



Designation: D4294 – 21

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 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 (ϵ) 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, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasoline-ethanol blends, 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 % by weight) 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 % by 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 quantitation² is ten times the reproducibility standard deviation.

1.3 Samples containing more than 4.6 % by 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 17](#) 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.

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 [6.2](#)). Matrix mismatch can be caused by C/H ratio differences between samples and standards (see [Section 6](#)) 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:³

[D4057](#) Practice for Manual Sampling of Petroleum and Petroleum Products

[D4175](#) Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

[D4177](#) Practice for Automatic Sampling of Petroleum and Petroleum Products

[D6259](#) Practice for Determination of a Pooled Limit of Quantitation for a Test Method

[D6299](#) Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

[D7343](#) Practice for Optimization, Sample Handling,

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 *Analytical Chemistry*, Vol 55, 1983, pp. 2210-2218.

³ 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^A

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

^A 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.

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

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 The sample is placed in the beam emitted 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 percent or mg/kg, or both. A minimum of three groups of calibration samples are required to span the concentration range: 0.0 % to 0.1 % by mass, 0.1 % to 1.0 % by mass, and 1.0 % to 5.0 % by mass sulfur. (See Practice D7343.)

5. Significance and Use

5.1 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 min to 5 min per sample.

5.2 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.

5.3 This test method provides a means of determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

5.4 When this test method is applied to petroleum materials with matrices significantly different from the calibration materials specified in 10.1, the cautions and recommendations in Section 6 should be observed when interpreting results.

6. Interferences

6.1 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

TABLE 2 Matrix Diluents

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

^A MOWH = mineral oil white heavy

^B MOWL = mineral oil white light

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.

6.2 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 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.

6.3 The interferences mentioned in 6.1 and 6.2 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.

6.4 In general, petroleum materials with compositions that vary from oils as specified in 10.1 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.

7. Apparatus

7.1 *Energy-dispersive X-ray Fluorescence Analyzer*—Energy dispersive X-ray fluorescence analyzer may be used if