



Designation: D7212 – 13 (Reapproved 2018)

Standard Test Method for Low Sulfur in Automotive Fuels by Energy-Dispersive X-ray Fluorescence Spectrometry Using a Low-Background Proportional Counter¹

This standard is issued under the fixed designation D7212; 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 the total sulfur content of automotive fuels with a concentration range from 7 mg/kg to 50 mg/kg.

1.1.1 The pooled limit of quantitation of this test method as obtained by statistical analysis of interlaboratory test results is 7 mg/kg sulfur.

1.2 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mg/kg sulfur.

1.3 *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.*

1.4 *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

[D4045 Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

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.

[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](#)

[D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories](#)

[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 *Definitions of Terms Specific to This Standard:*

3.1.1 *low background proportional counter, n*—an X-ray proportional counter that can suppress the noise generated when incident X rays are absorbed near the wall with resulting incomplete charge collection.

3.1.1.1 *Discussion*—An electrode shield close to the wall detects incomplete charge collection and associated electronic detection circuitry rejects those events. In comparison to conventional proportional counters, this gives lower spectral background and a lower limit of detection.

4. Summary of Test Method

4.1 The sample is placed in the beam emitted from an X-ray source with titanium target and primary filtration so that excitation is by essentially monochromatic radiation of 4.51 keV and virtually no background at 2.3 keV. A low background proportional counter measures the intensity of the fluorescent sulfur K series intensity and argon K series intensity (from residual air) and the accumulated counts are compared with counts from previously prepared calibration standards to obtain the sulfur concentration in mg/kg. If chlorine is expected to be present in some samples then other regions of the spectrum must be measured to provide compensation for

spectral overlap. One group of calibration standards is required to span the concentration range from 0 mg/kg to 150 mg/kg sulfur.

NOTE 1—Operation of analyzers using X-ray tubes is to be conducted in accordance with the manufacturer's safety instructions and federal, state, and local regulations governing the use of ionizing radiation.

4.2 Practice **D7343** should be consulted regarding standard operating protocols in XRF analysis.

5. Significance and Use

5.1 This test method determines total sulfur in automotive fuels with a typical analysis time around 10 min per sample.

5.2 The quality of automotive fuel is related to the amount of sulfur present. Knowledge of sulfur level is necessary for processing purposes.

5.3 Sulfur level in automotive fuels affects performance characteristics and air quality. Federal, state, and local agencies regulate the level of sulfur in fuel delivered at the pump.

5.4 This test method can be referenced in specification documents to determine if the material meets the desired sulfur content.

5.5 If this test method is applied to petroleum matrices with significantly different composition to those used in the interlaboratory precision study, then the caution and recommendations in Section 6 should be observed when interpreting the results.

6. Interferences

6.1 Spectral interferences result when some sample component element or elements emit X rays that the detector cannot resolve from sulfur X-ray emission. Overlapping peak lines are the result of this. This overlapping effect may be by lead alkyls, silicon, phosphorus, calcium, potassium, and halides if their aggregate concentration is more than 10 mg/kg. The most likely interference is chlorine that has been found in biodiesel derived from recycled waste vegetable oil.

6.2 The presence of oxygenates or water may alter the sensitivity for sulfur.

6.3 Follow the manufacturer's operating guide to compensate for the interferences.

7. Apparatus

7.1 *Energy-dispersive X-ray Fluorescence Analyzer*—Any energy dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum the following features:³

7.1.1 *Source of X-ray Excitation*, X-ray source with titanium target and primary filtration so that excitation is by essentially monochromatic radiation of 4.51 keV.

³ The sole source of supply of the apparatus known to the committee at this time is the Twin-X ULS from Oxford Instruments Analytical, Halifax Road, High Wycombe, Bucks, HP12 3SE, England. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

7.1.2 *Low Background Proportional Counter* (see 3.1.1), with sensitivity at 2.3 keV.⁴

7.1.3 *Multi-channel Analyzer*, with a channel width of 10eV or less, covering the energy range from 0 keV to 10 keV.

7.1.4 *Signal Conditioning and Data Handling Electronics*, that include the functions of X-ray intensity counting, a minimum of four energy regions (to correct for background X rays and spectral overlap), spectral overlap corrections, and conversions of sulfur X-ray intensity into sulfur concentration.

7.1.5 *Display or Printer*, that reads out in mg/kg sulfur.

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

7.1.7 *Helium Purged Optical Path*, to maximize sensitivity and minimize spectral overlap from argon in air. The helium shall be at least 99.9 % purity.

8. Reagents and Materials

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.⁵ 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 standard with certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards. (**Warning**—Di-n-butyl sulfide is flammable and toxic).

8.3 *Mineral Oil, White (MOW)*, with sulfur content less than 0.2 mg/kg as certified by a suitable analytical method, like Test Method **D4045**.

8.4 *X-ray Transparent Film*, any film that resists attack by the sample, is free of sulfur and other interfering elements (see 6.1), and is sufficiently X-ray transparent may be used.

NOTE 2—Polycarbonate with thickness of 5 or 6 µm most closely matches these requirements and eight of nine participants in the interlaboratory study⁶ used one of these films, while the other laboratory used 3 µm polyester.

8.4.1 Samples of high aromatic content may dissolve polycarbonate film and polypropylene has a tendency to absorb some hydrocarbons and may stretch during a long measurement time.

⁴ The low background proportional counter is covered by a pending patent. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patent-pending item to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington DC. For suggestions on testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory*, BDH Ltd., Poole Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1587. Contact ASTM Customer Service at service@astm.org.