



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, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, M-85 and M-100.

1.2 Interlaboratory studies on precision covered a variety of materials with sulfur concentrations ranging from approximately 3 mg/kg to 5.3 mass %. For a subset of these samples, with sulfur concentrations below 60 mg/kg, the repeatability standard deviation (S_r) was 1.5 mg/kg. An estimate of the limit of detection is $3 \times S_r$, and an estimate of the limit of quantitation² is $10 \times S_r$. 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.

1.3 Samples containing more than 5.0 mass % sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method.

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 matrix are well matched. Matrix mismatch can be caused by C/H ratio differences between samples and standards (see Tables 1 and 2) or by the presence of other heteroatoms (see Table 3).

1.6 The values stated in either SI units or angstrom units are to be regarded as 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.*

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.

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² *Analytical Chemistry*, Vol 55, 1983, pp. 2210-2218.

TABLE 1 Comparison of NIST and ASTM Interlaboratory Study (RR) Results

| NIST SRM | Sulfur, mass %, NIST | Sulfur, mass %, ASTM RR Average | C/H mass ratio | Apparent Bias, % Sulfur | Relative Bias, % | Significant |
|----------|----------------------|---------------------------------|----------------|-------------------------|------------------|-------------|
| 1616a | 0.0146 | 0.0148 | 5.205 | 0.0002 | 1.37 | No |
| 1617a | 0.1731 | 0.1776 | 5.205 | 0.0045 | 2.60 | Yes |
| 2724a | 0.0430 | 0.0417 | 5.986 | -0.0013 | -3.02 | Yes |
| 1623c | 0.3806 | 0.3661 | 7.504 | -0.0145 | -3.81 | Yes |
| 2717 | 3.0220 | 2.948 | 8.229 | -0.0736 | -2.44 | Yes |
| 1621e | 0.948 | 0.8973 | 8.553 | -0.0507 | -5.35 | Yes |
| 1624c | | 0.3918 | 6.511 | | | |
| 2723 | | 0.0299 | 5.937 | | | |

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

2. Referenced Documents

2.1 ASTM Standards:

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³

D 4294 Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy³

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy³

E 29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴

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 5.373 Å is measured. The background intensity, measured at a recommended wavelength of 5.190 Å (5.437 Å 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

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Index of ASTM Standards*, Vol 14.02.

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

TABLE 2 Comparison of NIST and ASTM Interlaboratory Study (RR) Corrected Results, Mass % Sulfur

NOTE—The correction factors were calculated from data determined with XRF-11.⁷ Application of these correction factors requires separate determination of the C/H mass ratio. The significance was determined based on a *t* test using a function of the NIST uncertainty at 1 sigma and the round robin reproducibility standard deviation. The correction formula, which is applicable when the base material used for the calibration standards is white oil, is:

$$S_{\text{corrected}} = S_{\text{uncorrected}} / (1.086 - 0.01511 \times C/H)$$

where:

C/H = mass ratio of carbon to hydrogen for the sample.

| SRM | RR ID | NIST | RR Corrected | Apparent Bias | Relative Bias, % | Significant |
|-------|-------|--------|--------------|---------------|------------------|-------------|
| 1616a | K2 | 0.0146 | 0.0147 | 0.0001 | 0.68 | No |
| 1617a | K1 | 0.1731 | 0.1763 | 0.0032 | 1.85 | No |
| 2724a | D2 | 0.0430 | 0.0419 | -0.0011 | -2.56 | No |
| 1623c | R1 | 0.3806 | 0.3763 | -0.0043 | -1.13 | No |
| 2717 | R4 | 3.0220 | 3.065 | 0.0430 | 1.42 | No |
| 1621e | R3 | 0.948 | 0.9382 | -0.0098 | -1.03 | No |
| 1624c | D3 | | 0.397 | | | |
| 2723 | D4 | | 0.0300 | | | |

TABLE 3 Concentration of Interfering Elements

| Element | Mass % Tolerated |
|--------------------|------------------|
| Phosphorus | 0.3 |
| Zinc | 0.6 |
| Barium | 0.8 |
| Lead | 0.9 |
| Calcium | 1 |
| Chlorine | 3 |
| Ethanol (Note 14) | 8.6 |
| Methanol (Note 14) | 6 |

the concentration of sulfur in mass %. (**Warning**—Exposure to excessive quantities of X-radiation 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.)

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 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 white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting results.

NOTE 1—Compared to other test methods for sulfur determination, Test Method D 2622 has high throughput, minimal sample preparation, and excellent precision, and is capable of determining sulfur over a wide range of concentrations. 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 Standards⁵ 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 3.

5.2 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. They have a high oxygen content leading to significant absorption of sulfur K α radiation. 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.

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 determination of sulfur in lubricating oils and lubricating oil additives because Test Methods D 4927 implements inter-element correction factors.

6. Apparatus

6.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF)*, equipped for X-ray detection in the 5.37 Å range. For optimum sensitivity to sulfur, the instrument should be equipped with the following.

6.1.1 *Optical Path*, of helium.

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

6.1.3 *Detector*, designed for the detection of long wavelength X-rays.

6.1.4 *Analyzing Crystal*, suitable for the dispersion of sulfur K α X-rays within the angular range of the spectrometer employed. Pentaerythritol and germanium are popular although other materials, such as EDDT, ADP, graphite, and quartz can be used.

6.1.5 *X-ray Tube*, capable of exciting sulfur K α radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

⁵ *Annual Book of ASTM Standards*, Vol 00.01.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ 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*, a high-purity standard with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (see 9.1).

NOTE 2—It is essential to know the concentration of sulfur in the di-n-butyl sulfide, not 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. Examples of sulfur containing materials that have been found to be suitable include a renewable liquid petroleum material, a semipermanent solid, a pressed powder sample, a metal alloy, or a fused glass disk. The monitor's count rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The count 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.

NOTE 3—Calibration standards may be used for this purpose. Because it is desirable to discard standards after each determination, a lower cost material is suggested for daily use.

7.4 *White Oil*, 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).

7.5 *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. Films can include polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

7.6 *Helium Gas*, minimum purity 99.9 %.

7.7 *Counting Gas*, for instruments equipped with flow proportional counters.

7.8 *Sample Cells*, compatible with the sample and the geometry requirements of the spectrometer. Disposable cells are preferred.

⁶ *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.

TABLE 4 Sulfur Standards

| Sulfur Concentration, mass % | Sulfur Concentration, mass % | Sulfur Concentration, mass % |
|------------------------------|------------------------------|------------------------------|
| 0.0000 ^A | 0.100 | 1.0 |
| 0.001 | 0.250 | 2.0 |
| 0.010 | 0.500 | 3.0 |
| 0.025 | | 4.0 |
| 0.050 | | 5.0 |
| 0.075 | | |

^A Base material.

7.9 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known sulfur content and not used in the generation of the calibration curve. The check samples shall be used to determine the accuracy of the initial calibration (see 9.5).

7.10 *Quality Control Samples*, stable petroleum or product samples representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (Section 13).

NOTE 4—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 5—Suitable QC samples can often be prepared by combining retains of typical samples.

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. 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 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, a small vent hole is provided.

8.3 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 shall be checked after starting each new roll or batch of film.

9. Calibration

9.1 Prepare calibration standards by careful mass dilution of the certified di-n-butyl sulfide with white oil or other suitable base material (see 5.3). The standards, with accurately known sulfur concentrations, shall approximate the nominal sulfur concentrations listed in Table 4 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 %.

NOTE 6—If desired, additional standards can be analyzed with concentrations between those listed in Table 4.