



Designation: D7041 – 16 (Reapproved 2021)

# Standard Test Method for Determination of Total Sulfur in Liquid Hydrocarbons and Hydrocarbon-Oxygenate Blends by Gas Chromatography with Flame Photometric Detection<sup>1</sup>

This standard is issued under the fixed designation D7041; 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.

## 1. Scope

1.1 This test method covers the determination of total sulfur in liquid hydrocarbons with a final boiling point less than 450 °C by gas chromatography using a flame photometric detector.

1.2 This test method is applicable for total sulfur levels from 0.5 mg/kg S to 100 mg/kg S.

NOTE 1—The pooled limit of quantification (PLOQ) derived from the 2002 interlaboratory cooperative test program was determined to be 1 mg/kg S.

NOTE 2—Samples can also be tested at other total sulfur levels, but the precision statements may not apply.

1.3 The values stated in SI units are to be regarded as 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements see Section 7.*

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:<sup>2</sup>

[D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Prod-](#)

[ucts by Hydrometer Method](#)

[D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[E840 Practice for Using Flame Photometric Detectors in Gas Chromatography](#)

## 3. Summary of Test Method

3.1 The sample is analyzed by gas chromatography with a flame photometric detector. A fixed amount of sample is injected into the gas chromatograph where it is vaporized. The air carrier stream carries the vaporized sample into a high temperature zone (>900 °C) where the compounds present in the sample are oxidized. Sulfur compounds are converted to sulfur dioxide (SO<sub>2</sub>). The carrier stream carries the oxidation components onto a chromatographic column where they are separated and the SO<sub>2</sub> is quantified by the flame photometric detector. Calibration of the detector is achieved by the use of an appropriate external standard.

## 4. Significance and Use

4.1 This test method can be used to determine total sulfur levels in process feeds and finished products that fall within the scope of this test method.

4.2 Low levels of sulfur in process feed stocks can poison expensive catalysts used in petroleum refining processes. This test method can be used to monitor sulfur levels in these feedstocks.

## 5. Apparatus

5.1 *Gas Chromatograph*, equipped with automatically controlled valves, capable of automatic calibration with an external standard and having a flame photometric detector with an overall sensitivity to detect at least 0.5 mg/kg of SO<sub>2</sub>. It must be able to automatically control all valve switching times. Although originally developed with online analytical measurement equipment in an offline mode of operation, suitable online

<sup>1</sup> 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 D02.03 on Elemental Analysis.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

or laboratory gas chromatographs may apply this test method as described. Typical instrument parameters are listed in Table 1.

5.1.1 *Carrier and Detector Gas Control*—The chromatograph must be equipped with flow controllers or pressure controllers capable of maintaining a constant supply of carrier gas and detector supply gases. Electronic pressure or flow control is highly recommended.

5.1.2 *Sample Injection System*—An automatic sample injection device is required. The injector must allow the introduction of small sample sizes (0.1 µL to 1 µL). The sample must be accurately and repeatably injected into the gas chromatograph. Rotary or stem type liquid injection valves or auto injectors are recommended. The valve or injector must be equipped with a heated vaporizer section capable of being heated to at least 285 °C.

5.2 *Pyrolysis Furnace*—A furnace capable of maintaining a sufficient temperature (>900 °C) to pyrolyze the entire sample and oxidize the sulfur compounds to SO<sub>2</sub>.

5.3 *Quartz Combustion Tube*—Quartz tube capable of withstanding temperatures up to 1200 °C. The oxidation section shall be large enough to ensure complete oxidation of the sample.

5.4 *Column*—A column that can provide complete separation of SO<sub>2</sub> from the CO<sub>2</sub> quench and the other oxidized components such as H<sub>2</sub>O.

5.5 *Detector*—Any flame photometric detector (FPD) can be used, provided it can detect a minimum peak height twice that of the baseline noise for a 1 µL injection of a 0.5 mg/kg S standard. Detector linearity shall be at least equal to or greater than 10<sup>3</sup>. The user is referred to Practice E840 for assistance in optimizing the operation and performance of the FPD.

5.6 *Data Acquisition System*—Use any integrator or computerized data acquisition system for peak area integration, as well as for recording the chromatographic trace. The device and software must have the following capabilities:

- 5.6.1 Identification of peak by retention time.
- 5.6.2 Calculation and use of response factors.
- 5.6.3 External standard calibration calculation.
- 5.6.4 Graphic presentation of the chromatogram.

5.7 *Analytical Balance*—Any balance capable of accurately weighing materials to the nearest 0.01 mg.

## 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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</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.

6.2 *Carrier-Gas*—Zero grade air is recommended. (**Warning**—Compressed air is a gas under high pressure that supports combustion.)

6.3 *Hydrogen*—Chromatographic grade recommended, minimum purity 99.995 %. (**Warning**—Hydrogen is an extremely flammable gas under high pressure.)

6.4 *Solvent (Reagent Grade)*—The solvent chosen should be capable of dissolving the sulfur-containing compound used to prepare the standard. The solvent of choice should have a density similar to the samples being analyzed and it should have sulfur concentrations less than the instrument detection limit. Mixed solvents such as an *isooctane* / toluene mixture can be used to reach the desired density. (**Warning**—Solvents used as reagents such as toluene and *isooctane* are flammable and may be harmful or fatal if ingested or inhaled.)

6.5 *Standards for Calibration and Peak Identification*—Standards are used for peak identification and retention time determination. Also standards of known concentrations are required for external standard calibration of the gas chromatograph.

6.5.1 *Preparation of Stock Solution (mass/volume)*, 100 µg S/mL (see Notes 3 and 4). Accurately weigh to the nearest 0.1 mg, 0.0456 g of butyl sulfide into a suitable container such as a 100 mL volumetric flask. Dilute to volume with the selected solvent. This stock solution can be further diluted to the desired sulfur concentration. Other sulfur containing compounds such as thiophene or thianaphthene can be substituted for n-butyl sulfide if desired. The concentration of the stock solution can be calculated as follows:

$$\mu\text{g S/mL} = (M \times 32.06) \times (1 \times 10^6) / (100 \text{ mL} \times FW) \quad (1)$$

where:

*M* = exact mass of sulfur reference compound (g), and  
*FW* = formula weight of sulfur reference compound.

NOTE 3—Commercial standards can be used provided they are checked for accuracy.

NOTE 4—Stock solutions will have a shelf life of approximately 2 to 3 months and should be remixed accordingly.

6.5.2 *Preparation of Stock Solution: (mass/mass)*, 100 µg S/g (see Notes 3 and 4). Accurately weigh to the nearest 0.1 mg, 0.0456 g of butyl sulfide into a suitable container. Add 100 g (accurately weighed to the nearest 0.1 g) of the selected

TABLE 1 Typical Instrument Parameters

Carrier gas	Zero air
Carrier flow rate	30 mL/min
Hydrogen flow rate	60 mL/min
Detector	Flame photometric detector
Detector temperature	120 °C
Injector temperature	285 °C
Furnace temperature	1000 °C
Column	40 ft by 1/8 in. stainless steel tubing, 12 % polyphenyl ether/1.5 % H <sub>3</sub> PO <sub>4</sub> on 40/60 Chromosorb T
Column temperature	115 °C

<sup>3</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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. Pharmacopial Convention, Inc. (USPC), Rockville, MD.

solvent. This stock solution can be further diluted to the desired sulfur concentration. Other sulfur containing compounds such as thiophene or thianaphthene can be substituted for butyl sulfide if desired. The concentration of the stock solution can be calculated as follows:

$$\text{mg/kg S} = (M \times 32.06) \times (1 \times 10^6) (\text{mg/kg}) / (100 \text{ g} \times \text{FW}) \quad (2)$$

6.6 *Butyl Sulfide*—FW 146.29, 21.92 % (m/m) S.

6.7 *Thiophene*—FW 84.14, 38.1 % (m/m) S.

6.8 *Thianaphthene*—FW 134.20, 23.89 % (m/m) S.

## 7. Hazards

7.1 Consult current Occupational Safety Health Administration (OSHA) regulations, supplier Material Safety Data Sheets, and local regulations for all materials used in this test method.

7.2 High temperatures are used in this method; extra precaution should be exercised when working with flammable materials near the pyrolysis furnace.

## 8. Sampling

8.1 *General Requirements:*

8.1.1 Collect samples in accordance with Practice D4057 or D4177.

8.1.2 To prevent the loss of volatile components, which may be present in some samples, protect samples from excess temperatures prior to testing. This can be done by storage in an ice bath or refrigerator.

8.1.3 Analyze samples as soon as possible to prevent loss of sulfur components or contamination.

8.1.4 Do not store samples in plastic containers, since volatile materials may diffuse through the walls of the container.

8.1.5 Do not test samples stored in leaky containers. Discard and obtain a new sample if leaks in the containers are detected.

## 9. Preparation of Apparatus

9.1 Place in service in accordance with the manufacturer's instructions. Typical instrument parameters are listed in Table 1.

9.2 Set gas flows and temperatures to the desired operating conditions, in accordance with the manufacturer's instructions.

9.3 Ignite the flame photometric detector according to the manufacturer's procedure.

9.4 Prepare the sample introduction accessories, if required, according to the manufacturer's instructions.

9.5 Load a sulfur standard (see 6.5) into the injection valve or auto injector and inject into the gas chromatograph. Determine the retention time of the SO<sub>2</sub> peak.

9.6 Set-up a chromatographic analysis method according to the manufacturer's instructions.

## 10. Calibration

10.1 Choose which type of calibration method is required (mass/volume or mass/mass) and prepare a calibration standard from the stock solution (see 6.5.1 or 6.5.2) by volumetric dilution or mass dilution (see Note 3). The concentration of the

calibration standard should be approximately 50 % of the full-scale concentration range of the test samples to be analyzed.

10.1.1 Load calibration standard into injection valve or auto injector.

10.1.2 Inject the calibration standard into the gas chromatograph. See Table 2 for recommended injection volumes.

10.1.3 Analyze the calibration standard and obtain a chromatogram. Calculate the relative response factor for the SO<sub>2</sub> peak:

$$RF_S = (C_n/A_S) \quad (3)$$

where:

$RF_S$  = relative response factor of SO<sub>2</sub>,  
 $C_n$  = sulfur concentration (mg/kg S) of the compound in the calibration mixture, and  
 $A_S$  = peak area of the SO<sub>2</sub> component.

## 11. Procedure

11.1 Obtain a test sample using the procedure outlined in Section 8.

11.2 Sample injection volumes can range from 0.1 μL to 1 μL. Experience dictates the best sample volume. The injection volume must be the same as used in the calibration procedure. Typical injection volumes are listed in Table 2.

11.3 Load the sample into the injection valve or auto injector according to the manufacturer's recommended procedure.

11.4 Inject the sample into the chromatograph by starting the chromatographic method, in accordance with the manufacturer's instructions.

11.5 Record concentration reading from gas chromatograph. See Fig. 1 for a typical chromatogram.

11.6 Density values needed for the calculations are to be tested using Test Methods D1298, D4052, or equivalent, at the temperature at which the sample specimen was taken for analysis by this test method.

## 12. Calculation

12.1 If the analyzer was calibrated on a mass/volume basis then calculate the sulfur content of the test sample in parts per million by mass (mg/kg) as follows:

$$\text{sulfur, ppm } (\mu\text{g/g, mg/kg}) = C_{Sv}/D_S \quad (4)$$

where:

$C_{Sv}$  = concentration reading from analyzer (μg/mL), and  
 $D_S$  = density of sample (g/mL).

12.1.1 If the analyzer was calibrated on a mass/mass basis then calculate the sulfur content of the test sample in parts per million by mass (mg/kg) as follows:

TABLE 2 Suggested Injection Volume

Sulfur, mg/kg	Sample Size, μL
Less than 1	0.5 to 1
1 to 100	up to 0.5
Greater than 100	0.1 to 0.25

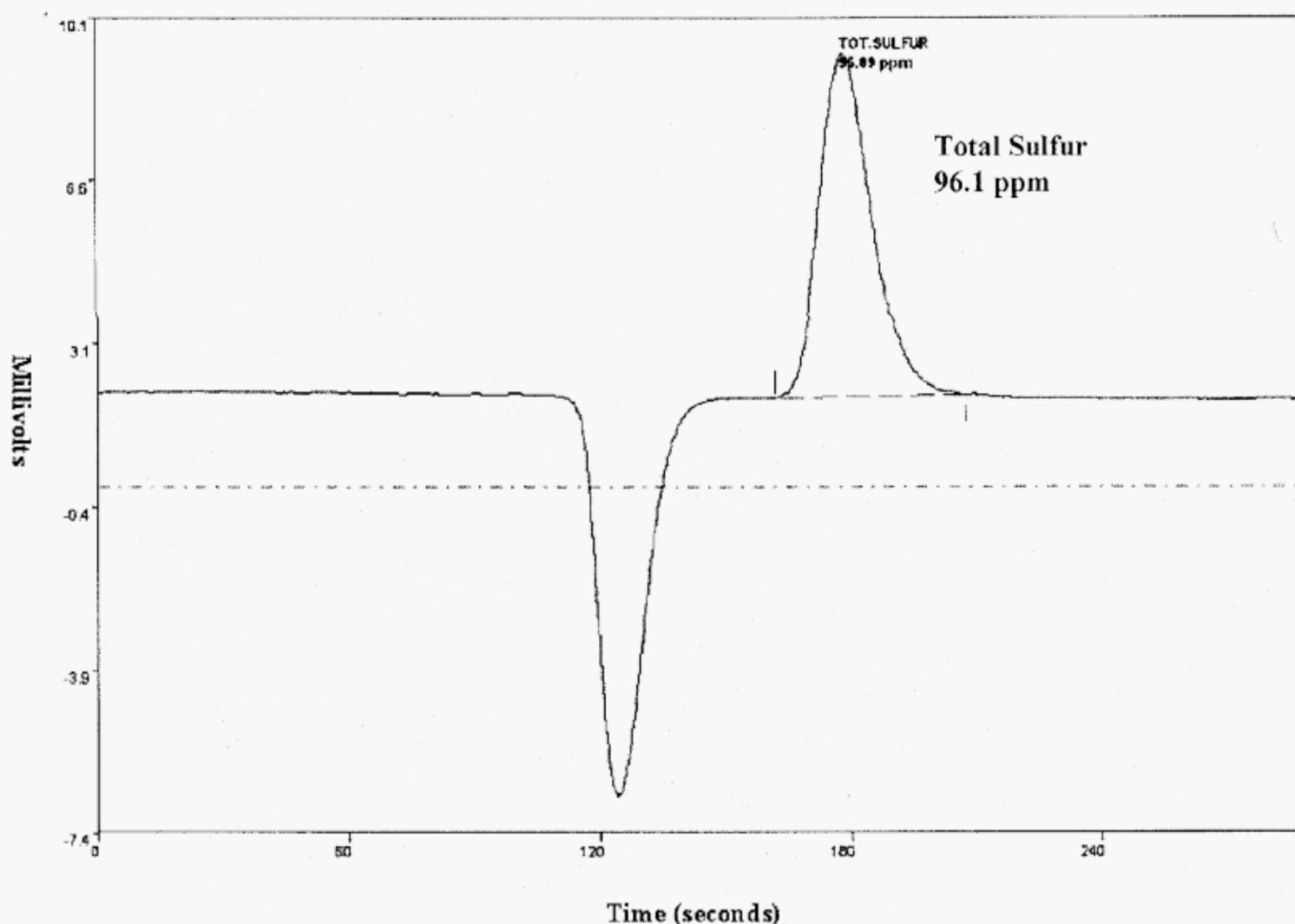


FIG. 1 Typical Chromatogram

$$\text{sulfur, ppm (mg/g, mg/kg)} = (C_{Sm})(D_C)/D_S \quad (5)$$

where:

- $C_{Sm}$  = concentration reading from analyzer (mg/kg),
- $D_C$  = density of calibration standard (g/mL), and
- $D_S$  = density of sample (g/mL).

### 13. Report

13.1 Report the total sulfur concentration in parts per million by mass (mg/kg) to the nearest 0.1 mg/kg S.

### 14. Precision and Bias<sup>4,5</sup>

14.1 *Precision*—The precision of this test method as determined by statistical examination of interlaboratory test results are as follows:

NOTE 5—The following precision data were developed in a 2002 interlaboratory cooperative test program. Nine participants analyzed sample sets of blind duplicates of 16 types of hydrocarbons and hydrocarbon-oxygenate blends. The sample set consisted of eight gasoline samples and eight diesel samples. For the gasoline sample set, the concentration range was approximately from 3 mg/kg S to 100 mg/kg S

and for the diesel sample set, approximately between 2 mg/kg S to 85 mg/kg S. To facilitate the calibration of the analyzers involved in the interlaboratory study, a calibration standard was provided for gasoline and a second calibration standard was provided for diesel. By providing calibration standards the uncertainty often introduced in the calibration process by variations in the standards was removed. By providing the calibration standards for each fuel tested, the precision could have been positively influenced.

14.1.1 *Repeatability*—The difference between two successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in normal and correct operation of the test method exceed the following values only in one case in twenty:

Gasoline	0.53 mg/kg S
Diesel	$0.2070 \cdot X^{0.2594}$ mg/kg S

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories with different apparatus on identical materials would, in the long run, in normal and correct operation of the test method exceed the following values only in one case in twenty:

Gasoline	$0.0657 (X + 28.626)$ mg/kg S
Diesel	$1.9771 \cdot X^{0.2594}$ mg/kg S

For repeatability and reproducibility estimates at several sulfur levels, see Table 3.

### 15. Keywords

15.1 flame photometric detector; gas chromatography; total sulfur

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1558. Contact ASTM Customer Service at service@astm.org.

<sup>5</sup> The following equipment was used to develop the precision statement: ABB Model PGC2007 configured with FPD Sulfur Addition Module, manufactured by ABB Inc., 843 N. Jefferson St, Lewisburg, WV, 24901. To date no other equipment has demonstrated through ASTM interlaboratory testing the ability to meet the precision statement. This is not an endorsement or certification by ASTM International.

**TABLE 3 Repeatability and Reproducibility Estimates**

X (mg/kg S)	Gasoline Repeatability	Gasoline Reproducibility	Diesel Repeatability	Diesel Reproducibility
3	0.53	2.08	0.28	2.63
6	0.53	2.28	0.33	3.15
9	0.53	2.47	0.37	3.50
15	0.53	2.87	0.42	3.99
30	0.53	3.85	0.50	4.78
50	0.53	5.17	0.57	5.45
80	0.53	7.14	0.65	6.16

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