



Designation: D7041 – 04

Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Online Gas Chromatography with Flame Photometric Detection¹

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 (ϵ) 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 to 100 mg S/kg.

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

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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*²

D1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products 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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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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.

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 (SO₂). The carrier stream carries the oxidation components onto a chromatographic column where they are separated and the SO₂ 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 SO₂. 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 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.

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 ₃ PO ₄ on 40/60 Chromosorb T
Column temperature	115°C

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 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 SO₂.

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 SO₂ from the CO₂ quench and the other oxidized components such as H₂O.

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 S/kg standard. Detector linearity shall be at least equal to or greater than 10³. 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.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.

6.2 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:

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

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 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:

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

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, 23.90 % (m/m) S.

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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.