Designation: D2622 – 10

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, gasohol 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 wt. % 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 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 14 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 12.2). Matrix mismatch 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

[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.

Current edition approved Feb. 15, 2010. Published March 2010. Originally approved in 1967. Last previous edition approved in 2008 as D2622–08. DOI: 10.1520/D2622-10.

[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.

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

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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

3. Summary of Test Method

3.1 The sample is placed in the X-ray beam, and the peak intensity of the sulfur 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 mg/kg or mass % (see Section 12).

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 2 minutes 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 white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 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.

5. Interferences

5.1 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.

5.2 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 11.5.

5.3 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 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.

5.4 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. 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.

6. Apparatus

6.1 *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:

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

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

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

6.1.4 *Analyzing Crystal,* suitable for the dispersion of sulfur 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.

6.1.5 *X-ray Tube,* capable of exciting sulfur 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.

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

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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 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.

7.2 *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 9.1). (**Warning—**Di-*n*-butyl sulfide is flammable and toxic. Prepared solutions 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 the 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.

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 9.4) and again at the time of analysis (see 10.1). These counting rates are used to calculate a drift correction factor (see 11.1).

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 (or other primary standards body) reference materials.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

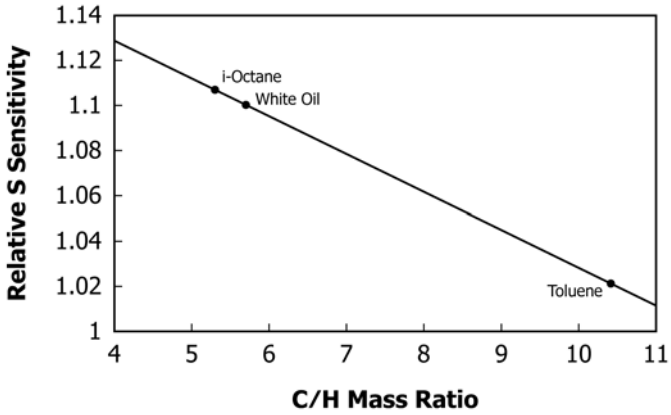

FIG. 1 Relative Sulfur Sensitivity versus C/H Ratio

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 grades for the preparation of calibration standards. It is also important to measure the C/H ratio (see Section 12 and Fig. 1).

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 and polycarbonate films.

7.7 *Helium Gas,* minimum purity 99.9 %.

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 9.5).

7.11 *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 13).

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

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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 the average value in the calibration.

8. Sampling and Specimen Preparation

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

8.2 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.

8.3 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.

8.4 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.

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

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

NOTE 9—If desired, additional standards can prepared and analyzed with concentrations between those listed in Table 2, see 9.1.1.

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.[4]

9.1.2 Alternatively, standards may be prepared by mass serial dilution of polysulfide oils (Note 6) with sulfur-free white oil. A freshly prepared polysulfide oil calibration curve should be verified using CRM's traceable to a national measurement institution 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 ppm to high weight percent 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 oils demonstrate excellent linearity and help the analyst visualize the full dynamic range of their analytical method.

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

9.2 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 10 and 11.

9.2.1 Standards containing 100 mg/kg total sulfur or less must be analyzed in duplicate. Either both of the individual values or the average value of these measurements can be used in the calibration. All samples in this sulfur concentration range must also be analyzed in duplicate, as in 10.12, and reported as in 12.1.1.

9.3 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):

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

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

[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. 1, 2007.

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