Designation: D 5453 – 93

Standard Test Method for
Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence

This standard is issued under the fixed designation D 5453; 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, boiling in the range from approximately 25°C to 400°C, with viscosities between approximately 0.2 and 10 cSt (mm²/S) at room temperature. This test method is applicable to naphthas, distillates, motor fuels and oils containing 1.0 to 8000 mg/kg total sulfur.

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 SI (Metric) units are regarded as standard.

1.4 This standard does not purport to address all of the safety problems, 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. See 3.2, 6.3, 6.4, 8.1 and Section 7.

2. Referenced Documents

2.1 ASTM Standards:
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

2.2 Referenced Documents:
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 A hydrocarbon sample is directly injected or placed in a sample boat. The sample or boat, or both, enter into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO₂) in an oxygen rich atmosphere. Water produced during the sample combustion is removed 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*). The 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.

4. Significance and Use

4.1 Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur bearing materials are contained in the feedstocks. This test method can be used to determine sulfur in process feeds and can also be used to control sulfur in finished products.

5. Apparatus

5.1 Furnace—An electric furnace held at a temperature (1100°C) sufficient to pyrolyze all of the sample and oxidize sulfur to SO₂.

5.2 Combustion Tube—A quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace or constructed so that the inlet end of the tube is large enough to accommodate a quartz sample boat. The combustion tube must have side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough (see Figs. 1 and 2) to ensure complete combustion of the sample. Figs. 1 and 2 depict conventional combustion tubes. Other configurations are acceptable if precision is not degraded.

5.3 Flow Control—The apparatus must be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.

5.4 Drier Tube—The apparatus must be equipped with a mechanism for the removal of water vapor. The oxidation reaction products include water vapor which must be eliminated prior to measurement by the detector. This can be accomplished with a membrane drying tube, permeation dryer, that utilizes a selective capillary action for water removal.

5.5 UV Fluorescence Detector—A qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

5.6 Microlitre Syringe—A microlitre syringe capable of accurately delivering 5 to 20-microlitre quantities. The needle should be 50 mm (± 5 mm) long.

5.7 Sample Inlet System—Either of two types of sample inlet systems can be used.

5.7.1 Direct Injection—A direct injection inlet system must be capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism which discharges the sample from the microlitre syringe at a rate of approximately 1 µL/s is required. See example, Fig. 3.

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1 This test method is under the jurisdiction of ASTM Committee D-02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03.03 on Electrometric Methods.

2 Annual Book of ASTM Standards, Vol 05.02.

3 Apparatus manufactured in several variations by Antek Instruments, Inc., Houston, TX has been found suitable for this purpose.
**Fig. 1** Direct Inject

**Fig. 2** Boat Inlet

**Fig. 3** Syringe Drive, Direct Injection
5.7.2 Boat Inlet System—An extended combustion tube provides a seal to the inlet of the oxidation area and is swept by a carrier gas. The system provides an area to position the sample carrying mechanism (boat) at a retracted position removed from the furnace. The boat drive mechanism will fully insert the boat into the hottest section of the furnace inlet. The sample boats and combustion tube are constructed of quartz. The combustion tube provides a coolant jacket for the area in which the retracted boat rests awaiting sample introduction from a microlitre syringe. A drive mechanism which advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate is required. See example, Fig. 4.

5.8 Refrigerated Circulator—An adjustable apparatus capable of delivering a coolant material at a constant temperature as low as 4°C could be required when using the boat inlet injection method (optional).

5.9 Strip Chart Recorder, (optional).

5.10 Balance with a Precision of ±0.01 mg, (optional).

6. Reagents

6.1 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. 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 Inert Gas—Argon or helium only, high purity grade (that is, chromatography or zero grade), 99.998 % min purity, moisture 5 ppm w/w max.

6.3 Oxygen—High purity (that is, chromatography or zero grade), 99.75 % min purity, moisture 5 ppm w/w max, dried over molecular sieves.

NOTE 2: Warning—Vigorously accelerates combustion.

6.4 Toluene, Xylenes, Isooctane, Reagent grade. (Other solvents similar to those occurring in samples to be analyzed are also acceptable.) Correction for sulfur contribution from solvents (solvent blank) used in standard preparation and sample specimen dilution is required. Alternatively, use a solvent with nondetectable sulfur contamination relative to the sample unknown makes the blank correction unnecessary.

NOTE 3: Warning—Flammable solvents.

6.5 Dibenzothiophene, FW184.26, 17.399 % (m/m) S (Note 4).

6.6 Butyl Sulfide, FW146.29, 21.927 % (m/m) S (Note 4).

6.7 Thionaphthene (Benzothiophene), FW134.20, 23.907 % (m/m) S (Note 4).

NOTE 4—A correction for chemical impurity can be required.

6.8 Quartz Wool:

6.9 Sulfur Stock Solution, 1000 µg S/mL—Prepare a stock solution by accurately weighing 0.5748 g of dibenzothiophene or 0.4652 g of Butyl Sulfide or 0.4184 g of thionaphthene into a tared 100 mL volumetric flask. Dilute to volume with selected solvent. This stock can be further diluted to desired sulfur concentration (Note 5).

NOTE 5—Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, stock solutions have a useful life of about 3 months.

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4 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.
7. Hazards

7.1 High temperature is employed in this test method. Extra care must be exercised when using flammable materials near the oxidative pyrolysis furnace.

8. Sampling

8.1 Obtain a test unit in accordance with Practice D 4057 or Practice D 4177. To preserve volatile components which are in some samples, do not uncover samples any longer than necessary. Samples should be analyzed as soon as possible after taking from bulk supplies to prevent loss of sulfur or contamination due to exposure or contact with sample container.

Note 6: Warning—Samples that are collected at temperatures below room temperature can undergo expansion and rupture the container. For such samples, do not fill the container to the top; leave sufficient air space above the sample to allow room for expansion.

8.2 If the test unit is not used immediately, then thoroughly mix in its container prior to taking a test specimen.

9. Preparation of Apparatus

9.1 Assemble and leak check apparatus according to manufacturer’s instructions.

9.2 Adjust the apparatus, dependent upon the method of sample introduction, to meet conditions described in Table 1.

9.3 Adjust instrument sensitivity, baseline stability and perform instrument blanking procedures following manufacturer’s guidelines.

10. Calibration and Standardization

10.1 Select one of the suggested curves outlined in Table 2. Prepare a series of calibration standards by making dilutions of the stock solution to cover the range of operation.

10.2.1 For the boat inlet, quantitatively discharge the remaining sample into the combustion tube or delivery into the sample boat for analysis (Note 6). There are two alternative techniques available.

TABLE 1 Typical Operating Conditions

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Syringe Drive (Direct Inject) Drive Rate (700–750)</td>
<td>1 µL/s</td>
</tr>
<tr>
<td>Boat Drive (Boat Inlet) Drive Rate (700–750)</td>
<td>140–160 mm/min</td>
</tr>
<tr>
<td>Furnace Temperature</td>
<td>1100 ± 25°C</td>
</tr>
<tr>
<td>Furnace Oxygen Flowmeter Setting (3.8–4.1)</td>
<td>450–500 cc/min</td>
</tr>
<tr>
<td>Inlet Oxygen Flowmeter Setting (0.4–0.8)</td>
<td>10–30 cc/min</td>
</tr>
<tr>
<td>Inlet Carrier Flowmeter Setting (3.4–3.6)</td>
<td>150–160 cc/min</td>
</tr>
</tbody>
</table>

10.2.2 For direct injection, carefully insert the syringe into the inlet of the combustion tube and the syringe drive. Allow time for sample residues to be burned from the needle (Needle Blank). Once a stable baseline has reestablished, promptly start the analysis. Remove syringe once the apparatus has returned to a stable baseline.

10.3 For the boat inlet, quantitatively discharge the contents of the syringe into the boat containing quartz wool at a slow rate being careful to displace the last drop from the syringe needle. Remove the syringe and promptly start the analysis. The instrument baseline should remain stable until the boat has been completely withdrawn from the furnace (Note 8). Once the boat has reached its fully retracted position, allow one min for cooling before the next sample injection (Note 9).

TABLE 2 Sulfur Standards

<table>
<thead>
<tr>
<th>Injection Size</th>
<th>Curve I</th>
<th>Curve II</th>
<th>Curve III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur ng/g</td>
<td>100.00</td>
<td>500.00</td>
<td>1000.00</td>
</tr>
<tr>
<td>5.00</td>
<td>50.00</td>
<td>25.00</td>
<td>10.00</td>
</tr>
<tr>
<td>0.50</td>
<td>5.00</td>
<td>2.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Note 7—An automatic sampling and injection device can be used in place of the described manual injection procedure.

10.3.1 The volumetric measurement of the injected material can be obtained by filling the syringe to the selected level. Retract the plunger so that air is aspirated and the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. After injection, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected (Note 7).

Note 8—Slowing boat speed or briefly pausing the boat in the furnace can be necessary to assure complete sample combustion.

Note 9—The level of boat cooling required and the onset of sulfur detection following sample injection are directly related to the volatility of the materials analyzed. The use of a refrigerated circulator to minimize the vaporization of the sample until the boat begins approaching the furnace could be required.

10.5 Calibrate the instrument using one of the following two techniques.

10.5.1 Perform measurements for the calibration standards and blank using one of the procedures described in Sections 10.2 through 10.4. Measure the calibration standards and blank three times. Subtract the average blank response from each standard measurement before determining the average integrated response (see 6.4). Construct a curve plotting average integrated detector response (y-axis) versus µg sulfur injected (x-axis). This curve should be linear and system performance must be checked with the calibration standards at least once per day.

10.5.2 If the apparatus features an internal calibration routine, measure the calibration standards and blank three
times using one of the procedures described in Sections 10.2 through 10.4. If blank correction is required and is not available (see 6.4), calibrate the analyzer as per manufacturer's instructions using the average response for each standard versus ng of sulfur. This curve should be linear and system performance must be checked with the calibration standards at least once per day.

10.5 If analyzer calibration is performed using a different calibration curve than listed in Table 2, select an injection size based on the curve closest in concentration to the measured solution(s) (Note 10).

Note 10—Injection of 10 μL of the 100 ng/μL standard would establish a calibration point equal to 1000 ng or 1.0 μg.

11. Procedure

11.1 Obtain a test specimen using the procedure described in Section 8. The sulfur concentration in the test specimen must 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 can be performed on either a weight or volume basis.

11.1.1 Gravimetric Dilution—Record the mass of the test specimen and the total mass of the test specimen and solvent.

11.1.2 Volumetric Dilution—Record the mass of the test specimen and the total volume of the test specimen and solvent.

11.2 Measure the response for the test specimen solution using one of the procedures described in Sections 10.2 through 10.4.

11.3 Inspect the combustion tube and other flow path components to verify complete oxidation of the test specimen.

11.3.1 Direct Inject Systems—Reduce the sample size or the rate of injection, or both, of the specimen into the furnace if coke or sooting is observed.

11.3.2 Boat Inlet Systems—Increase the residence time for the boat in the furnace if coke or soot is observed on the boat. Decrease the boat drive introduction rate or specimen sample size, or both, if coke or soot is observed on the exit end of the combustion tube.

11.3.3 Cleaning and Recalibration—Clean any coked or sooted parts per manufacturer's instructions. After any cleaning or adjustment, assemble and leak check the apparatus. Repeat instrument calibration prior to reanalysis of the test specimen.

11.4 Measure each test specimen solution three times and calculate the average detector responses.

12. Calculation

12.1 For analyzers calibrated using a standard curve, calculate the sulfur content of the test specimen in parts per million (ppm) as follows:

\[
\text{Sulfur, ppm (μg/g)} = \frac{(I - Y)}{S \times M \times K_s} \quad (1)
\]

or,

\[
\text{Sulfur, ppm (μg/g)} = \frac{(I - Y)}{S \times V \times K_v} \quad (2)
\]

where:

- \(D\) = density of test specimen solution, g/mL,
- \(I\) = average of integrated detector response for test specimen solution, counts,
- \(K_s\) = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,
- \(K_v\) = volumetric dilution factor, mass of test specimen/volume of test specimen and solvent, g/mL,
- \(M\) = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, \(V \times D, \mu L\),
- \(S\) = slope of standard curve, counts/μg S,
- \(V\) = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, \(M/D, \mu L\), and \(Y\) = y-intercept of standard curve, counts.

12.2 For analyzers calibrated using internal calibration routine without blank correction, calculate the sulfur of the test specimen in parts per million (ppm) as follows:

\[
\text{Sulfur, ppm (μg/g)} = \frac{G}{M \times K_s \times g/1000 mg} \quad (3)
\]

or,

\[
\text{Sulfur, ppm (μg/g)} = \frac{G}{V \times D \times g/1000 mg} \quad (4)
\]

where:

- \(D\) = density of test specimen solution, mg/μL (neat injection), or concentration of solution, mg/μL (volumetric dilute injection),
- \(K_s\) = gravimetric dilution factor, mass of test specimen/mass of test specimen and solvent, g/g,
- \(M\) = mass of test specimen solution injected, either measured directly or calculated from measured volume injected and density, \(V \times D, \mu L\),
- \(V\) = volume of test specimen solution injected, either measured directly or calculated from measured mass injected and density, \(M/D, \mu L\),
- \(G\) = sulfur found in test specimen, μg.

13. Precision

13.1 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.

\[
r = 0.1867(x)^{0.63} \quad (5)
\]

13.2 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 the two test results,

\[
R = 0.2217(x)^{0.92} \quad (6)
\]

13.3 Bias—The bias of this method was determined in a
1992 research report, by analysis of standard reference materials (SRMs) containing known levels of sulfur in hydrocarbon. This report indicated that the results obtained on the SRMs were within the repeatability of the test method.

13.4 Examples of the above precision estimates for selected absolute values of $x$ are set out in Table 3.

14. Keywords

14.1 fluorescence; sulfur; ultraviolet

### TABLE 3 Repeatability ($r$) and Reproducibility ($R$)

<table>
<thead>
<tr>
<th>Concentration (mg/kg S)</th>
<th>$r$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.187</td>
<td>0.222</td>
</tr>
<tr>
<td>5</td>
<td>0.515</td>
<td>0.975</td>
</tr>
<tr>
<td>10</td>
<td>0.795</td>
<td>1.844</td>
</tr>
<tr>
<td>50</td>
<td>2.195</td>
<td>8.106</td>
</tr>
<tr>
<td>100</td>
<td>3.397</td>
<td>15.338</td>
</tr>
<tr>
<td>500</td>
<td>9.364</td>
<td>67.426</td>
</tr>
<tr>
<td>1000</td>
<td>14.492</td>
<td>127.575</td>
</tr>
<tr>
<td>5000</td>
<td>39.948</td>
<td>560.813</td>
</tr>
</tbody>
</table>

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