



# Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection<sup>1</sup>

This standard is issued under the fixed designation D 5623; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Warning statements were placed in the text in November 1999.

## 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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 2622 Test Method for Sulfur in Petroleum Products (X-Ray Spectrographic Method)<sup>2</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0L on Gas Chromatography.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry<sup>2</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards<sup>3</sup>

D 4626 Practice for Calculation of Gas Chromatographic Response Factors<sup>3</sup>

## 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 sulfur chemiluminescence detector or atomic emission detector (AED<sup>4</sup>) 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:

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>4</sup> The AED is manufactured by Hewlett-Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610.

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: (a) linearity of  $10^4$ , (b) 5 pg sulfur/s minimum detectability, (c) approximate equimolar response on a sulfur basis, (d) 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- $\mu$ m thick film of methylsilicone.

5.2.1.2 *Sample size*—0.1 to 2.0- $\mu$ L.

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

5.2.1.4 *Column Oven*—10°C for 3 min, 10°C/min to 250°C, held 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: (a) graphic presentation of the chromatogram, (b) digital display of chromatographic peak areas, (c) identification of peaks by retention time or relative retention time, or both, (d) calculation and use of response factors, (e) 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.<sup>5</sup> 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 D 2622 and D 3120 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

<sup>5</sup> *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 *Analar 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.

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 to 1 g of the internal standard on a sulfur basis to 1 kg of solvent.

**6.1.7 Sulfur Compound Standards**—99 + % purity (if available). Obtain pure standard material of all sulfur compounds of interest (**Warning**—Sulfur compounds can be flammable and harmful or fatal when ingested or inhaled.). If purity is unknown or questionable, analyze the individual standard material by any appropriate means and use the result to provide accurate standard quantities.

**6.1.8 System Test Mixture**—Gravimetrically prepare a stock solution of sulfur compounds in accordance with Practice D 4307. This solution should cover the volatility range encountered in samples of interest; for example, dimethyl sulfide (~0.1 g/kg), 2-propanethiol (~0.1 g/kg), dimethyl disulfide (~10 g/kg), 3-methylthiophene (~100 g/kg), and (~10 g/kg) benzothiophene. Prepare a working test mix solution by making a 1000:1 dilution of the stock solution in a mixture of 10 % toluene in iso-octane. Although 2-propanethiol is not stable in the long term, peak asymmetry of a thiol (mercaptan) is an indicator of GC system activity.

## 7. Sampling

**7.1** Appropriate sampling procedures are to be followed. This test method is not suitable for liquified petroleum gases. Volatile liquids to be analyzed by this test method shall be sampled using the procedures outlined in Practice D 4057. A sufficient quantity of sample should be taken for multiple analyses to be performed (at least 10 to 20 g for quantitation by internal standardization). Store all samples and standard blends at a temperature of 7 to 15°C (45 to 60°F). Do not open the sample or standard container at temperatures above 15°C (60°F).

## 8. Preparation of Apparatus

**8.1 Chromatograph**—Place in service in accordance with the manufacturer's instructions. Typical chromatograph and detector operating conditions are shown in 5.2.1.

**8.2 Detector**—Place in service in accordance with the manufacturer's instructions. After sufficient equilibration time (for example, 5 to 10 min), 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.

**8.3 System Performance Specification**—The inlet system should be evaluated for compatibility with trace quantities of reactive sulfur compounds. Inject and analyze a suitable amount (for example, 0.1 to 2.0-μL) of the system test mixture (6.1.8). All sulfur compounds should give essentially equimolar response and should exhibit symmetrical peak shapes. Relative response factors should be calculated for each sulfur compound in the test mixture (relative to a referenced component) in accordance with Practice D 4626 or Eq 1:

$$R_m = \frac{C_n \times A_r}{C_r \times A_n} \quad (1)$$

where:

$R_m$  = relative response factor for a given sulfur compound,

$C_n$  = concentration of the sulfur compound as sulfur,

$A_n$  = peak area of the sulfur compound,

$C_r$  = concentration of referenced sulfur standard as sulfur, and

$A_r$  = peak area of the referenced sulfur standard.

The relative response factor ( $R_m$ ) for each sulfur compound should not deviate from unity by more than ±10 %. Deviation of response by more than ±10 % or severe peak asymmetry indicates a chromatography or detector problem that must be corrected to ensure proper selectivity, sensitivity, linearity, and integrity of the system. If necessary, optimize the system according to instructions from the manufacturers.

## 9. Procedure

**9.1** A list of typical apparatus and conditions is provided in 5.2.1. Table 2 provides a listing of the retention times for common sulfur compounds that are typical for the column and conditions specified in 5.2.1. Whenever possible, the retention times of sulfur compounds of interest should be determined experimentally. Fig. 1 shows a chromatogram from a typical analysis.

**9.2 Sample Preparation for Analysis by Internal Standardization**—Add a quantity of suitable internal standard dissolved in iso-octane or another suitable solvent (internal standard stock solution, 6.1.6.1), to an accurately measured quantity of sample on a gravimetric (mass) basis. The final concentration of the internal standard in the sample aliquot, on a sulfur basis, should be approximately one half of the concentration range of sulfur compounds in the original sample. A concentration of approximately 1 to 50 mg/kg of internal standard on a sulfur basis has been used successfully for most samples.

**9.3 Sample Analysis by External Standardization**—At least once a day, or as frequently as deemed expedient, use the external standard(s) (6.1.5) to calibrate the instrument. The volume of external standard injected for calibration must be exactly the same as the sample volume injected for analysis.

**9.4 Chromatographic Analysis**—Introduce a representative aliquot of sample into the gas chromatograph. For internal standardization, the sample aliquot must contain a measured quantity of internal standard (6.1.6). Exercise care that the amount of sample and standard injected does not cause detector

saturation (indicated by flat-topped peaks). Typical sample size ranges from 0.1 to 2.0- $\mu$ L. Obtain the chromatographic data by way of a potentiometric recorder (graphic), digital integrator, or computer based chromatographic data system. Examine the graphic display or digital data for any errors.

## 10. Calculations

10.1 *Mass Concentration of Sulfur Compounds as Sulfur*—After identifying the sulfur compounds of interest by retention time, measure the area of each sulfur peak.

10.1.1 *Sulfur Concentration by Internal Standardization*—Compare the area response of each sulfur compound of interest to that of the internal standard. Calculate the concentration of each sulfur peak according to Eq 2:

$$C_n = \frac{C_i \times W_i \times A_n}{W_{sx} \times A_i} \quad (2)$$

where:

- $C_n$  = concentration (mg/kg) of sulfur compound as sulfur,
- $C_i$  = concentration (mg/kg) of internal standard in stock solution calculated as sulfur,
- $W_i$  = mass of internal standard stock solution added to the sample,
- $A_n$  = peak area of the sulfur compound,
- $W_{sx}$  = mass of sample aliquot, and
- $A_i$  = peak area of the internal standard.

10.1.2 *Sulfur Concentration by External Standardization*—An appropriate external standard (6.1.5) is chosen for calibration. The sulfur compound(s) and matrix of the external standard chosen should be representative of the sample(s) being analyzed. Compare the area response of each sulfur compound of interest to that of the external standard. Calibrate the concentration of each sulfur peak according to Eq 3:

$$C_n = \frac{C_e \times D_e \times A_n}{D_{sx} \times A_e} \quad (3)$$

where:

- $C_n$  = concentration (mg/kg) of sulfur compound as sulfur,
- $C_e$  = concentration (mg/kg) of external standard calculated as sulfur,
- $D_e$  = density of external standard matrix,
- $A_n$  = peak area of the sulfur compound,
- $D_{sx}$  = density of sample matrix, and
- $A_e$  = peak area of the external standard.

This equation assumes that equivalent volumes of sample and standard are injected.

10.2 Report the concentration of each sulfur compound as sulfur in units of mg/kg (ppm wt) to the appropriate number of significant figures.

10.3 *Mass Concentration of Total Sulfur in Sample*—Sum the sulfur content of all sulfur components (knowns and unknowns) in the sample to arrive at its total sulfur value according to Eq 4:

$$C_{Stot} = \Sigma C_n \quad (4)$$

where:

$C_{Stot}$  = concentration of total sulfur in the sample.

10.4 Report the concentration of total sulfur in units of mg/kg to the appropriate number of significant figures.

10.5 *Mass Concentration of Sulfur Compounds as Compound*—In 9.1 the concentration of sulfur compounds is reported on a sulfur basis. In some instances the concentration of sulfur compounds as compound is of interest. This conversion is made according to Eq 5:

$$C_w = \frac{C_n \times M}{S \times 32.07} \quad (5)$$

where:

- $C_w$  = concentration of the sulfur compound as compound,
- $C_n$  = concentration of sulfur compound as sulfur,
- $M$  = Molar mass of the compound in g/mol,
- $S$  = number of sulfur atoms in the molecular formula of the compound, and,
- 32.07 = the mass of one mol of sulfur, g.

## 11. Precision and Bias <sup>6</sup>

11.1 Data is insufficient for determining precision and bias of AED use in this test method. Data is sufficient, however, for determining precision of sulfur chemiluminescence detector used in this test method. The precision of this test method as determined by the statistical examination of the interlaboratory test results is as follows:

11.1.1 *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 only in one case in twenty (see Table 2 and Table 3).

11.1.2 *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 in one case in twenty (see Table 4 and Table 5).

11.2 *Bias*—Since there is no accepted reference material suitable for measuring bias for this test method, no statement of bias can be made.

## 12. Keywords

12.1 atomic emission detection; gas chromatography; sulfur chemiluminescence detection; sulfur compounds

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR:D02-1335.

**TABLE 1 Typical Retention Times for Common Sulfur Compounds<sup>A</sup>**

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

<sup>A</sup>Conditions specified in 5.2.1.

**TABLE 2 Sulfur Chemiluminescence Detection and Internal Standardization**

	Concentration, mg/kg S	Repeatability, mg/kg S
Single stable component	1 to 100	0.11 × Concentration
Total sulfur	10 to 200	0.12 × Concentration

**TABLE 3 Sulfur Chemiluminescence Detection and External Standardization**

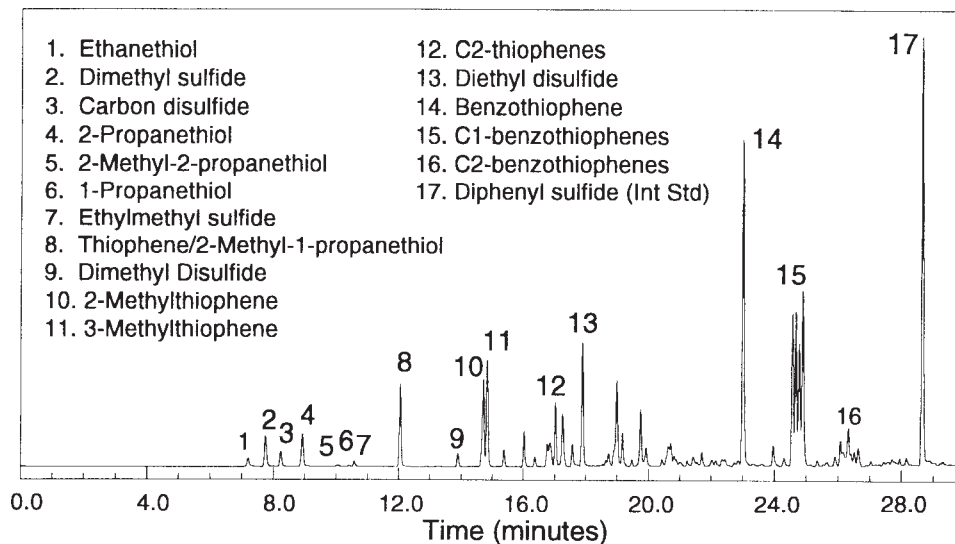
	Concentration, mg/kg S	Repeatability, mg/kg S
Single stable component	1 to 100	0.31 × Concentration
Total sulfur	10 to 200	0.24 × Concentration

**TABLE 4 Sulfur Chemiluminescence Detection and Internal Standardization**

	Concentration, mg/kg S	Reproducibility, mg/kg S
Single stable component	1 to 100	0.42 × Concentration
Total sulfur	10 to 200	0.33 × Concentration

**TABLE 5 Sulfur Chemiluminescence Detection and External Standardization**

	Concentration, mg/kg S	Reproducibility, mg/kg S
Single stable component	1 to 100	0.53 × Concentration
Total sulfur	10 to 200	0.52 × Concentration



NOTE 1—Conditions as shown in 5.2.1, column: 30 m, 0.32 mm inside diameter, 4 μm methyl silicone wall coated open tube fused silica; temperature program: – 10°C for 3 min to the final required temperature at a rate of 10°C/min.

**FIG. 1 Chromatogram from the analysis of a typical gasoline sample containing approximately 85 ppm wt total sulfur**

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