1.1) of this test method; thus both unidentified and known individual compounds are determined. However, many sulfur compounds, for example, hydrogen sulfide and mercaptans, are reactive and their concentration in samples may change during sampling and analysis. Coincidently, the total sulfur content of samples is estimated from the sum of the individual compounds determined; however, this test method is not the preferred method for determination of total sulfur.

1.3 The values stated in SI units are to be regarded as ~~the~~ standard. The values given in parentheses ~~are for information only.~~ after SI units are provided for information only and are not considered standard.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
D4626 Practice for Calculation of Gas Chromatographic Response Factors
D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

2.2 *Other Standard:*

GPA 2199 Determination of Specific Sulfur Compounds by Capillary Gas Chromatography and Sulfur Chemiluminescence Detection

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography Methods.

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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.

***A Summary of Changes section appears at the end of this standard**

3. Summary of Test Method

3.1 The sample is analyzed by gas chromatography with an appropriate sulfur selective detector. Calibration is achieved by the use of an appropriate internal or external standard. All sulfur compounds are assumed to produce equivalent response as sulfur.

3.2 *Sulfur Detection*— As sulfur compounds elute from the gas chromatographic column they are quantified by a sulfur selective detector that produces a linear and equimolar response to sulfur compounds; for example, a sulfur chemiluminescence detector or atomic emission detector used in the sulfur channel.

4. Significance and Use

4.1 Gas chromatography with sulfur selective detection provides a rapid means to identify and quantify sulfur compounds in various petroleum feeds and products. Often these materials contain varying amounts and types of sulfur compounds. Many sulfur compounds are odorous, corrosive to equipment, and inhibit or destroy catalysts employed in downstream processing. The ability to speciate sulfur compounds in various petroleum liquids is useful in controlling sulfur compounds in finished products and is frequently more important than knowledge of the total sulfur content alone.

5. Apparatus

5.1 *Chromatograph*—Use a gas chromatograph (GC) that has the following performance characteristics:

5.1.1 *Column Temperature ~~Programmer —~~Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range sufficient for separation of the components of interest. The programming rate must be sufficiently reproducible to obtain retention time repeatability of ~~0.05 min (3 s)~~ 0.05 min (3 s) throughout the scope of this analysis.

5.1.2 *Sample Inlet System*—The sample inlet system must have variable temperature control capable of operating continuously at a temperature up to the maximum column temperature employed. The sample inlet system must allow a constant volume of liquid sample to be injected by means of a syringe or liquid sampling valve.

5.1.3 *Carrier and Detector Gas ~~Control —~~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 or mass flow controllers capable of maintaining gas flow constant to ±1 % at the required flow rates. The gas flow rate is measured by any appropriate means. The supply pressure of the gas delivered to the gas chromatograph must be at least ~~70 kPa (10 psig)~~ 70 kPa (10 psig) greater than the regulated gas at the instrument to compensate for the system back pressure of the flow controllers. In general, a supply pressure of ~~550 kPa (80 psig)~~ 550 kPa (80 psig) is satisfactory.

5.1.4 *Cryogenic Column Cooling*—An initial column starting temperature below ambient temperature may be required to provide complete separation of all of the sulfur gases when present in the sample. This is typically provided by adding a source of either liquid carbon dioxide or liquid nitrogen, controlled through the oven temperature circuitry.

5.1.5 *Detector*—A sulfur selective detector is used and shall meet or exceed the following specifications: (*1*) linearity of 10^4, (*2*) ~~5 pg~~ 5 pg sulfur/s minimum detectability, (*3*) approximate equimolar response on a sulfur basis, (*4*) no interference or quenching from co-eluting hydrocarbons at the GC sampling volumes used.

5.2 *Column*—Any column providing adequate resolution of the components of interest may be used. Using the column and typical operating conditions as specified in 5.2.1, the retention times of some sulfur compounds will be those shown in Table 1. The column must demonstrate a sufficiently low liquid phase bleed at high temperature, such that loss of the detector response is not encountered while operating at the highest temperature required for the analysis.

5.2.1 *Typical Operating Conditions:*

5.2.1.1 *Column*—~~30 m by 0.32 mm~~ 30 m by 0.32 mm inside diameter fused silica wall coated open tube (WCOT) column, ~~4 µm~~4 µm thick film of methylsilicone.

5.2.1.2 *Sample size*—~~0.1~~ 0.1 µL to ~~2.0 µL.~~2.0 µL.

5.2.1.3 *Injector*—Temperature ~~275°C;~~275 °C; Split ratio: 10:1 (10 % to column).

5.2.1.4 *Column Oven*—~~10°C for 3 min,~~10 °C for 3 min, 10 °C ~~10°C/min /~~min to ~~250°C,~~250 °C, hold as required.

5.2.1.5 *Carrier Gas*—Helium, Head pressure: ~~70 to 86 kPa (10 to 13 psig).~~70 kPa to 86 kPa (10 psig to 13 psig).

5.2.1.6 *Detector*—Sulfur chemiluminescence detector.

5.3 *Data Acquisition:*

~~5.3.1 *Recorder*—The use of a 0 to 1 mV recording potentiometer, or equivalent, with a full-scale response time of 2 s, or less, is suitable to monitor detector signal.~~

5.3.1 *Integrator*—The use of an electronic integrating device or computer is recommended for determining the detector response. The device and software must have the following capabilities: (*1*) graphic presentation of the chromatogram, (*2*) digital display of chromatographic peak areas, (*3*) identification of peaks by retention time or relative retention time, or both, (*4*) calculation and use of response factors, (*5*) internal standardization, external standardization, and data presentation.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such

TABLE 1 Typical Retention Times for Common Sulfur Compounds[A]

Sulfur Compounds	Retention Time (min)
Hydrogen Sulfide	0.95
Carbonyl Sulfide	1.21
Sulfur Dioxide	1.34
Methanethiol	3.43
Ethanethiol	7.20
Dimethyl Sulfide	7.76
Carbon Disulfide	8.24
2-Propanethiol	8.92
2-methyl-2-propanethiol	10.04
1-Propanethiol	10.42
Ethylmethyl sulfide	10.53
2-Butanethiol	12.01
Thiophene	12.04
2-methyl-1-propanethiol	12.18
Diethyl Sulfide	12.82
1-Butanethiol	13.33
Dimethyl Disulfide	13.90
2-Methylthiophene	14.71
3-Methylthiophene	14.84
Diethyl Disulfide	17.89
Methylbenzothiophene	24.55
Methylbenzothiophene	24.66
Methylbenzothiophene	24.77
Methylbenzothiophene	24.88
Diphenyl sulfide	28.64

[A]Conditions specified in 5.2.1.

specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.1.1 *Alkane Solvent*—Such as, iso-octane (2,2,4-trimethylpentane), Reagent grade, for use as solvent (diluent) in preparation of system test mixtures and for preparation of internal standard stock solution. (**Warning—**Iso-octane is flammable and can be harmful when ingested or inhaled.)

6.1.2 *Aromatic Solvent*—Such as, toluene, Reagent grade, for use as solvent (diluent) in preparation of system test mixtures. (**Warning—**Reagent grade toluene is flammable and is toxic by inhalation, ingestion, and absorption through skin.)

6.1.3 *Carrier Gas*—Helium or nitrogen of high purity. (**Warning—**Helium and nitrogen are compressed gases under high pressure.) 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 5.1.3).

6.1.4 *Detector Gases*—Hydrogen, nitrogen, air, and oxygen may be required as detector gases. These gases must be free of interfering contaminants, especially sulfur compounds. (**Warning—**Hydrogen is an extremely flammable gas under high pressure. **Warning—**Compressed air and oxygen are gases under high pressure and they support combustion.)

6.1.5 *External Standards*—The sulfur compounds and matrices of external standards should be representative of the sulfur compounds and sample matrices being analyzed. Test Methods D2622 and D3120 can be used to analyze materials for calibration of this test method. The internal standardization procedure can also be used for generating external standards. Alternatively, primary standards prepared as described in 6.1.4 can be used for method calibration when it is demonstrated that the matrix does not affect calibration. Only one external standard is necessary for calibration, provided that the system performance specification (8.3) is met. An external standard must contain at least one sulfur compound at a concentration level similar, for example, within an order of magnitude to those in samples to be analyzed.

6.1.6 *Internal Standards*—Diphenyl sulfide, 3-chlorothiophene, and 2-bromothiophene are examples of sulfur compounds that have been used successfully as internal standards for samples within the scope of this test method (**Warning—**Sulfur compounds can be flammable and harmful or fatal when ingested or inhaled.). Any sulfur compound is suitable for use as an internal standard provided that it is not originally present in the sample, and is resolved from other sulfur compounds in the sample. Use the highest purity available (99 + % when possible). When purity is unknown or questionable, analyze the material by any appropriate means and use the result to provide accurate internal standard quantities.

6.1.6.1 An internal standard stock solution should be made up in the range of ~~0.1~~0.1 g to ~~1 g~~ 1 g of the internal standard on a sulfur basis to ~~1 kg~~ 1 kg of solvent.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.