



Designation: D7620 – 10 (Reapproved 2020)

Standard Test Method for Determination of Total Sulfur in Liquid Hydrocarbon Based Fuels by Continuous Injection, Air Oxidation and Ultraviolet Fluorescence Detection¹

This standard is issued under the fixed designation D7620; 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 hydrocarbon based fuel with a final boiling point of up to 450 °C. It is applicable to analysis of natural, processed and final product materials containing sulfur in the range of 4.0 mg/kg to 830 mg/kg (see [Note 1](#)).

NOTE 1—For liquid hydrocarbons containing less than 4.0 mg/kg total sulfur or more than 830 mg/kg total sulfur, Test Method [D5453](#) may be more appropriate.

1.2 This test method is applicable for total sulfur determination in liquid hydrocarbons containing less than 0.35 % (m/m) halogen(s).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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 [4.1](#), [8.3](#), and Section [9](#).

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:²

¹ 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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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.

- [D1298](#) Test Method for Density, Relative Density, 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
- [D4175](#) Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- [D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products
- [D5453](#) Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
- [D6299](#) Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- [D6300](#) Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
- [D6792](#) Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

3. Terminology

3.1 Definitions:

3.1.1 See Terminology [D4175](#) for definitions of other terms used in this test method.

3.1.2 *oxidative pyrolysis, n*—process in which a sample undergoes complete combustion in an appropriate oxygen containing environment at a sufficiently elevated temperature.

3.1.2.1 *Discussion*—Organic compounds pyrolytically oxidize to carbon dioxide and water and oxides of other elements that are in the sample.

4. Summary of Test Method

4.1 A small, very controlled flow of hydrocarbon sample is continuously injected during measurement. It is introduced via a syringe into a high temperature combustion tube containing air where sulfur is oxidized to sulfur dioxide (SO₂). Water produced during the sample combustion is removed, as

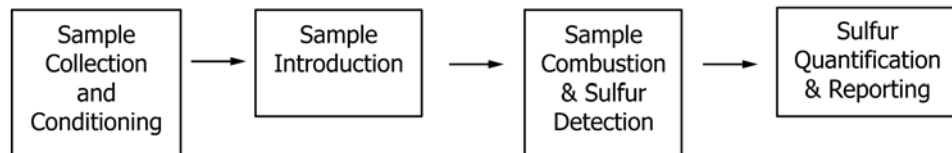


FIG. 1 Basic Block Diagram Describing Sulfur Determination

required, and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO₂ absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO₂*). Fluorescence emitted from the excited SO₂* as it returns to a stable state SO₂ is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample. (**Warning**—Exposure to excessive quantities of ultraviolet light is injurious to health. The operator shall avoid exposing their body, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.)

4.2 Fig. 1 illustrates a basic block diagram describing sulfur determination. Sample collection and conditioning, sample introduction, detection system and data handling are depicted.

5. Significance and Use

5.1 Some process catalysts used in refining can be poisoned when trace amounts of sulfur bearing materials are contained in the feedstocks. There are also government regulations as to how much sulfur is permitted to be present in commercial transportation fuels. This test method can be used to determine sulfur in process and downstream distribution streams. It can also be used for purposes of screening and quality control of finished hydrocarbon fuel products.

6. Interferences

6.1 Halogens above 0.35 % (mass/mass) will interfere with accurate sulfur determination.

6.2 Bound nitrogen at concentration greater than 150 mg N/kg can cause a 1 mg S/kg positive bias.

6.3 Excessive moisture produced during the combustion step will interfere if not removed prior to the detector.

7. Apparatus

7.1 *Furnace*—An electric furnace held at a temperature sufficient to pyrolyze the entire sample (typically 1050 °C ± 25 °C) and oxidize sulfur to SO₂.

7.2 *Combustion Tube*—A quartz combustion tube constructed to allow the direct injection of a continuous flow of sample into the heated oxidation zone of the furnace. The oxidation section shall be large enough to ensure complete combustion of the sample. Fig. 2 illustrates a typical combustion tube (**Note 2**).

NOTE 2—Other combustion tube configurations are acceptable if precision and accuracy are not degraded.

7.3 *Flow Control*—The apparatus shall be equipped with suitable flow control apparatus capable of maintaining a constant supply of air.

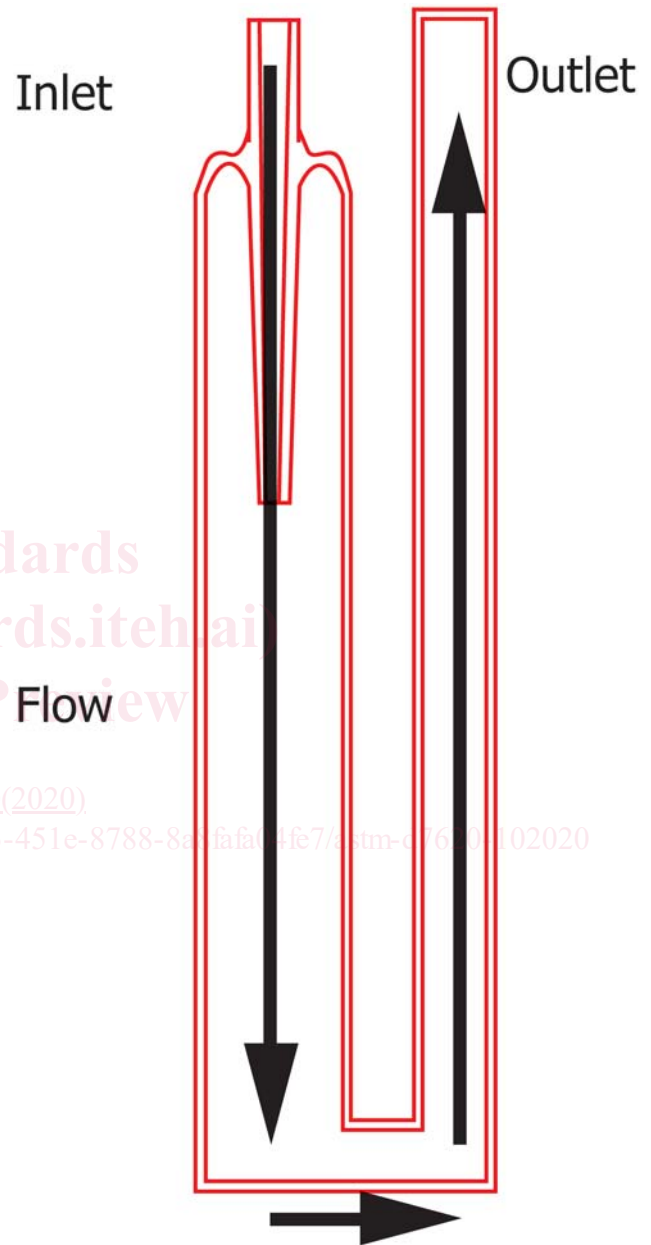


FIG. 2 Typical Combustion Tube

7.4 *Drier Tube*—The apparatus shall be equipped with a mechanism for the removal of excessive water vapor. The oxidation reaction produces water vapor which must be eliminated prior to measurement by the detector. This may be accomplished with a membrane drying tube, or a permeation dryer, that utilizes a selective capillary action for water removal.

7.5 UV Fluorescence Detector—A quantitative detector capable of measuring the energy emitted from the fluorescence of sulfur dioxide by UV light.

7.6 Millilitre Syringe—A disposable 1 mL syringe capable of accurately delivering a controlled and constant flow of calibration and sample materials. The syringe shall accommodate a disposable tip to aid the filling of the syringe and a disposable septum seal to accommodate penetration and sample flow.

7.7 Sample Inlet System—An automatic sample injection device that is compatible with a disposable 1 mL syringe is required. The injector shall allow the introduction of an appropriate continuous flow of sample into a combustion tube carrier stream, which directs the sample into the oxidation zone at a controlled and repeatable rate.

7.8 Strip Chart Recorder—Equivalent electronic data logger, integrator or recorder (optional).

7.9 Balance—With a precision of ± 0.01 mg (optional).

8. Reagents and Materials

8.1 Purity of Reagents—Reagent grade chemicals shall be used in 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.

8.2 Air—Filtered (with a 2 μ m filter).

8.3 Iso-octane, Toluene, Xylenes—Reagent grade. (**Warning**—Organic solvents are flammable.)

8.4 Thiophene—FW84.14, Sulfur content 38.10 % (m/m).

8.4.1 Other sources of sulfur and diluent materials may be used if precision and accuracy are not degraded.

8.4.2 Apply the appropriate correction for chemical impurity.

8.5 Sulfur Stock Solution—1000 μ g S/mL. Prepare a stock solution by accurately weighing 0.2624 g \pm 0.013 g of thiophene into a tared 100 mL volumetric flask. Dilute to volume with selected solvent. This stock may be further diluted to desired sulfur concentration.

8.5.1 Working standards should be rebled on a regular basis depending upon frequency of use and age.

NOTE 3—Typically, stock solutions have a useful life of about 3 months.

8.6 Quality Control (QC) Samples—Preferably, these are portions of one or more hydrocarbon materials that are stable and representative of the samples of interest. These QC samples may be used to check the validity of the testing process as described in Section 16.

³ 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Typical Operating Conditions

Furnace Temperature	1050 °C
Furnace Pressure	28 kPa
Photo Multiplier Tube (PMT) Temperature	40 °C
PMT Voltage	900 V
Optics Purge Flow	80 mL/min to 100 mL/min

9. Hazards

9.1 Consult current OSHA regulations, suppliers' Material Safety Data Sheets, and local regulations for all materials used in this test method.

9.2 High temperature is employed in this test method. Exercise extra care when using flammable materials near the oxidative pyrolysis furnace.

9.3 Due to the types of samples analyzed in this test method, chemical resistant gloves should be worn when performing this test method.

10. Sampling

10.1 Collect the samples in accordance with Practice **D4057** or Practice **D4177**. To preserve volatile components which are in some samples, do not uncover samples any longer than necessary.

11. Preparation of Apparatus

11.1 Place the analyzer in service in accordance with the manufacturer's instructions.

11.2 Typical instrument parameters are listed in **Table 1**.

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

11.4 Adjust the instrument sensitivity and baseline stability and perform instrument blanking procedure following manufacturer's guidelines.

12. Calibration

12.1 Choose which type of calibration method is required (mass/volume or mass/mass), and prepare a calibration standard from the stock solution (**8.5**) by volume or mass dilution.

12.2 If a mass/mass analysis is being done with a calibration standard in a different matrix than the sample, the calibration is set for the product derived from the weight/weight concentration estimate (see **Eq 1** in **14.1** and **Note 4**).

NOTE 4—Apparatus capable of accepting a fixed or variable density input and utilizing an automatic density compensation and result calculation are acceptable if precision and accuracy are not degraded.

12.3 Based on anticipated sulfur concentration carefully prepare a series of calibration standards that bracket the concentrations of the samples being analyzed. **Table 2** lists typical calibration curves. The calibration curve shall contain at least three points, otherwise the number of standards used per curve can vary.

12.3.1 Prepare the instrument for calibration and fill the millilitre syringe to approximately the 0.75 mL mark with sample prior to analysis. Eliminate any bubbles that are present in the liquid column and cap the syringe with a septum seal.