Designation: D2622 – 21

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

This standard is issued under the fixed designation D2622; 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, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasoline-ethanol blends, and biodiesel.

1.2 The range of this test method is between the PLOQ value (calculated by procedures consistent with Practice D6259) of 3 mg/kg total sulfur and the highest level sample in the round robin, 4.6 % by weight total sulfur.

Note 1—Instrumentation covered by this test method can vary in sensitivity. The applicability of the test method at sulfur concentrations below 3 mg/kg may be determined on an individual basis for WDXRF instruments capable of measuring lower levels, but precision in this test method does not apply.

1.2.1 The values of the limit of quantitation (LOQ) and method precision for a specific laboratory's instrument depends on instrument source power (low or high power), sample type, and the practices established by the laboratory to perform the method.

1.3 Samples containing more than 4.6 % by mass sulfur should 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 15 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 13.2). Matrix mis-match can be caused by C/H ratio differences between samples and standards or by the presence of other interfering heteroatoms or species (see Table 1).

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:*[2]
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
D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
D4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy
D6259 Practice for Determination of a Pooled Limit of Quantitation for a Test Method

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[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] 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.

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

TABLE 1 Concentrations of Interfering Species

Species	Mass % Tolerated
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Oxygen	2.8
FAME (see Note 16)	25
Ethanol (see Note 16)	8.6
Methanol (see Note 16)	6

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. 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 X-ray beam, and the peak intensity of the sulfur K-$L_{2,3}$ (Kα) line at 0.5373 nm is measured. The background intensity, measured at a recommended wavelength of 0.5190 nm (0.5437 nm for a Rh target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in milligrams per kilogram (mg/kg) or mass percent (see Section 13).

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 2 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 white oil calibration materials specified in this test method, the cautions and recommendations in Section 6 should be observed when interpreting results.

NOTE 2—The equipment specified for Test Method D2622 tends to be more expensive than that required for alternative test methods, such as

Test Method D4294. Consult the Index to ASTM Standards for alternative test methods.

6. Interferences

6.1 When the elemental composition (excluding sulfur) of samples differs significantly from the standards, errors in the sulfur determination can result. For example, differences in the carbon-hydrogen ratio of sample and calibration standards introduce errors in the determination. Some other interferences and action levels are listed in Table 1. If a sample is known from its history or another analysis to contain any of the species listed in Table 1 at or above the values listed there, that sample should be diluted with blank sulfur solvent to reduce the interferent concentration below the value to mitigate the effect of this interference.

NOTE 3—The concentrations of the first seven substances in Table 1 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. Refer to Note 16 for additional information regarding FAME, ethanol, and methanol.

6.2 Fuels containing large quantities of FAME, ethanol, or methanol (see Table 1) have a high oxygen content leading to significant absorption of sulfur Kα radiation and low sulfur results. Such fuels can, however, be analyzed using this test method provided either that correction factors are applied to the results (when calibrating with white oils) or that the calibration standards are prepared to match the matrix of the sample. See 12.5.

6.3 In general, petroleum materials with compositions that vary from white oils as specified in 10.1 can 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 expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

6.4 Test Method D4927 is the recommended test method for the determination of sulfur >100 mg/kg in lubricating oils and lubricating oil additives because method D4927 implements inter-element correction factors. Test Method D2622 is not suitable because it does not encompass the measurement of the additional elements present in lubricating oils and their additives making matrix correction impossible.

7. Apparatus

7.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF),* equipped for X-ray detection in the wavelength range from about 0.52 nm to about 0.55 nm (specifically at 0.537 nm). For optimum sensitivity to sulfur, the instrument should be equipped with the following items:

7.1.1 *Optical Path,* vendor specified, helium preferred, ambient air or nitrogen are inferior.

7.1.2 *Pulse-Height Analyzer,* or other means of energy discrimination.

7.1.3 *Detector,* for the detection of X-rays with wavelengths in the range of interest (from about 0.52 nm to about 0.55 nm).

7.1.4 *Analyzing Crystal,* suitable for the dispersion of sulfur K-L$_{2,3}$ (Kα) and background X-rays within the angular range of the spectrometer employed. Germanium or pentaerythritol (PET) are generally found to be acceptable. Other crystals may be used, consult with the instrument vendor.

7.1.5 *X-ray Tube,* capable of exciting sulfur K-L$_{2,3}$ (Kα) radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

NOTE 4—Exposure to excessive quantities of high energy radiation such as those produced by X-ray spectrometers is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation.

7.2 *Analytical Balance,* capable of weighing to the nearest 0.1 mg and up to 100 g.

8. Reagents

8.1 *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.[3] 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.

8.2 *Di-n-Butyl Sulfide (DBS),* a high-purity material 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 10.1). (**Warning**—Di-*n*-butyl sulfide is flammable and toxic. **Warning**—Solutions prepared in a volatile or un-stabilized matrix may not be stable several months after preparation.)

NOTE 5—It is essential to know the concentration of sulfur in the di-*n*-butyl sulfide, not only its purity, since impurities may also be sulfur containing compounds. The sulfur content may be determined via mass dilution in sulfur-free white oil followed by a direct comparison analysis against NIST (or other primary standards body) reference materials.

8.3 *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 10.4) and again at the
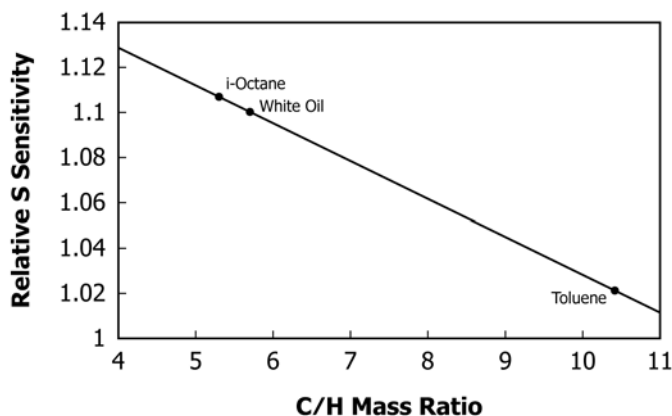

FIG. 1 Relative Sulfur Sensitivity versus C/H Ratio

time of analysis (see 11.1). These counting rates are used to calculate a drift correction factor (see 12.1).

8.3.1 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.

8.4 *Polysulfide Oil,* generally nonyl polysulfides containing a known percentage of sulfur diluted in a hydrocarbon matrix. (**Warning**—May cause allergic skin reactions. **Warning**—Solutions prepared in a volatile or un-stabilized matrix may not be stable several months after preparation.)

NOTE 6—Polysulfide oils are high molecular weight oils that contain high concentrations of sulfur, as high as 50 % by weight. They exhibit physical properties such as low viscosity, low volatility, and durable shelf life while being completely miscible in white oil. 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 (or other primary standards body) reference materials.

8.5 *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 10.1). When the sulfur content of the solvent or reagent is not certified, verify the absence of sulfur. Use the purest grades for the preparation of calibration standards. It is also important to measure the C/H ratio (see Section 13 and Fig. 1).

8.6 *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 and polycarbonate films.

8.7 *Helium Gas,* minimum purity 99.9 %.

8.8 *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.

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[3] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

8.9 *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.

8.10 *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 10.5).

8.11 *Quality Control 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 14).

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

9. Sampling and Specimen Preparation

9.1 Samples shall be taken in accordance with the instructions in Practices D4057 or D4177 when applicable.

9.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, or the instrument window (if the instrument is so equipped) 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 intensity of the sulfur X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer may need recalibration if the type or thickness of the window film is changed. After the sample cell is filled, create a small vent hole except when the cell is of the sealed type.

9.3 Employ adequate storage, mixing, and sampling procedures. Refrigerate gasolines or other similar volatile materials to retain sample integrity in storage, but allow them to return to room temperature before testing. Expose these materials to ambient conditions only as long as necessary to obtain a sample for analysis.

9.4 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in polyester films and may vary from lot to lot. Therefore, the calibration should be checked after starting each new lot of film.

9.5 See Practice D7343 for more detailed sample handling and preparation information.

10. Calibration

10.1 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 8.5). The concentrations of the unknown samples must lie within the calibration range that is used. Approximate recommended nominal sulfur concentration

TABLE 2 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 both values or the average value in the calibration.

standards are listed in Table 2 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 % by mass (200 mg/kg), as shown in Eq 1:

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

where:

S = mass percent sulfur of the prepared standards,
DBS = actual mass of DBS, g,
S_{DBS} = mass percent sulfur in DBS, typically 21.91 %,
WO = actual mass of white oil, g, and
S_{WO} = mass percent sulfur in the white oil.

NOTE 9—If desired, additional standards can prepared and analyzed with concentrations between those listed in Table 2, see 10.1.1.

10.1.1 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.[4]

10.1.2 Alternatively, standards may be prepared by mass serial dilution of polysulfide oils (Note 6) with sulfur-free white oil. A freshly prepared calibration curve should be verified using CRMs traceable to a national measurement institution that has demonstrated proficiency for measuring sulfur in the matrix of interest.

NOTE 10—Commercially available standards may be used provided their sulfur concentrations are accurately known and they approximate the nominal concentrations listed in Table 2.

10.2 Establish calibration curve data by carefully determining the net intensity of the emitted sulfur radiation from each of the standards by the procedures described in Sections 11 and 12.

10.2.1 Analyze standards containing 100 mg/kg total sulfur or less in duplicate. Either both of the individual values or the average value of these measurements may be used in the calibration. All samples in this sulfur concentration range must also be analyzed in duplicate, as in 11.12, and reported as in 13.1.1.

10.3 Construct a calibration model by using the software and algorithms supplied by the equipment vendor. The calibration model typically takes one of the following forms (refer to the equipment vendor's software documentation to determine the exact form):

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[4] 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.

$$C_S = a + bI \qquad \text{linear calibration} \qquad (2)$$

$$C_S = (a + bI)\left(1 + \sum \alpha_{ij} C_j\right) \qquad \text{correction for matrix effects} \qquad (3)$$

$$C_S = a + bI\left(1 + \sum \alpha_{ij} C_j\right) \qquad \text{alternative correction for matrix effects} \qquad (4)$$

$$C_S = a + bI + cI^2 \qquad \text{2nd order polynomial} \qquad (5)$$

where:

C_S = mass fraction of sulfur. The concentration units depend on the fitted calibration constants a, b and c,
I = measured net intensity for the sulfur radiation,
a = fitted calibration line offset (intercept),
b = fitted calibration line slope,
c = fitted calibration line 2nd order polynomial,
a_{ij} = correction factor for the effect of an interfering element (*j*) on sulfur (*i*). The interfering element can be sulfur when "matrix eliminated alphas" or empirical corrections are used, and
C_j = concentration of the interfering element (*j*).

Note 11—The a_{ij} factors can be determined empirically through multiple regression, or theoretically through fundamental parameters. Equipment vendors typically have provisions in their software for calculating theoretical a's.

10.3.1 Fit the calibration data over several ranges if necessary, depending on the sulfur concentrations to be covered. For example (Table 2): 0 % to 0.10 % by mass sulfur, 0.10 % to 1.0 % by mass sulfur, and 1.0 % to 5.0 % by mass sulfur.

Note 12—Calibration curves are typically linear to about 0.10 % by mass sulfur. The analyst should choose a linear calibration model when fitting within this range. One of the other calibration models (correction for matrix effects or a 2nd order polynomial) should be chosen when fitting to higher concentrations of sulfur.

10.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s) during the calibration procedure. The value determined corresponds to the factor A in Eq 7 in 12.1.

10.5 Immediately after completing the calibration, determine the sulfur concentration of one or more of the calibration check samples (8.10). The differences between two measured values shall be within the repeatability of this test method (see 15.1.1). When this is not the case, the stability of the instrument and the repeatability of the sample preparation are suspect and corrective measures should be taken. The degree of matrix mismatch between samples and standards should also be considered when evaluating a calibration. Statistical quality control charts may be prepared for these materials to establish if the method is in statistical control, as described in Section 14.

11. Procedure

11.1 *Instrument Setup*—Before using any WDXRF spectrometer, it is essential that the instrument is performing to the manufacturer's specifications. Consult with the manufacturer on how to perform spectrometer quality control checks. Practice D7343, Section 7 also provides more detailed information in this area.

11.2 Place particular attention on goniometer settings for sequential instruments, that is, ensuring goniometer positions are set correctly. Before performing a calibration of the goniometer angles carry out pulse height discriminator settings (PHD's) for each element and background to be used. The angle should be checked first, then the PHD, then the angle re-checked if the PHD settings are changed significantly. A very poor angle calibration may lead to bad PHD. The only reasonable alternate line is the sulfur K-$M_{2,3}$ (Kβ) with significantly less than 10 % of the sensitivity of the K-$L_{2,3}$ (Kα); this will only be practical for samples with high sulfur concentrations.

11.3 Account for observations of known instrument interferences. These include crystal fluorescence, tube line overlaps and any element spectral contamination from the materials within the instrument construction. Lead is a particularly bad interference for sulfur measurement. A number of these interferences can be avoided by careful selection of window settings during PHD set-up and for element interference the selection of an alternative line or minimizing overlap using higher resolution collimators and crystal selection.

11.4 When the factor F' is used in Eq 8, regularly analyze a blank sample to determine the factor F'. On a sulfur free sample, such as the base material, determine the counting rate at the appropriate sulfur peak and background angles.

11.5 Place the sample in an appropriate cell using techniques consistent with good practice for the particular instrument being used. Although incident radiation may penetrate a significant distance into the sample, sulfur radiation will escape from only a small distance into the sample, and scatter from the sample cell and the sample can vary. Ensure that the sample cell is filled above a minimum depth, beyond which additional sample does not significantly affect the counting rate. Generally, fill the sample cell to a minimum of two-thirds of the cell's capacity. Provide a small vent hole in the sample cell unless using a sealed cell.

11.6 Place the sample in the X-ray beam and allow the X-ray optical path to come to equilibrium.

11.7 Determine the intensity of the sulfur K-$L_{2,3}$ (Kα) radiation at 0.5373 nm by making counting rate measurements at the precise angular settings for this wavelength.

Note 13—It is suggested that a sufficient number of counts be taken to satisfy an expected coefficient of variation (% rsd) of 1.0 % or less when practical. When sensitivity or concentration, or both, make it impractical to collect a sufficient number of counts to achieve a 1.0 % coefficient of variation, accepted techniques, which will allow the greatest statistical precision in the time allotted for each analysis, should be used.

11.8 The coefficient of variation, CV, is calculated as follows:

$$CV = \left(100(N_p + N_b)^{1/2}\right)/(N_p - N_b) \qquad (6)$$

where:

CV = Coefficient of Variation, %,
N_p = number of counts collected at sulfur line peak, 0.5373 nm, and
N_b = number of counts collected at background wavelength in the same time interval taken to collect N_p counts.

11.9 Measure background counting rate at a previously-selected fixed angular setting, adjacent to the sulfur Kα peak.

TABLE 3 2θ Angles for Most Common Crystals

Crystal	2d (nm)	S Kα (0.5373 nm) Deg 2θ	Background (0.5190 nm) Deg 2θ	Background (0.5437 nm) Deg 2θ
Pentaerythritol (002)	0.8742	75.85	72.84	76.92
GE (111)	0.6532	110.68	105.23	112.68

NOTE 14—Suitability of any background setting will depend on the X-ray tube anode employed. A wavelength of 0.5190 nm is recommended where chromium or scandium is used whereas 0.5437 nm has been found suitable for rhodium, 2θ, peak and background, angles for various crystals are listed in Table 3.

11.10 Determine the corrected counting rate and calculate the concentration of the sample as described in Section 12.

11.11 When, from the measurements made in accordance with 11.5 – 11.10, the counting rate is higher than that of the highest point of the calibration curve, dilute the sample with the base material used to prepare the calibration standards until the sulfur counting rate is within the limits of the calibration curve and repeat the procedure described in 11.5 – 11.10.

11.12 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 11.5 – 11.10. The difference between the duplicate analyses should be equal to or less than the repeatability values indicated in 15.1.1. 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.

11.13 When the sample is known or believed to contain concentrations of interfering substances higher than those listed in Table 1, dilute the sample by mass with base material to concentrations below those listed.

11.13.1 The data collected (see Note 3) showed reasonable X-ray results when the calculated sum of mass absorption coefficients times mass fractions for samples was not greater than 4 % to 5 % above the sum of mass absorption coefficients times mass fractions for the calibration standards. Absorption interferences are additive, and they are only minimized by dilution, not completely eliminated. Table 1 is therefore to be used as a guide to concentrations that can be tolerated without significant error, not as an absolute quantity.

NOTE 15—The effect of matrix interferences can also be corrected on an empirical or theoretical basis.

NOTE 16—The concentrations of ethanol and methanol were calculated assuming 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 D2622 for determining sulfur in FAME blends (biodiesel), gasohol, M-85, or M-100 of the nature of the error involved.

11.13.2 Thoroughly mix the blend to ensure homogeneity (mixing method will depend on the matrix type), and transfer it to the instrument for measurement.

11.13.3 Determine the sulfur content of the blend in the normal manner as described in 11.5 – 11.9, and calculate the sulfur content of the original sample as described in Section 12.

12. Calculations

12.1 When using the drift correction monitor described in 8.3, calculate a correction factor for changes in daily instrument sensitivity as follows:

$$F = A/B \qquad (7)$$

where:

F = correction factor,
A = counting rate of the drift correction monitor as determined at the time of calibration (see 10.4), and
B = counting rate of the drift correction monitor as determined at the time of analysis.

12.2 Determine the corrected net counting rate (intensity) as follows:

$$R = [(N_p/S_1) - (N_b F'/S_2)] F \qquad (8)$$

where:

R = corrected net counting rate,
N_p = total counts collected at 0.5373 nm,
N_b = total counts collected at the background location chosen in 11.8,
S_1 and S_2 = seconds required to collect N_p and N_b counts, respectively,
F' = the ratio of counts/s at 0.5373 nm to the counts/s at background using a sample containing no sulfur, and
F = optional factor (see Note 17).

NOTE 17—The inclusion of the factor F in Eq 8 may not be necessary or desirable with some instrumentation. In this case F is set to unity. It is recommended that the user chart the F factor and develop criteria for its application based on the stability of the instrumentation and standard SQC principles.

12.2.1 The inclusion of the factor F' in Eq 8 is optional. In general it is needed for multi-channel spectrometers, which use different spectrometer channels to measure peak and background intensities.

NOTE 18—Charting the F' factor, even if it is not used in Eq 8, will alert the user to changes in instrument operation due to contamination of system elements, such as crystals, collimators, and fixed windows.

12.3 Calculate the sulfur content of the sample by inserting the corrected net counting rate from Eq 8 in the chosen calibration model from Section 10. In many cases the instrument vendor will provide software for the required calculations.

12.4 Calculate the concentration of sulfur in samples, which have been diluted, as follows:

$$S = S_b[(W_s + W_o)/W_s] \qquad (9)$$

where:

S = mass percent total sulfur in the sample,
S_b = mass percent sulfur in diluted blend,
W_s = mass of original sample, g, and
W_o = mass of diluent, g.

12.4.1 The instrument vendor may have provided software to perform this calculation when required masses are input.

12.5 When analyzing fuels containing high levels of FAME, ethanol, or methanol (Table 1) with a calibration determined with white oil based standards, divide the result obtained in 12.3 as follows (see Note 16):

$$S_{Fuel} = M/F \qquad (10)$$

where:

S_{Fuel} = mass percent sulfur present in the fuel sample, wt.%,
M = measured mass percent, wt.%, and
F = correction factor, for example, equals 0.59 for M-85 and 0.55 for M-100

12.5.1 This correction is not required if the standards are prepared in the same matrix as the samples, as described in 6.2.

12.6 Additional information regarding regression calculations may be found in Practice D7343.

NOTE 19—There are multiple options for correcting the interference from the presence of oxygenates in the determination of sulfur in fuels using WD-XRF method. A survey of D02.SC 3 members conducted in December 2014 revealed that the majority of users of this test method use the option given in Section 2 (that is, use of fundamental parameter calculation which is built into the software. This is done automatically by the instrument after the measurement is completed for each sample). Some members use the option of matrix matching described in 6.2. This is a challenging task due to the variability of the oxygen content in a series of samples. Fewer members use the option of automatic correction of the final data done by an independent program, using the approach similar to that given in 13.2. This would be similar to Fig. 1 depicted in the standard where the carbon/hydrogen ratio is being manually corrected. The option given in 11.13 does not appear to be used by the members.

13. Reporting

13.1 For samples analyzed without dilution, report the result calculated in 12.3. For samples that have been diluted, report the result calculated in 12.4. Report the result as the total sulfur content, mass percent, to three significant figures for concentrations greater than 0.1000 % by mass. Below 0.1000 % by mass (1000 mg/kg) report results in mg/kg to three significant figures between 1000 mg/kg and 10 mg/kg, and to two significant figures below 10 mg/kg. For guidance in properly rounding significant figures, refer to the rounding method in Practice E29. State that the results were obtained according to Test Method D2622.

13.1.1 For samples containing 100 mg/kg total sulfur or less, average the duplicate determinations and report that value as in 13.1.

13.2 The carbon/hydrogen (C/H) ratio correction formula, which is applicable when the base material used for the calibration standards is white oil and is derived from the best straight line shown in Fig. 1, is shown in Eq 11:

$$S_{C/H} = \frac{1.195 - 0.0164\,(C/H)_{whiteoil}}{1.195 - 0.0164\,(C/H)} \cdot S_{whiteoil} \qquad (11)$$

where:

$S_{C/H}$ = sulfur concentration corrected for C/H ratio matrix differences,
$(C/H)_{whiteoil}$ = mass ratio of carbon to hydrogen for white oil, 5.7 from Fig. 1,
(C/H) = mass ratio of carbon to hydrogen for the sample, and

TABLE 4 Precision Values, All Sample Types

S, mg/kg	Repeatability r, mg/kg Eq 12 values	Reproducibility R, mg/kg Eq 14 values
3.0	0.4	1.0
5.0	0.5	1.6
10.0	0.9	2.7
25.0	1.9	5.6
50.0	3.4	9.8
100.0	5.9	17.1
500	21	62
1000	37	108
5000	135	394
10 000	235	687
46 000	798	2333

$S_{whiteoil}$ = sulfur concentration as derived from the calibration graph.

13.2.1 The value for C/H mass ratio is input for each unknown sample. The $S_{whiteoil}$ will be corrected for the different C/H ratios. Accordingly, if standards are prepared with a different solvent, the C/H ratio for that solvent should be used in place of $(C/H)_{whiteoil}$. Any difference between the C/H ratio between standards and samples will contribute to error in the measured result (see Table 6 for examples). It is the analyst's discretion as to when this error is large enough to be corrected by Eq 11.

14. Quality Control

14.1 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[5] of quality control samples (see 8.11). 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.

14.2 In addition to running a quality control sample (8.11), it is strongly recommended that the calibration blank (for example, diluent oil) be analyzed on a daily basis.

14.2.1 The measured concentration for the blank should be less than 2 mg/kg (0.0002 % by mass) sulfur. If the measured concentration for the blank is greater than 2 mg/kg (0.0002 % by 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.

14.2.2 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. It may also be beneficial to change the weighting method used. Many software packages default to square root error weighting but have the possibility of using linear error weighting or no error weighting.

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