
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. 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.

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:
   - D2622 Test Method for Sulfur in Petroleum Products (X-Ray Spectrographic Method)²
   - D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry²
   - D4057 Practice for Manual Sampling of Petroleum and Petroleum Products²

2.2 Other Standards:
   - D4367 Practice for Preparation of Liquid Blends for Use as Analytical Standards²
   - D4626 Practice for Calculation of Gas Chromatographic Response Factors²

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 (AED³) 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—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.

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² Annual Book of ASTM Standards, Vol 05.02.

³ The AED is manufactured by Hewlett-Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610.
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. 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, isooctane (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—See Note 1).

NOTE 1: Warning—Isooctane 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—See Note 2).

NOTE 2: 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—See Note 3). 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).

NOTE 3: Warning—Helium and nitrogen are compressed gases under high pressure.

6.1.4 Detector Gases—Hydrogen, nitrogen, air, and ox-

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**TABLE 1 Typical Retention Times for Common Sulfur Compounds**

<table>
<thead>
<tr>
<th>Sulfur Compounds</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.95</td>
</tr>
<tr>
<td>Carbonyl Sulfide</td>
<td>1.21</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>1.34</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>3.43</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>7.20</td>
</tr>
<tr>
<td>Dimethyl Sulfide</td>
<td>7.76</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>8.24</td>
</tr>
<tr>
<td>2-Propanethiol</td>
<td>8.92</td>
</tr>
<tr>
<td>2-methyl-2-propanethiol</td>
<td>10.04</td>
</tr>
<tr>
<td>1-Propanethiol</td>
<td>10.42</td>
</tr>
<tr>
<td>Ethylmethyl sulfide</td>
<td>10.53</td>
</tr>
<tr>
<td>2-Butanethiol</td>
<td>12.01</td>
</tr>
<tr>
<td>Thiophene</td>
<td>12.04</td>
</tr>
<tr>
<td>2-methyl-1-propanethiol</td>
<td>12.18</td>
</tr>
<tr>
<td>Diethyl Sulfide</td>
<td>12.82</td>
</tr>
<tr>
<td>1-Butanethiol</td>
<td>13.33</td>
</tr>
<tr>
<td>Dimethyl Disulfide</td>
<td>13.90</td>
</tr>
<tr>
<td>2-Methylthiophene</td>
<td>14.71</td>
</tr>
<tr>
<td>3-Methylthiophene</td>
<td>14.84</td>
</tr>
<tr>
<td>Diethyl Disulfide</td>
<td>17.89</td>
</tr>
<tr>
<td>Methylbenzothiophene</td>
<td>24.55</td>
</tr>
<tr>
<td>Methylenebithiophene</td>
<td>24.69</td>
</tr>
<tr>
<td>Methylbithiophene</td>
<td>24.77</td>
</tr>
<tr>
<td>Dimethylbithiophene</td>
<td>24.88</td>
</tr>
<tr>
<td>Diphenyl sulfide</td>
<td>28.64</td>
</tr>
</tbody>
</table>

*Conditions specified in 5.2.1.*
Ygen may be required as detector gases. These gases must be free of interfering contaminants, especially sulfur compounds. (Warning—See Note 4).

Note 4: 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 performance specification (7.3) 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—See Note 5). 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—See Note 5). If purity is unknown or questionable, analyze the individual standard material by any appropriate means and use the result to provide accurate standard quantities.

Note 5: Warning—Sulfur compounds can be flammable and harmful or fatal when ingested or inhaled.

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) benzo thiophene. Prepare a working test mix solution by making a 1000:1 dilution of the stock solution in a mixture of 10 % toluene in isooctane. Although 2-propanethiol is not stable in the long term, peak asymmetry of a thiol (mercaptan) is an indicator of GC system activity.

7. Preparation of Apparatus

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

7.2 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.

7.3 System Performance Specification—The inlet system must 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:

\[
R_m = \frac{C_m \times A_r}{C_r \times A_m}
\]

where:
- \( R_m \) = relative response factor for a given sulfur compound,
- \( C_m \) = concentration of the sulfur compound as sulfur,
- \( A_r \) = peak area of the referenced sulfur compound,
- \( C_r \) = concentration of referenced sulfur standard as sulfur, and
- \( A_m \) = 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.

8. Sampling

8.1 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).

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

| 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 |
determined experimentally. Figure 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-μL. 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:

\[ C_n = \frac{C_i \times W_i \times A_n}{W_{sx} \times A_i} \]  

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:

\[ C_n = \frac{C_e \times D_e \times A_e}{D_{sx} \times A_e} \]  

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:

\[ C_{Stot} = \sum C_n \]  

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:

\[ C_w = \frac{C_n \times M}{S \times 32.07} \]  

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

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:

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5 Supporting data are available from ASTM Headquarters. Request RR:D02-1335.
1. Ethanethiol
2. Dimethyl sulfide
3. Carbon disulfide
4. 2-Propanethiol
5. 2-Methyl-2-propanethiol
6. 1-Propanethiol
7. Ethylmethyl sulfide
8. Thiophene/2-Methyl-1-propanethiol
9. Diethyl disulfide
10. 2-Methylthiophene
11. 3-Methylthiophene
12. C2-thiophenes

13. Diethyl disulfide
14. Benzothiophene
15. Cl-benzothiophenes
16. C2-benzothiophenes
17. Diphenyl sulfide (Int Std)

**Note**—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.

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

<table>
<thead>
<tr>
<th>Concentration, mg/kg S</th>
<th>Repeatability, mg/kg S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single stable component</td>
<td>1 to 100</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>10 to 200</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration, mg/kg S</th>
<th>Reproducibility, mg/kg S</th>
</tr>
</thead>
<tbody>
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<td>Single stable component</td>
<td>1 to 100</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>10 to 200</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Concentration, mg/kg S</th>
<th>Reproducibility, mg/kg S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single stable component</td>
<td>1 to 100</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>10 to 200</td>
</tr>
</tbody>
</table>

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 Tables 2 and 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 Tables 4 and 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