Designation: D7620 – 10 (Reapproved 2015)

Standard Test Method for
Determination of Total Sulfur in Liquid Hydrocarbon Based Fuels by Continuous Injection, Air Oxidation and Ultraviolet Fluorescence Detection[1]

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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 4.1, 8.3, and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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, Petroleum Products, 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 and Lubricants

D6792 Practice for Quality System in Petroleum Products 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 (SO_2). Water produced during the sample combustion is removed, as required, and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2^*). Fluorescence emitted from the excited SO_2^* as it returns to a stable state SO_2 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

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[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.

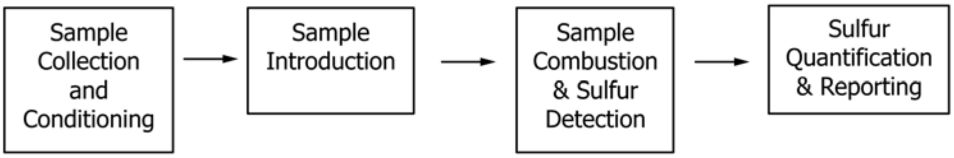

FIG. 1 Basic Block Diagram Describing Sulfur Determination

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 SO_2.

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.

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.

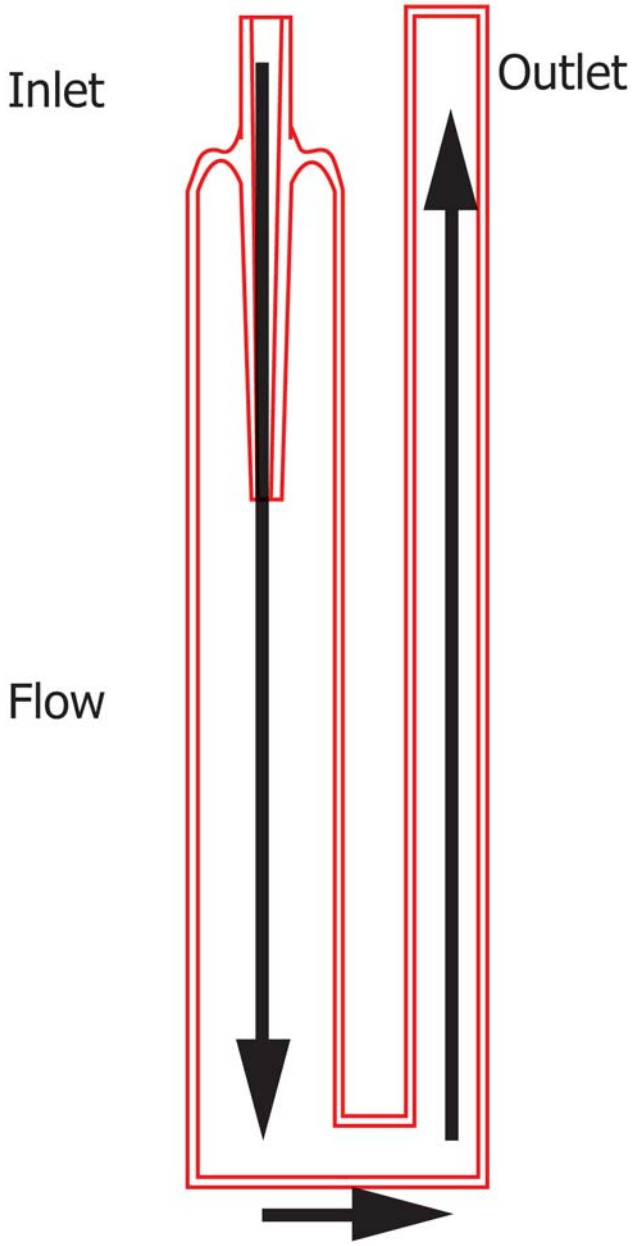

FIG. 2 Typical Combustion Tube

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 µm 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 µg S/mL. Prepare a stock solution by accurately weighing 0.2624 g ± 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 reblended 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.

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.

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[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 *Annual 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 2 Typical Sulfur Calibration Ranges and Standard Concentrations

Curve I Sulfur, ng/µL	Curve II Sulfur, ng/µL	Curve III Sulfur, ng/µL
1.0	5.00	100.00
2.5	25.00	500.00
5.0	50.00	1000.00
10.0	100.00	...

12.3.2 Install the millilitre syringe, enter the density of the calibration standard and inject the standard into the analyzer according to the manufacturer's instructions.

12.3.3 Continue instrument calibration (by repeating 12.3.1 through 12.3.2) to construct a calibration curve. The calibration curve shall be linear and system performance shall be checked each day of use. See Section 16.

13. Procedure

13.1 Obtain a test specimen using the procedure described in Section 10. The sulfur concentration in the test specimen shall be less than the concentration of the highest standard and greater than the concentration of the lowest standard used in the calibration. If required, a dilution may be performed on either a weight or volume basis.

13.1.1 *Gravimetric Dilution (mass/mass)*—Record the mass of the test specimen and the total mass of the test specimen and solvent.

13.1.2 *Volumetric Dilution (mass/volume)*—Record the mass of the test specimen and the total volume of the test specimen and solvent.

13.2 The injection rate shall be consistent with that used in the calibration procedure (See Section 12).

13.3 Measure the response for the test specimen solution using the procedures described in 12.3.

13.4 Determine sulfur concentration in accordance with the manufacturer's instructions.

13.5 *Cleaning and Recalibration*—Clean any coked or sooted parts per the manufacturer's instructions. After any cleaning or adjustment, assemble and verify operation by analyzing a calibration check standard (see Section 16).

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

14. Calculations

14.1

$$\frac{\mu\text{g Sulfur}}{\text{g Solvent}} \times \frac{\text{Density of solvent}}{\text{Density of Sample}} = \frac{\mu\text{g Sulfur}}{\text{g Solvent}} \tag{1}$$

$$RF_S = C_n / A_n \tag{2}$$

$$C_u = RF_S \times A_u \tag{3}$$

where:

RF_S = response factor for sulfur,
C_n = sulfur concentration in mg/kg in the calibration mixture,
A_n = counts from the detector from calibration mixture,
C_u = sulfur concentration in mg/kg of the sample, and
A_u = counts from the detector from the sample.

15. Report

15.1 For results equal to or greater than 10 mg/kg, report the sulfur result to the nearest mg/kg. For results less than 10 mg/kg, report the sulfur results to the nearest tenth of a mg/kg. State that the results were obtained according to this Test Method D7620.

16. Quality Control

16.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (8.6) after each calibration and at a frequency in accordance with local site requirements.

16.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

16.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 may be used as the QC/QA system.

17. Precision and Bias[4]

17.1 *Precision*—The precision of this test method as determined by statistical examination of interlaboratory test results using Practice D6300 is as follows.

NOTE 5—The following precision data were developed in a 2008 interlaboratory cooperative test program. Six laboratories analyzed 14 sample sets each of gasoline, gasoline with 10 % ethanol, diesel, biodiesel (B100), and jet fuel. Their sulfur concentration ranges were from 4.0 mg/kg to 830 mg/kg.

17.1.1 *Repeatability*—The difference between two 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 in only 1 case in 20, where x = the average of the two test results.

$$r = 0.180 * X^{0.75} \text{ mg/kg} \tag{4}$$

17.1.2 *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, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where x = the average of two test results.

$$R = 0.495 * X^{0.75} \text{ mg/kg} \tag{5}$$

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

17.2 *Bias*—The bias of this test method by analysis of National Institute of Standards and Technology (NIST) standard reference materials (SRMs) containing known levels of sulfur in gasoline and diesel has not been determined.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1701.

TABLE 3 Repeatability (r) and Reproducibility (R)

Concentration, (mg/kg S)	r	R
1	0.2	0.5
5	0.6	1.7
10	1.0	2.8
50	3.4	9.3
100	5.7	15.6
400	16.1	44.2

17.2.1 *Relative Bias*—Relative bias to Test Method D5453 has not been determined.

18. Keywords

18.1 diesel; gasoline; total sulfur analysis; UV-fluorescence detection

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample (see Test Methods D6299, D6792, and ASTM MNL 7[5]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process (see Test Methods D6299, D6792, and ASTM MNL 7[5]). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM Test Method precision to ensure data quality.

X1.5 It is recommended that, if possible, the types of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Test Methods D6299, D6792, and ASTM MNL 7[5] for further guidance on QC and control charting techniques.

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[5] ASTM MNL7, *Manual on Presentation of Data and Control Chart Analysis*, ASTM International, W. Conshohocken, PA.