
This standard is issued under the fixed designation D 4294; 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 measurement of sulfur in hydrocarbons such as naphthas, distillates, fuel oils, residues, lubricating base oils and nonleaded gasoline. The concentration range is from 0.05 to 5 mass %.

1.2 This standard may involve hazardous materials, operations, and equipment. 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 precautionary statements, see Section 7.

1.3 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mass % sulfur.

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 Other Standards:
X-ray Source, for Energy-Dispersive X-ray Analysis

3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray source. The excitation energy may be derived from a radioactive source or from an X-ray tube. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass %. Three groups of calibration samples are required to span the concentration range 0.05 to 5 mass % sulfur.

4. Significance and Use

4.1 The quality of many petroleum products is related to the amount of sulfur present. Knowledge of sulfur concentration is necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies which restrict the amount of sulfur present in some fuels.

5. Interferences

5.1 Samples containing heavy metal additives, lead alkyls, etc., may interfere with the test method. Elements such as silicon, phosphorus, calcium, potassium, and halides interfere if present in concentrations of more than a few hundred milligrams per kilogram. Consult instrument manufacturers' instructions for specific interference data. Materials used in the study to determine precision contained up to 250 mg/kg vanadium, 50 mg/kg nickel, and 15 mg/kg iron with no detectable bias introduced.

6. Apparatus

6.1 Energy-dispersive X-ray Fluorescence Analyzer—Energy-dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum, the following features and if test results from it are shown to be equivalent on the samples of interest. Required design features include:

6.1.1 Source of X-ray Excitation, with significant energy above 2.5 KeV.
6.1.2 Removable Sample Cup, equipped with replaceable X-ray transparent plastic film windows and providing a sample depth of at least 3 mm.
6.1.3 X-ray Detector, with high sensitivity at 2.3 KeV.
6.1.4 Filters or other means of discriminating between sulfur Ka radiation and other X-rays.
6.1.5 Signal Conditioning Electronics that include the functions of pulse counting and pulse height analysis.
6.1.6 Display or Printer that reads out in counts, % sulfur, or both.

NOTE 1—Precaution—In addition to other precautions, if a radioactive source is used, it must be well shielded to international standard requirements and, therefore, not present any safety hazard. However, attention to the source is only to be carried out by a fully trained and competent person using the correct shielding techniques.

6.2 Analytical Balance, capable of weighing to the nearest 0.1 mg.

NOTE 2—Operation of analyzers using X-ray tube sources is to be conducted in accordance with the manufacturer's safety instructions.

7. Reagents and Materials

7.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

7.2 Di-n-Butyl Sulfide, sulfur content 21.91 mass %.

NOTE 3: Warning—Di-n-butyl sulfide is flammable and toxic.

7.3 White Oil, ACS reagent grade or less than 20 mg/kg sulfur.

8. Sample Cell Preparation

8.1 Clean and dry cells before use. Disposable sample cups are not to be reused. Window material usually is 6 μm polyester or polycarbonate film. Handling of the film must be kept to an absolute minimum to prevent contamination. Renewal of the window is essential for the measurement of each sample.

NOTE 4: Caution—Samples of high-aromatic content will probably dissolve polycarbonate films.

9. Calibration and Standardization

9.1 Preparation of Standards:

9.1.1 Make primary standards by weighing the components separately and not from dilution by a concentrate at three concentrations: 5, 2.5, and 1 mass % sulfur. The exact sulfur content in each standard is to be calculated to three decimal places.

9.1.2 Accurately weigh approximately the appropriate quantity of white oil, shown in Table 1, into a suitable, narrow-necked container and then accurately weigh in approximately the appropriate quantity of di-n-butyl sulfide. Mix thoroughly (a glass-coated magnetic stirrer is advisable) at room temperature.

9.1.3 Make calibration standards in three ranges by diluting primary standards with white oil (Table 2).

9.1.4 Prepare the aforementioned standards and suitable dilutions for the calibration graphs to cover the three ranges. A computer included with the analyzer may be used, if an internal multi-point calibration curve is provided.

9.2 Certified Calibration Standards

9.2.1 Calibration standards which are certified by a responsible standards organization may be used when applicable to the sample of interest. Such standards included Standard Reference Materials (SRM) prepared and certified by the National Institute of Standards and Technology (NIST), and Standard Sample of Sulfur in Residual Fuel Oil certified by the Japan Petroleum Institute.

9.2.2 NIST certified materials used in the study of this test method were designated as 1620, 1621, 1622, 1623, and 1624, and contained from 0.2 to 4.5 mass % sulfur.

9.2.3 Storage of Standards—Store standards in dark, glass-stoppered bottles in a cool, dark place until required. As soon as any sediment or change of concentration is observed, discard the standard.

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10. Preparation of Apparatus

10.1 Set up the apparatus in accordance with the manufacturer’s instructions. Whenever possible the instrument is run continuously to maintain optimum stability.

11. Sampling

11.1 Obtain a test specimen in accordance with Practice D 4057 or D 4177. If the test specimen is not used immediately, then thoroughly mix in the container prior to taking a portion for analysis.

12. Procedure

12.1 Prepare the sample cell and fill with sample to a minimum depth of 3 mm. Provide adequate head space, and if required, a cell vent hole to prevent bowing of the window when testing volatile samples.

NOTE 4: Warning—Avoid spilling flammable liquids inside the analyzer.

12.2 Standards—Obtain four readings on each standard using the recommended counting time for the instrument (typically acceptable counting times are 50 to 300 s). Immediately repeat the procedure using freshly prepared cells and fresh portions of samples. From the data obtained, calculate the average reading for each sulfur concentration. Prepare a calibration graph from the averaged results. A computer included with the analyzer may be used, if an internal multi-point calibration curve is provided.

12.3 Samples for Analysis—Before filling the cell, it may be necessary to heat viscous samples so that they are easy to pour into the cell. Fill the cell to the required depth and ensure there are no air bubbles between the window and the liquid. Obtain two consecutive counts using the recommended counting time for the instrument on a portion of the sample. Calculate the average count for the sample.

13. Calculation

13.1 The concentration of sulfur in the sample is read from the calibration curve using the averaged counts for each oil. Record the results to two decimal places. If the analyzer includes a computer and provides for automatic multi-point calibration, the concentration values so computed are to be recorded.

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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 Analytical 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.

4 Available from Phillips Petroleum Co., Bartlesville, OK.
14. Report

14.1 Report the results as the total sulfur content, mass %, and state that the results were obtained according to Test Method D 4294.

15. Precision and Bias

15.1 Precision—The precision of this test method as obtained by statistical analysis of interlaboratory test results is as follows:

15.1.1 Repeatability—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty (see Table 3).

\[
\text{Repeatability} = 0.029(S + 0.6) \quad (1)
\]

where \( S \) = average value of two results, mass %.

15.1.2 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, exceed the following values only in one case in twenty (see Table 3).

\[
\text{Reproducibility} = 0.063(S + 0.6) \quad (2)
\]

where \( S \) = average value of two results, mass %.

15.2 Bias—There was no observed bias within the reproducibility of the test method as determined in an interlaboratory test using NIST certified standards.

16. Keywords

16.1 sulfur; XRF; X-ray fluorescence

### TABLE 3 Repeatability and Reproducibility

<table>
<thead>
<tr>
<th>Average Value of Two Results, mass % sulfur</th>
<th>Repeatability, mass % sulfur</th>
<th>Reproducibility, mass % sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>1.0</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>2.0</td>
<td>0.08</td>
<td>0.16</td>
</tr>
<tr>
<td>3.0</td>
<td>0.10</td>
<td>0.23</td>
</tr>
<tr>
<td>4.0</td>
<td>0.13</td>
<td>0.29</td>
</tr>
<tr>
<td>5.0</td>
<td>0.16</td>
<td>0.35</td>
</tr>
</tbody>
</table>

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