



Designation: D5623 – 94(Reapproved 2009)

Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection¹

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

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) 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 to 100 mg/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. Coincidentally, 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.

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.*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.01 on Gas Chromatography Methods.

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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

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

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.

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*—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) 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*—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 $\pm 1\%$ 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) 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) 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 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 inside diameter fused silica wall coated open tube (WCOT) column, 4- μ m thick film of methylsilicone.

5.2.1.2 *Sample size*— 0.1 to 2.0- μ L.

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

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

^AConditions specified in 5.2.1.

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

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

5.3.2 *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 specifications are available.³ Other grades may be used,

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.