



Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry¹

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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosine, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. In addition, sulfur in other products, such as M-85 and M-100, may be analyzed using this technique. The applicable concentration range is 0.0150 to 5.00 mass % sulfur.

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

1.3 *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 warning statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

- D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry²
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts

from previously prepared calibration standards that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation. A typical analysis time is 2 to 4 min per sample.

4.2 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 that restrict the amount of sulfur present in some fuels.

4.3 This test method provides a means of compliance with specifications or limits set by regulations for sulfur content of petroleum products.

4.4 If this test method is applied to petroleum matrices with significantly different composition than the white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting the results.

4.5 Compared to other test methods for sulfur determination, Test Method D 4294 has high throughput, minimal sample preparation, good precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified is in most cases less costly than that required for alternative methods. Consult the ASTM Subject Index⁵ for names of alternative test methods.

5. Interferences

5.1 Spectral interferences result when some sample component element or elements emit X-rays that the detector cannot resolve from sulfur X-ray emission. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing water, lead alkyls, silicon, phosphorus, calcium, potassium, and halides if present at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred

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

Current edition approved April 10, 2002. Published July 2002. Originally published as D 4294-83. Last previous edition D 4294-98.

² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ *Annual Book of ASTM Standards*, Vol 00.01.

milligrams/kilogram. Follow the manufacturer's operating-guide to compensate for the interferences.

5.2 Matrix effects are caused by concentration variations of the elements in a sample. These variations directly influence X-ray absorption and change the measured intensity of each element. For example, performance enhancing additives, such as oxygenates in gasoline, can affect the apparent sulfur reading. These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

5.3 Both types of interferences are compensated for in contemporary instruments with the use of built-in software. It is recommended that these interferences be checked from time to time and that the software corrections offered by the manufacturer not be accepted at face value. Corrections should be verified for new formulations.

5.4 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. As such, they have a high oxygen content, hence, absorption of sulfur $K\alpha$ radiation. Such fuels can, however, be analyzed using this test method provided that the calibration standards are prepared to match the matrix of the sample. There may be a loss of sensitivity and precision. The repeatability, reproducibility, and bias obtained in this test method did not include M-85 and M-100 samples.

5.5 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 may be analyzed with standards made from base materials that are of the same, or similar, composition. Thus, a gasoline may be simulated by mixing *isooctane* and toluene in a ratio that approximates the true aromatic content of the samples to be analyzed. Standards made from this simulated gasoline will produce results that are more accurate than results obtained using white oils.

NOTE 1—In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and immediately tested. The interference is greatest if the water creates a layer over the transparent film as it will attenuate the X-ray intensity for sulfur. One such method to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.

6. Apparatus

6.1 *Energy-dispersive X-ray Fluorescence Analyzer*—Any energy dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum, the following features:

6.1.1 *Source of X-ray Excitation*, X-ray source with energy above 2.5 keV. (**Warning**—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.)

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

6.1.2 *Sample Cell*, providing a sample depth of at least 4 mm and equipped with a replaceable X-ray transparent plastic film window.

6.1.3 *X-ray Detector*, with sensitivity at 2.3 keV and a resolution value not to exceed 800 eV. A gas filled proportional counter has been found to be suitable to use.

6.1.4 *Filters*, or other means of discriminating between sulfur $K\alpha$ radiation and other X-rays of higher energy.

6.1.5 Signal conditioning and data handling electronics that include the functions of X-ray intensity counting, a minimum of two energy regions (to correct for background X-rays), spectral overlap corrections, and conversion of sulfur X-ray intensity into percent sulfur concentration.

6.1.6 *Display or Printer*, that reads out in mass % sulfur.

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.⁶ 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 (DBS)*, a high purity standard with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (9.1.7). (**Warning**—*Di-n-butyl sulfide* is flammable and toxic.)

NOTE 3—It is essential to know the concentration of the sulfur in the *di-n-butyl sulfide*, not the purity, since impurities may also be sulfur containing compounds.

7.3 *Mineral Oil, White (MOW)*, ACS reagent grade or less than 2 mg/kg sulfur.

7.4 *X-ray Transparent Film*, any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent may be used. Films found to be suitable are polyester, polypropylene, polycarbonate, and polyimide films.

7.4.1 Samples of high aromatic content may dissolve polyester and polycarbonate films. In these cases, other materials besides these films may be used for X-ray windows, provided that they do not contain any elemental impurities. An optional window material is polyimide foil. Although polyimide foil absorbs sulfur X-rays more than other films, it may be a preferred window material as it is much more resistant to chemical attack by aromatics and exhibits higher mechanical strength.

7.5 *Sample Cells*, resistant to sample attack and meet geometry requirements of spectrometer.

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practice D 4057 or D 4177, where appropriate.

⁶ *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.