Designation: D4294 – 10

# Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry[1]

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, 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[2] 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.

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:*[3]

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

[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

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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.

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

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 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 Kα radiation and other X-rays of higher energy.

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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.[4] 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).

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

[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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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TABLE 3 Composition of Primary Standards

| Sulfur Content, mass % | Mass of Matrix Diluent, g | Mass of Di-*n*-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 <10 µm 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 µm 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.[5]

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

[5] 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.

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TABLE 4 Suggested Sulfur Standard Calibration Ranges

| 0–1000 mg/kg | 0.10–1.00 mass % | 1.0–5.0 mass % |
|---|---|---|
| 0.0[A,B] | 0.100 | 1.0 |
| 5[B] | 0.250 | 2.0 |
| 10[B] | 0.500 | 3.0 |
| 100[B] | 1.000 | 4.0 |
| 250 | | 5.0 |
| 500 | | |
| 750 | | |
| 1000 | | |

[A] Base material.
[B] Analyze these standards in duplicate and use either both individual values or the average in the calibration.

with concentrations between those listed in Table 4, see 9.1.1.

9.1.5 Alternatively, prepared standards for the above referenced matrices are commercially available.

9.1.6 If the matrix diluent being used for the preparation of standards contains sulfur, add this value to the calculated sulfur content of the prepared standards as per Eq 1 (consult your supplier for an accurate sulfur concentration or test the mineral oil using some other low level sulfur analyzing method).

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 or other national metrology institute that has demonstrated proficiency in measuring sulfur in the matrix of interest.

9.2.2 Standards containing 100 mg/kg total sulfur or less must be analyzed in duplicate. Use either both individual values or the average value of these measurements in the calibration.

9.3 *Instrument Calibration*—Calibrate the instrument for the appropriate range as listed in Table 4, following manufacturer's instructions. Typically, the calibration procedure involves setting up the instrument for recording of net sulfur X-ray intensity, followed by the measurement of known standards. Obtain one reading on each standard using the recommended counting time for the instrument as per Table 5. In the case of calibration standards less than 100 mg/kg, repeat the measurement using a freshly prepared sample cup and a fresh portion of the sample. Immediately repeat the procedure using freshly prepared cells and fresh portions of samples. Once all the standards have been analyzed, follow manufacturers instructions for generating the optimum calibration curve based on the net sulfur counts for each standard. (**Warning**—Avoid spilling flammable liquids inside the analyzer.)

9.4 *Quality Control Samples*—Several additional standards (quality control standards) may prove useful. Quality control standards, independently prepared as per 9.1, may be used as well as any appropriate certified standards as per 9.2. The concentration of the QC standards should be near the expected concentration of the samples being analyzed.

TABLE 5 Typical Counting Times For Sulfur Content Determination

| Sulfur Content Range, Mass % | Counting Time, seconds |
|---|---|
| 0.0000 to 0.1000 | 200 to 300 |
| 0.1 to 5.0 | 100 |
| 1.0 to 5.0 | 100 |

9.5 *Storage of Standards*—Store all standards in dark, glass bottles, with screw caps with a chemically resistant lining, in a cool, dark place until required. As soon as any sediment or change of concentration is observed, discard the standard.

## 10. Preparation of Apparatus

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

## 11. Sampling

11.1 Obtain a test specimen in accordance with Practice D4057 or D4177. Samples should be analyzed immediately after pouring into a sample cup and allowing for the escape of the air bubbles caused by mixing.

## 12. Procedure

12.1 A quality control sample is measured prior to analyzing unknowns to verify that the test method is in control. It is run identically to any unknown sample. If the chosen quality control sample's repeatability varies by more than the repeatability value of this test method expected for that concentration (acceptance value obtained from Table 6) then the procedure is deemed to be out of control and the instrument should be recalibrated before running any further analysis. A synthetic solid quality control sample may be used in lieu of liquid samples (see Section 15).

12.2 *Analysis of Unknown Samples*—Fill the cup with the sample to be measured to about 75 % of cup capacity. Before filling the cell, it may be necessary to heat viscous samples so that they are easy to pour into the cell. Ensure that no air bubbles are present between the cup window and the liquid sample. Measure each sample once. If the concentration from the first analysis is less than 100 mg/kg, repeat the measurement using a freshly prepared sample cup and a fresh portion of the sample, and obtain the average of the readings for the sulfur content in the unknown sample.

12.3 When analyzing more than a single unknown sample, measure a quality control sample at the end of each batch of unknown samples, but no less than every ten unknown samples, to verify that the method is in control. In all situations where the quality control samples vary by more than the repeatability expected for that concentration (Table 6), the analysis must be discontinued and corrective action taken to find the source of error. Use a quality control sample close to the unknown samples' sulfur concentration. Refer to Section 15.

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TABLE 6 Precision Values, All Sample Types

| X, mg/kg | Repeatability *r*, mg/kg Eq 3 Values | Reproducibility *R*, mg/kg Eq 5 Values |
|---|---|---|
| 16.0 | 2.6 | 11 |
| 25.0 | 3.4 | 15 |
| 50.0 | 5.4 | 24 |
| 100.0 | 8.5 | 37 |
| 500 | 24 | 105 |
| 1000 | 37 | 165 |
| 5000 | 105 | 465 |
| 10 000 | 165 | 727 |
| 46 000 | 440 | 1943 |

12.4 For samples containing 100 mg/kg total sulfur or less, duplicate determinations are required. Each determination must be made on a new portion of sample material and analyzed in accordance with 12.1 and 12.2. The difference between the duplicate analyses should be equal to or less than the repeatability values indicated in Table 6. If the difference is larger, investigate sample preparation to identify any possible sources of sample contamination, and repeat the analysis. The reason for duplicate measurements is to identify problems associated with sample contamination, leading to improved results precision at the lower sulfur levels.

NOTE 11—The concentrations of ethanol and methanol were calculated assuring a theoretical mixture of hydrocarbons and di-butyl sulfide to which ethanol (or methanol) was added until the sum of the mass coefficients times mass fractions increased by 5 %. In other words, the amount of ethanol (or methanol) that caused a negative 5 % error in the sulfur measurement was calculated. This information is included in Table 1 to inform those who wish to use Test Method D4294 for determining sulfur in gasohol (or M-85 and M-100) of the nature of the error involved.

## 13. Calculation

13.1 The concentration of sulfur in the sample is automatically calculated from the calibration curve.

## 14. Report

14.1 Report the results as total sulfur content mass % to three significant figures for concentrations greater than 0.01 %. For concentrations less than or equal to 0.01 %, report results in mg/kg. Report results in mg/kg to two significant figures between 100 and 10 mg/kg, and to one significant figure below 10 mg/kg. Report that results were obtained according to Test Method D4294. Use Practice E29 as a guide for rounding purposes.

14.1.1 For samples containing less than 100 mg/kg total sulfur, average the duplicate determinations and report that value as in 14.1.

## 15. Quality Control

15.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in this test method is in statistical control. One part of such a program might be the regular use and charting[6] of quality control samples (see 7.11). It is recommended that at least one type of quality control sample be analyzed that is representative of typical laboratory samples as defined in Practice D6299.

15.2 In addition to running a quality control sample (7.11), it is strongly recommended that the calibration blank (for example, diluent oil) be analyzed on a daily basis.

15.2.1 The measured concentration for the blank should be less than 2 mg/kg (0.0002 mass %) sulfur. If the measured concentration for the blank is greater than 2 mg/kg (0.0002 mass %), re-standardize the instrument and repeat the measurement of the blank (use a fresh sample and fresh cell). If the result falls outside the acceptable range, carry out a full calibration. If the sample loading port becomes contaminated, especially when analyzing <20 mg/kg sulfur level samples, it is necessary to open and clean it according to manufacturer's recommendations before further use.

15.2.2 It should be noted that in order to obtain a good fit for the calibration at low concentrations, it may be necessary to change the weighting factor in the regression.

15.3 *Results Validation*—Once a standard or sample has been measured, a procedure should be carried out to validate that measurement. This requires the operator to check for obvious signs of damage to the sample such as leaking sample cells, crinkled sample cell window and inspection of any secondary film.

15.4 Observation of the resultant analysis. If a result is considered outside normal thresholds, a repeat of the analysis should be carried out to confirm anomalous results.

15.5 Regular checks should be carried out to ensure that purging gas performance is within the instrument manufacturer's specification.

15.6 Drift and quality control standards/monitors must be run on a regular basis while drift monitors may also be run on a regular basis. . The tolerance levels of the checks made using these monitors should be such that a protocol of either drift correction or total recalibration is carried out if the results fall outside these levels. All measurements should be repeated between the last accepted monitor result and point of noncompliance should a current monitor measurement prove to be outside acceptable levels.

## 16. Precision and Bias[7]

16.1 *Precision*—The precision of the test method was determined by statistical analysis of results obtained in an interlaboratory study that included 27 samples including distillates, gasoline with or without oxygenates, kerosine, diesel, biodiesel E-85, residual oils, and crude oils. The laboratory study on precision covered a variety of materials with sulfur concentrations ranging from approximately 1 mg/kg to 4.6 mass %. A pooled limit of quantitation (PLOQ) of 16.0 mg/kg sulfur, was determined for all sample types. Separate precision statements for diesel and gasoline are included in Appendix X1. The ranges of sulfur concentrations represented by the sample sets, together with the precisions, are

[6] *ASTM MNL 7, Manual on Presentation of Data and Control Chart Analysis*, Section 3, Control Chart for Individuals, ASTM International, W. Conshohocken, PA.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1635.

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TABLE 7 Comparison of NIST and ASTM Interlaboratory Study (RR) Results

| NIST SRM Number | Sulfur, mg/kg, NIST | RR Sample Number | Matrix | Sulfur, mg/kg ASTM RR avg | Apparent Bias mg/kg Sulfur | Relative Bias, % | Significant? |
|---|---|---|---|---|---|---|---|
| 2296 | 40.0 | 2 | Reformulated Gasoline (nominal 13 % ETBE) | 46.3 | +6.3 | +15.8 | No |
| 2299 | 13.6 | 3 | Reformulated Gasoline | 18.1 | +4.5 | +33.1 | No |
| 2770 | 41.6 | 7 | Diesel | 49.4 | +7.8 | +18.8 | No |
| 2724b | 426.5 | 8 | Diesel | 430.8 | +4.3 | +1.01 | No |
| 2721 | 15 832 | 9 | Crude Oil (light-sour) | 16 118 | +288 | +1.82 | Yes |
| 2722 | 2104 | 10 | Crude Oil (heavy-sweet) | 2082 | -21 | -1.00 | No |
| 1619b | 6960 | 12 | Residual Fuel Oil | 6654 | -306 | -4.40 | Yes |
| 1620c | 45 610 | 13 | Residual Fuel Oil | 45 801 | +191 | +0.42 | No |

listed in 16.1.1 and 16.1.2. These statistics apply only to samples having less than the level of interfering materials present shown in Table 1.

NOTE 12—Volatile materials may not meet the stated precision of the method because selective loss of light materials is possible before and during analysis by this method. Another possible mechanism is the sulfur enrichment of the sample cup window resulting in higher sulfur values.

16.1.1 *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. Repeatability ($r$) may be calculated as shown in Eq 3 for all materials covering the full scope of this method. See Table 6 for calculated values.

$$\text{Repeatability } (r) = 0.4347 * X^{0.6446} \text{ mg/kg} \quad (3)$$

$$\text{Repeatability } (r) = \{0.4347 * ((Y * 10\ 000)^{0.6446})\}/10\ 000 \text{ mass \%} \quad (4)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

16.1.2 *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, in the normal and correct operation of the test method exceed the following values only in one case in twenty. Reproducibility ($R$) may be calculated as shown in Eq 5 for all materials covering the full scope of this method. See Table 6 for calculated values.

$$\text{Reproducibility } (R) = 1.9182 * X^{0.6446} \text{ mg/kg} \quad (5)$$

$$\text{Reproducibility } (R) = \{1.9182 * ((Y * 10\ 000)^{0.6446})\}/10\ 000 \text{ mass \%} \quad (6)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

16.1.3 Repeatability and reproducibility values for diesel in the aforementioned interlaboratory study[7] may be found in Appendix X1.

16.2 *Bias*—The interlaboratory study[7] included ten NIST standard reference materials (SRM's). The certified sulfur value, interlaboratory round robin (RR) value, apparent bias, and relative bias are given in Table 7. The white oil was assumed to have a C/H mass ratio of 5.698 ($C_{22}H_{46}$). There was no apparent bias that could be attributed to C/H ratio.

16.2.1 Based on the analysis of eight NIST Standard Reference Materials (SRM's), there was no significant bias based on D2PP calculations between the certified values and the results obtained in this interlaboratory study for any sample type.

## 17. Keywords

17.1 analysis; diesel; gasoline; jet fuel; kerosine; petroleum; spectrometry; sulfur; X-ray

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# APPENDIXES

(Nonmandatory Information)

## X1. ADDITIONAL DIESEL PRECISION STATEMENTS

X1.1 *Diesel Precision*—Six samples in the interlaboratory study[7] were diesels; they contained between approximately 20 and 5500 mg/kg total sulfur:

| | |
|---|---|
| Number 5 | Diesel |
| Number 7 | NIST SRM 2770 |
| Number 8 | NIST SRM 2724b |
| Number 15 | Diesel |
| Number 17 | Diesel |
| Number 22 | B-5 diesel containing 5 % biodiesel |

X1.1.1 *Repeatability (r)*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material 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. Repeatability ($r$) may be calculated as shown in Eq X1.1 for the six diesel samples. See Table X1.1 for calculated values.

$$\text{Repeatability } (r) = 1.6658 * X^{0.3363} \text{ mg/kg} \quad (X1.1)$$

$$\text{Repeatability } (r) = (1.6658 * ((Y * 10\ 000)^{0.3363}) / 10\ 000 \text{ mass } \% \quad (X1.2)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

X1.1.2 *Reproducibility (R)*—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 only in one case in twenty. Reproducibility ($R$) may be calculated as shown in Eq X1.3 for all materials covering the full scope of this test method. See Table X1.1 for calculated values.

$$\text{Reproducibility } (R) = 8.9798 * X^{0.3360} \text{ mg/kg} \quad (X1.3)$$

$$\text{Reproducibility } (R) = (8.9798 * ((Y * 10\ 000)^{0.3360})) / 10\ 000 \text{ mass } \% \quad (X1.4)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

## X2. ADDITIONAL GASOLINE PRECISION STATEMENTS

**TABLE X1.1 Precision Values, Diesel**

| S, mg/kg | Repeatability ($r$), mg/kg Eq X1.1 Values | Reproducibility ($R$), mg/kg Eq X1.3 Values |
|---|---|---|
| 25 | 4.8 | 26 |
| 100 | 7.6 | 41 |
| 500 | 13 | 70 |
| 1000 | 16 | 88 |
| 5500 | 29 | 154 |

X2.1 *Gasoline Precision*—Five samples in the interlaboratory study[7] were gasolines; they contained between approximately 11 and 5500 mg/kg total sulfur:

| | |
|---|---|
| Number 2 | Gasoline with 13 % ETBE |
| Number 3 | Reformulated gasoline |
| Number 4 | Gasoline with 5 % ethanol |
| Number 11 | Gasoline |
| Number 20 | E-85 |

X2.1.1 *Repeatability (r)*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material 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. Repeatability ($r$) may be calculated as shown in Eq X2.1 for the five gasoline samples. See Table X2.1 for calculated values.

$$\text{Repeatability } (r) = 1.4477 * X^{0.3661} \text{ mg/kg} \quad (X2.1)$$

$$\text{Repeatability } (r) = (1.4477 * ((Y * 10000)^{0.3661})) / 10000 \text{ mass } \% \quad (X2.2)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

X2.1.2 *Reproducibility (R)*—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 only in one case in twenty. Reproducibility ($R$) may be calculated as shown in Eq X2.3 for all materials covering the full scope of this test method. See Table X2.1 for calculated values.

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$$\text{Reproducibility } (R) = 7.1295 * X^{0.3601} \text{ mg/kg} \quad (X2.3)$$

$$\text{Reproducibility } (R) = \{7.1295 * [(Y * 10\ 000)^{0.3601}]\}/10\ 000 \text{ mass \%} \quad (X2.4)$$

*where:*

$X$ = sulfur concentration in mg/kg total sulfur, and
$Y$ = sulfur concentration in mass % total sulfur.

## X3. HANDLING OXYGENATED FUELS

TABLE X2.2 Precision Values, Gasoline

| S, mg/kg | Repeatability (*r*), mg/kg Eq X2.1 Values | Reproducibility (*R*), mg/kg Eq X2.3 Values |
|---|---|---|
| 50 | 6.0 | 30 |
| 100 | 7.8 | 38 |
| 500 | 14 | 69 |
| 1000 | 18 | 89 |
| 5500 | 34 | 167 |

X3.1 M-85 and M-100 are fuels containing 85 and 100% methanol, respectively. E-85 contains 85% ethanol. As such, they have a high oxygen content, hence, absorption of sulfur Kα 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.

X3.2 When analyzing M-85 or M-100 fuels with a calibration determined with white oil based standards, divide the result obtained in 12.3 as in the following equations. This correction is not required if the standards are prepared in the same matrix as the samples, as described in 5.2.

$$S \text{ (in M} - 85), \text{ mass \%} = S, \text{ mass \%}/0.59 \quad (X3.1)$$

$$S \text{ (in M} - 100), \text{ mass \%} = S, \text{ mass \%}/0.55 \quad (X3.2)$$

## SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4294–08a$^{\epsilon 1}$) that may impact the use of this standard. (Approved Feb. 15, 2010.)

*(1)* Updated 1.2, 7.7, 12.1, 12.3, 15.6, 16.1.1, 16.1.2, X1.1.1, X1.1.2, X2.1.1, and X2.1.2.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D4294–08) that may impact the use of this standard. (Approved Oct. 15, 2008.)

*(1)* Updated Section 16 to include additional ILS data not previously included in the research report.

*(2)* Updated Appendix X1 and Appendix X3.

*(3)* Added Appendix X2.

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EXHIBIT A

# FUEL OIL SPECIFICATIONS NO. 6

| PARAMETER | ASTM METHOD | MINIMUM | MAXIMUM |
|---|---|---|---|
| Sampling | D-4057 | 3 levels composite | (UML) |
| Gravity, API Degree at 60° F | D-287 | 10.5 | 18 |
| Viscosity, SFS at 122° F. | D-445<br>D-88 | 150 | 350 |
| Water and Sediment, % vol. | D-1796<br>D-473 | | 1 |
| Flash Point, Degree F., PMCT | D-93 | 150 | |
| Sulfur, % weight [1] | D-4294 | | 0.50 |
| Ash, % weight | D-482 | | 0.1 |
| Asphaltenes, % weight | D-3279 | | 8.0 |
| Pour Point, Degree F | D-97 | | 75 |
| Sodium plus Potassium, PPM[2] | D-1318 | | 35 |
| Vanadium, PPM | D-1548<br>D-5708<br>D-5863-A | | 150 |
| Calcium, PPM | D-5863-B | | 75 |
| Heating Value, BTU/gal. (Gross) at 60° F | D-240 | 150,000 | |

[1]Reproducibility and repeatability must be taken into consideration in order to comply with the maximum sulphur per cent weight specification. Additional Top, Middle, and bottom analysis shall be performed to insure cargo is homogeneous.

[2]Method D-1318 for sodium analysis, however, sodium as well as potassium can be analyzed by other acceptable atomic absorption or spectrometric analysis.