



Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry¹

This standard is issued under the fixed designation D 2622; 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 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 An estimate of this method's pooled limit of quantitation (PLOQ) is 3 mg/kg as calculated by the procedures in Practice D 6259.

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 the standard. The values given in parentheses are for information only.

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 appro-*

priate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy

D 6259 Practice for Determination of a Pooled Limit of Quantitation

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

D 7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-Ray Fluorescence Spectrometry Methods for the Elemental Analysis of Petroleum Products and Lubricants

E 29 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 X-ray beam, and the peak intensity of the sulfur $K\alpha$ 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).

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved July 15, 2007. Published August 2007. Originally approved in 1967. Last previous edition approved in 2005 as D 2622-05.

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.

TABLE 1 Concentrations of Interfering Species

Element	Mass % Tolerated
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Oxygen	2.8
FAME (see Note 15)	25
Ethanol (see Note 15)	8.6
Methanol (see Note 15)	6

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 1—The equipment specified for Test Method D 2622 tends to be more expensive than that required for alternative test methods, such as Test Method D 4294. 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 2—The concentrations of 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.

5.2 Fuels containing large quantities of ethanol or methanol (see Table 1) have a high oxygen content leading to significant absorption of sulfur $K\alpha$ 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 D 4927 is the recommended test method for the determination of sulfur >100 mg/kg in lubricating oils and lubricating oil additives because method D 4927 implements inter-element correction factors. Method D 2622 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 $K\alpha$ 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 $K\alpha$ radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

NOTE 3—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.

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 4—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 5—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.

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 (for example, Mylar®), 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 6—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 7—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.

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practices D 4057 or D 4177 when applicable.

8.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused.

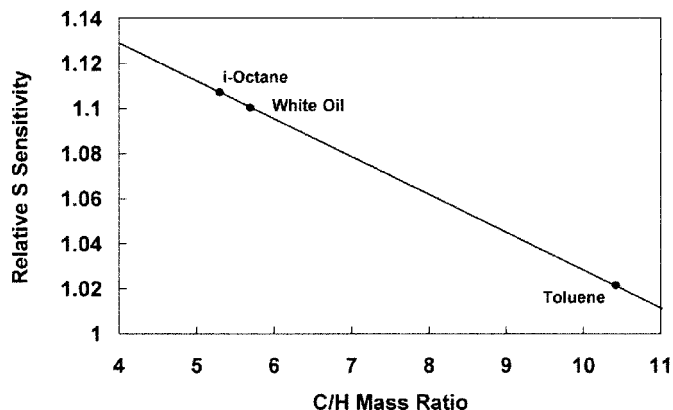


FIG. 1 Relative Sulfur Sensitivity versus C/H Ratio

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 *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.