



Designation: D4294 – 10

# Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D4294; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

## 1. Scope\*

1.1 This test method covers the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel (see **Note 2**), and similar petroleum products.

NOTE 1—Oxygenated fuels with ethanol or methanol contents exceeding the limits given in **Table 1** can be dealt with using this test method, but the precision and bias statements do not apply (see **Appendix X3**).

NOTE 2—For samples with high oxygen contents (>3 wt %) sample dilution as described in **1.3** or matrix matching must be performed to assure accurate results.

1.2 Interlaboratory studies on precision revealed the scope to be 17 mg/kg to 4.6 mass %. An estimate of this test method's pooled limit of quantitation (PLOQ) is 16.0 mg/kg as calculated by the procedures in Practice **D6259**. However, because instrumentation covered by this test method can vary in sensitivity, the applicability of the test method at sulfur concentrations below approximately 20 mg/kg must be determined on an individual basis. An estimate of the limit of detection is three times the reproducibility standard deviation, and an estimate of the limit of quantitation<sup>2</sup> is ten times the reproducibility standard deviation.

1.3 Samples containing more than 4.6 mass % sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method. Samples that are diluted can have higher errors than indicated in **Section 16** than non-diluted samples.

1.4 Volatile samples (such as high vapor pressure gasolines or light hydrocarbons) may not meet the stated precision because of selective loss of light materials during the analysis.

<sup>1</sup> 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.

Current edition approved Feb. 15, 2010. Published March 2010. Originally approved in 1983. Last previous edition approved in 2008 as D4294-08a<sup>ε1</sup>. DOI: 10.1520/D4294-10.

<sup>2</sup> *Analytical Chemistry*, Vol 55, 1983, pp. 2210-2218.

1.5 A fundamental assumption in this test method is that the standard and sample matrices are well matched, or that the matrix differences are accounted for (see **5.2**). Matrix mismatch can be caused by C/H ratio differences between samples and standards (see **Section 5**) or by the presence of other heteroatoms.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards*:<sup>3</sup>

**D4057** Practice for Manual Sampling of Petroleum and Petroleum Products

**D4177** Practice for Automatic Sampling of Petroleum and Petroleum Products

**D6259** Practice for Determination of a Pooled Limit of Quantitation

**D6299** Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

**D7343** Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

**E29** Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

## 3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray tube. The resultant excited characteristic X radiation is

<sup>3</sup> 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.

\*A Summary of Changes section appears at the end of this standard

**TABLE 1 Concentrations of Interfering Species<sup>A</sup>**

Element	Mass % Tolerated
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Ethanol (Note 11)	8.6
Methanol (Note 11)	6
Fatty Acid Methyl Ester (FAME)	5

<sup>A</sup> The concentrations of substances in this table were determined by the calculation of the sum of the mass absorption coefficients times mass fraction of each element present. This calculation was made for dilutions of representative samples containing approximately 3 % of interfering substances and 0.5 % sulfur.

measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass % and/or mg/kg. A minimum of three groups of calibration samples are required to span the concentration range: 0.0 to 0.1 mass %, 0.1 to 1.0 mass %, and 1.0 to 5.0 mass % sulfur. (See Practice D7343.)

#### 4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1 to 5 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 determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

4.4 When this test method is applied to petroleum materials with matrices significantly different from the calibration materials specified in 9.1, the cautions and recommendations in Section 5 should be observed when interpreting results.

#### 5. Interferences

5.1 Spectral interferences are caused by the closeness of the X-ray characteristic lines of the elements present in a sample and the limited detector ability to completely resolve them. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing lead alkyls, silicon, phosphorus, calcium, potassium, halides and catalyst particles if present at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred milligrams/kilogram (parts per million—mass ppm). 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, may affect the apparent sulfur reading. Other matrix related interferences may arise from

**TABLE 2 Matrix Diluents**

Matrix	Matrix Diluent	Alternate Diluent
#2 Diesel	#2 Diesel	Kerosine
Naphtha	Kerosine	—
Kerosine	Kerosine	#2 Diesel
Residuals	Lube Oil	MOWH <sup>A</sup>
Lubricating Base Oils	Lube Oil	MOWL <sup>B</sup>
Hydraulic Oils	Lube Oil	MOWL <sup>B</sup>
Crude Oil	Lube Oil	MOWH <sup>A</sup>
Jet Fuels	Kerosine	—
Gasoline	Gasoline	—

<sup>A</sup> MOWH = mineral oil white heavy

<sup>B</sup> MOWL = mineral oil white light

heavy metal additives, lead alkyls, and elements such as silicon, phosphorus, calcium, potassium, and the halides, especially if present at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred milligrams/kilogram (parts per million—ppm). These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

5.3 The interferences mentioned in 5.1 and 5.2 may be compensated for in contemporary instruments with the use of built-in software for spectra deconvolution or overlap correction and inter-element correction by multiple regression or by other mathematical methods.

5.4 In general, petroleum materials with compositions that vary from 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. Suggestions are given in Table 2.

NOTE 3—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*—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*, X-ray tube with excitation 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 4 mm and a diameter of at least 10 mm.

6.1.3 *X-ray Detector*, with high sensitivity and a resolution value (Full Width at Half Maximum, FWHM) not to exceed 800 eV at 2.3 keV.

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, spectral overlap corrections, and conversion of sulfur X-ray intensity into mass percent sulfur concentration.

6.1.6 The analyzer shall have the sensitivity under optimized measurement conditions to measure the concentration of sulfur at the 0.05 % level with a demonstrated error due to counting statistics with one standard deviation not greater than 0.5 percent relative at the 500 mg/kg level. This requirement pertains to sample measurements of less than 1000 mg/kg.

6.1.7 *Display or Printer* that reads out in mass % sulfur and/or mg/kg sulfur.

6.2 *Analytical Balance*, with an accuracy and resolution of 0.1 mg and capable of weighing up to 100 g.

NOTE 4—Operation of analyzers using X-ray tube sources is to be conducted in accordance with the manufacturer's safety instructions.

## 7. Reagents

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 (ACS) where such specifications are available.<sup>4</sup> 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 and the material purity when calculating the exact concentrations of the calibration standards (see 9.1). **(Warning—Di-n-butyl sulfide is flammable and toxic.)**

NOTE 5—It is essential to know the concentration of sulfur in the di-n-butyl sulfide, not only the purity, since impurities may also be sulfur containing compounds.

7.3 *Drift Correction Monitor(s) (Optional)*—Several different materials have been found to be suitable for use as drift correction monitors. Appropriate drift monitor samples should be permanent materials that are stable with respect to repeated exposure to X-rays. Stable liquids like polysulfide oils, glass or metallic specimens are recommended. Liquids, pressed powders, and solid materials that degrade with repeated exposure to X-rays should not be used. Examples of sulfur containing materials that have been found to be suitable include a renewable liquid petroleum material, a metal alloy, or a fused glass disk. The monitor's counting rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The counting rate for the monitor sample is determined during calibration (see 9.2.1) and again at the time of analysis (see 12.2). These counting rates are used to calculate a drift correction factor (see 15.6).

<sup>4</sup> *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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.3.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

7.4 *Polysulfide Oil*, generally nonyl polysulfides containing a known percentage of sulfur diluted in a hydrocarbon matrix. **(Warning—May cause allergic skin reactions.)**

NOTE 6—Polysulfide oils are high molecular weight oils that contain high concentrations of sulfur, as high as 50 weight percent. They exhibit excellent physical properties such as low viscosity, low volatility, and durable shelf life while being completely miscible in white oil. Polysulfide oils are readily available commercially. The sulfur content of the polysulfide oil concentrate is determined via mass dilution in sulfur-free white oil followed by a direct comparison analysis against NIST reference materials.

7.5 *Mineral Oil, White (MOW)*, ACS Reagent Grade containing less than 2 mg/kg sulfur or other suitable base material containing less than 2 mg/kg sulfur. When low level (<200 mg/kg) measurements are anticipated, then the sulfur content, if any, of the base material needs to be included in the calculation of calibration standard concentration (see 9.1). When the sulfur content of the solvent or reagent is not certified, verify the absence of sulfur. Use the purest available grades for chemicals to be used for preparing calibration standards.

7.6 *X-ray Transparent Film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent can be used. Film types can include polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polypropylene, polycarbonate and polyester films.

7.7 *Helium Purge Gas (optional)*, Follow manufacturer's recommendations for corresponding specifications when use of helium purge gas is required.

7.8 *Counting Gas*, for instruments equipped with flow proportional counters. The purity of the counting gas should be in agreement with the specification provided by the instrument manufacturer.

7.9 *Sample Cells*, compatible with the sample and the geometry requirements of the spectrometer. Disposable cells are preferred over reusable ones for ultra low (<50 mg/kg) sulfur levels.

7.10 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known or certified sulfur content (including polysulfide oils, di-n-butyl sulfide, thiophenes, etc.) and not used in the generation of the calibration curve. The check samples shall be used to determine the precision and accuracy of the initial calibration (see Section 9).

7.11 *Quality Control (QC) Samples*, stable petroleum or product samples or solids representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (see Section 15).

NOTE 7—Verification of system control through the use of QC samples and control charting is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

NOTE 8—Suitable QC samples can often be prepared by combining retains of typical samples if they are stable. For monitors, solid materials

**TABLE 3 Composition of Primary Standards**

Sulfur Content, mass %	Mass of Matrix Diluent, g	Mass of Di- <i>n</i> -Butyl Sulfide, g
5	48.6	14.4
0.1	43.6	0.2

are recommended. QC samples must be stable over long periods.

## 8. Sample Cell Preparation

8.1 If you employ reusable cups, clean and dry cells before use. Disposable sample cups are not to be reused. Window material usually is <math>10\ \mu\text{m}</math> polyester or polycarbonate film (see 7.6). Polycarbonate is preferred due to its high transmissivity of sulfur X-rays. Renewal of the window of the sample cup is essential for the measurement of each sample. Avoid touching the inside of the sample cup or portion of the window film in the cup or in the instrument window that is exposed to X-rays. Oil from fingerprints can affect the reading when analyzing for low levels of sulfur. Wrinkles in the film will affect the number of sulfur X-rays transmitted. Therefore, the importance of the film's smoothness and cleanliness cannot be over stressed to ensure reliable results. The analyzer will need recalibration if the type or thickness of the window film is changed.

8.2 Impurities which may affect the measurement of low levels of sulfur have been found in polyester films and may vary from lot to lot. Therefore, if using a polyester film, the calibration should be checked after starting each new roll.

8.3 Samples of high aromatic content may dissolve polyester, polypropylene 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  $6\ \mu\text{m}$  thick polyimide foil. While 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.

## 9. Calibration

9.1 Prepare Calibration Standards by careful mass dilution of the certified di-*n*-butyl sulfide with a sulfur-free white oil or other suitable base material (see 7.5). The concentrations of the unknown samples must lie within the calibration range that is used. Approximate recommended nominal sulfur concentration standards are listed in Table 3 for the sulfur concentration ranges of interest. Take into account any sulfur in the base material when calculating the concentration of standards below 0.02 mass % (200 mg/kg), as shown in Eq 1. Weigh the DBS and matrix diluent to the recommended mass as closely as possible. It is important that the exact mass is known and thus the exact concentration of the prepared standards can be calculated and entered into the instrument for calibration purposes. The concentration of sulfur can be calculated using the following equation:

$$S = [(DBS \times S_{DBS}) + (MOW \times S_{MOW})] / (DBS + MOW) \quad (1)$$

where:

$S$  = mass % sulfur of the prepared standards,

$DBS$  = actual mass of DBS, g,

$S_{DBS}$  = the mass % sulfur in DBS, typically 21.91 %,

$MOW$  = actual mass of white oil, g, and

$S_{MOW}$  = mass % sulfur in the white oil.

For any generic source of sulfur use the following equation:

$$S = [(M_{SC} \times S_{SC}) + (M_D \times S_D)] / (M_{SC} + M_D) \quad (2)$$

where:

$S$  = mass % of sulfur in standard,

$M_{SC}$  = mass of sulfur compound, g,

$S_{SC}$  = mass % of sulfur in sulfur compound,

$M_D$  = mass of diluent, g, and

$S_D$  = mass % of sulfur in diluent.

9.1.1 Calibration standards can also be prepared by careful mixing of certified reference materials (CRM) of the same matrix, so long as the sulfur values of the resulting blends and their uncertainties are characterized by the certifying body.<sup>5</sup>

9.1.2 Alternatively, standards may be prepared by mass serial dilution of polysulfide oils (Note 5) with sulfur-free white oil. A freshly prepared polysulfide oil calibration curve should be verified using CRMs traceable to NIST, or other national metrology institute that has demonstrated proficiency for measuring sulfur in the matrix of interest. Once a polysulfide oil calibration curve is established, the calibration standards are stored at room temperature, out of direct sunlight, and in amber glass bottles. Polysulfide oil standards can be prepared over a wide concentration range from low mg/kg to high mass % levels of sulfur. They are easily prepared in quantity and make excellent quality control standards. Shaking polysulfide oil standards before fresh aliquots are taken is recommended to ensure the standard is uniformly blended. The high molecular weight of these sulfur compounds results in a very low vapor pressure that inhibits X-ray film diffusion. Therefore, an autosampler can be employed during the measurement process. Calibration curves prepared from polysulfide also demonstrate excellent linearity and help the analyst visualize the full dynamic range of their analytical method.

NOTE 9—Commercially available standards can be used provided their sulfur concentrations are accurately known and they approximate the nominal concentrations listed in Table 3.

9.1.3 Accurately weigh the appropriate quantity of matrix diluent, shown in Table 3, into a suitable, narrow-necked container and then accurately weigh in the appropriate quantity of completely pure di-*n*-butyl sulfide. Mix thoroughly (a polytetrafluoroethylene (PTFE)-coated magnetic stirrer is advisable) at room temperature.

9.1.4 Make calibration standards using one or more of the three ranges suggested in Table 4, according to the expected level of sulfur of the samples to be analyzed, by diluting primary standards with the applicable matrix diluent. Alternatively, standards may be prepared by mixing of certified reference materials (as in 9.1.1) or diluting polysulfide oils (as in 9.1.2).

NOTE 10—If desired, additional standards can be prepared and analyzed

<sup>5</sup> Refer to Kelly, W. R., MacDonald, B. S., and Leigh, S. D., "A Method for the Preparation of NIST Traceable Fossil Fuel Standards with Concentrations Intermediate to SRM Values," *Journal of ASTM International*, Vol 4, No. 2, 2007.