



Designation: D7220 – 12

Standard Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry¹

This standard is issued under the fixed designation D7220; 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.

1. Scope

1.1 This test method specifies an energy-dispersive X-ray fluorescence (EDXRF) method for the determination of total sulfur in automotive, No. 2 heating, and jet fuels with a concentration range of 3 to 942 mg/kg.

1.1.1 The pooled limit of quantitation of this test method as obtained by statistical analysis of inter laboratory test results is 3 mg/kg sulfur.

1.1.2 This test method is applicable to gasoline, oxygen enriched gasoline (RFG), diesel, diesel/biodiesel blends containing up to twenty volume percent biodiesel, kerosene, jet fuel, jet fuel/biodiesel blends containing up to five volume percent biodiesel and No. 2 home heating oil.

1.2 A fundamental assumption in this test method is that the standard and sample matrix is well matched. Matrix mismatch can be caused by C/H ratio differences between samples and standards or by the presence of other heteroatoms.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3.1 The preferred concentration units are mg/kg sulfur.

1.4 *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

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 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.

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

3. Terminology

3.1 *Definitions:*

3.1.1 *monochromatic X-radiation, n*—an incident X-ray beam on a sample having a selected photon energy with a narrow energy bandwidth of $\pm 5\%$ relative to the selected energy.

3.1.1.1 *Discussion*—Monochromatic X-ray radiation in EDXRF instrumentation can be obtained by using Bragg optics (at an angle of $\theta = 45 \pm 5^\circ$, in the low energy range). Bragg optics (monochromators) create very intense mono-energetic radiation. A combination of a selected X-ray tube (typically a Pd or Ag anode) with a highly ordered pyrolytic graphite (HOPG) Bragg optic can be used to create monochromatic radiation of the characteristic radiation of the anode material of the X-ray tube. The use of such radiation for sample excitation results in increased sensitivity for the determination of sulfur in petroleum products.

3.2 *Abbreviations:*

3.2.1 *DBS*—actual mass of Di-*n*-butyl sulfide, g

3.2.2 *Kcps*—kilo-counts per second.

3.2.3 *EDXRF*—Energy dispersive X-ray spectrometry

3.2.4 *PTFE*—Polytetrafluorethylene

3.2.5 *SDBS*—mass % of sulfur in Di-*n*-butyl sulfide, typically 21.91%

3.2.6 *SStd*—mg/kg sulfur in the calibration standard

3.2.7 *SStock*—mg/kg of sulfur in the stock standard

3.2.8 *STK*—actual mass of stock standard, g

4. Summary of Test Method

4.1 The sample is placed in the monochromatic X-ray beam, and the peak area of the sulfur $K\alpha$ line at 2.307 keV is measured. The background spectrum, measured with a sulfur free white oil or other matrix matching blank sample (see 8.4) is adapted to the measured spectrum using adjustment regions following the instrument manufacturer's instructions and then subtracted from the measured spectrum. 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. (**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.)

5. Significance and Use

5.1 This test method provides measurement of total sulfur in automotive, No. 2 heating, and jet fuels with a minimum of sample preparation. A typical analysis time is 180 to 360 s per sample.

5.2 The quality of automotive, No. 2 heating, and jet fuel can be 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 fuel.

5.3 If this test method is applied to petroleum materials with matrices significantly different from the calibration materials specified in this test method, the cautions and recommendations in Section 6 should be observed when interpreting the results.

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.

6.2 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 $K\alpha$ 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.

6.3 In general, petroleum materials with compositions that vary from the calibration samples as specified in Section 11 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.

7. Apparatus

7.1 *Monochromatic X-ray Fluorescence Analyzer*—A Monochromatic Excitation Energy Dispersive XRF spectrometer may be used if its design incorporates as a minimum, the following features:

7.1.1 *Source of X-ray Excitation*, X-ray end window tube with Ag or Pd anode, in combination with HOPG Bragg monochromating X-ray optics. The monochromator must produce monochromatic Ag or Pd L radiation. Other anode materials and monochromators may be utilized, however stated precision and bias may not apply.

7.1.2 *Sample Cell*, providing a sample depth of at least 4 mm and equipped with replaceable X-ray transparent film window.

7.1.3 *X-ray Detector*, with a resolution value not to exceed 175 eV at 5.9 Kcps (10 000 cps). A Si drift chamber has been found suitable for use. Using a detection system with this minimum spectral resolution has been shown to eliminate the potential effect of interference from chlorine on sulfur should either salt contamination, or chlorine from other sources (for example, recycled vegetable oils) occur.

7.1.4 *He-flush*, the system must allow flushing of the optical path with helium (see 8.6). Alternatively, a vacuum of ≤ 4.0 kPa (≤ 30.4 Torr) is applied to the optical path.

7.1.5 *Signal Conditioning and Data Handling Electronics*, including the functions of X-ray intensity counting, spectra handling by background subtraction and deconvolution, calculation of overlap corrections and conversion of sulfur X-ray intensity into mg/kg sulfur concentration.

8. Reagents and Materials

8.1 *Purity of Reagents*³—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. 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*—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 11.1). (**Warning**—Di-n-butyl sulfide is both flammable and toxic.)

NOTE 1—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.

8.3 *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 or a fused glass disk. The monitor's count

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.