



Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry¹

This standard is issued under the fixed designation D7039; 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 covers the determination of total sulfur by monochromatic wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in single-phase gasoline, diesel fuel, refinery process streams used to blend gasoline and diesel, jet fuel, kerosine, biodiesel, biodiesel blends, and gasoline-ethanol blends.

NOTE 1—Volatile samples such as high-vapor-pressure gasolines or light hydrocarbons might not meet the stated precision because of the evaporation of light components during the analysis.

1.2 The range of this test method is between the pooled limit of quantitation (PLOQ) value (calculated by procedures consistent with Practice D6259) of 3.2 mg/kg total sulfur and the highest level sample in the round robin, 2822 mg/kg total sulfur.

1.3 Samples containing oxygenates can be analyzed with this test method provided the matrix of the calibration standards is either matched to the sample matrices or the matrix correction described in Section 5 or Annex A1 is applied to the results. The conditions for matrix matching and matrix correction are provided in the Interferences section (Section 5).

1.4 Samples with sulfur content above 2822 mg/kg can be analyzed after dilution with appropriate solvent (see 5.4). The precision and bias of sulfur determinations on diluted samples has not been determined and may not be the same as shown for neat samples (Section 15).

1.5 When the elemental composition of the samples differ significantly from the calibration standards used to prepare the calibration curve, the cautions and recommendation in Section 5 should be carefully observed.

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 appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard information, see 3.1.

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

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

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

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

2.2 EPA Documents:³

40 CFR 80.584 Code of Federal Regulations; Title 40; Part 80; U.S. Environmental Agency, July 1, 2005

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.

³ Available from U.S. Government Printing Office, 732 N. Capitol Street, NW, Washington, DC 20401.

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

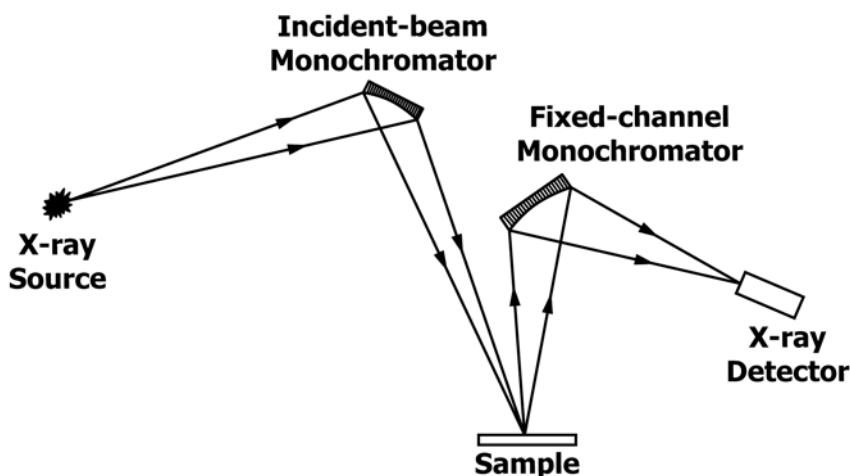


FIG. 1 Schematic of the MWDXRF Analyzer

3. Summary of Test Method

3.1 A monochromatic X-ray beam with a wavelength suitable to excite the K-shell electrons of sulfur is focused onto a test specimen contained in a sample cell (see Fig. 1). The fluorescent $K\alpha$ radiation at 0.5373 nm (5.373 Å) emitted by sulfur is collected by a fixed monochromator (analyzer). The intensity (counts per second) of the sulfur X rays is measured using a suitable detector and converted to the concentration of sulfur (mg/kg) in a test specimen using a calibration equation. Excitation by monochromatic X rays reduces background, simplifies matrix correction, and increases the signal/background ratio compared to polychromatic excitation used in conventional WDXRF techniques.⁴ (**Warning**—Exposure to excessive quantities of X-ray radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of his/her 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 for the precise measurement of the total sulfur content of samples within the scope of this test method with minimal sample preparation and analyst involvement. The typical time for each analysis is five minutes.

4.2 Knowledge of the sulfur content of diesel fuels, gasolines, and refinery process streams used to blend gasolines is important for process control as well as the prediction and control of operational problems such as unit corrosion and catalyst poisoning, and in the blending of products to commodity specifications.

4.3 Various federal, state, and local agencies regulate the sulfur content of some petroleum products, including gasoline

and diesel fuel. Unbiased and precise determination of sulfur in these products is critical to compliance with regulatory standards.

5. Interferences

5.1 Differences between the elemental composition of test samples and the calibration standards can result in biased sulfur determinations. For samples within the scope of this test method, elements contributing to bias resulting from differences in the matrices of calibrants and test samples are hydrogen, carbon, and oxygen. A matrix-correction factor (C) can be used to correct this bias; the calculation is described in Annex A1. For general analytical purposes, the matrices of test samples and the calibrants are considered to be matched when the calculated correction factor C is within 0.98 to 1.04. No matrix correction is required within this range. A matrix correction is required when the value of C is outside the range of 0.98 to 1.04. For most testing, matrix correction can be avoided with a proper choice of calibrants. For example, based on the example graph in Annex A1 (Fig. 2), a calibrant with 86 mass % carbon and 14 mass % hydrogen can cover non-oxygen containing samples with C/H ratios from 5.4 to 8.5. For gasolines with oxygenates, up to 2.3 mass % oxygen (12 mass % MTBE) can be tolerated for test samples with the same C/H ratio as the calibrants.

5.2 Fuels containing large quantities of oxygenates, such as biodiesel, biodiesel blends, and gasoline-ethanol blends, can have a high oxygen content leading to significant absorption of sulfur $K\alpha$ radiation and low sulfur results.

5.2.1 Biodiesel and biodiesel blends may be analyzed using this test method by applying correction factors to the results or using calibration standards that are matrix-matched to the test sample (see Table 1). Correction factors may be calculated (see Annex A1), or obtained from Table 2 if the sample has been measured on a mineral oil calibration curve.

5.2.2 Gasoline-ethanol blends may be analyzed using this test method by applying correction factors to the results or using calibration standards that are matrix matched to the test sample (see Table 1). Correction factors may be calculated (see

⁴ Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1975, pp. 115–118.

Matrix Correction vs. C/H for total oxygen wt. %

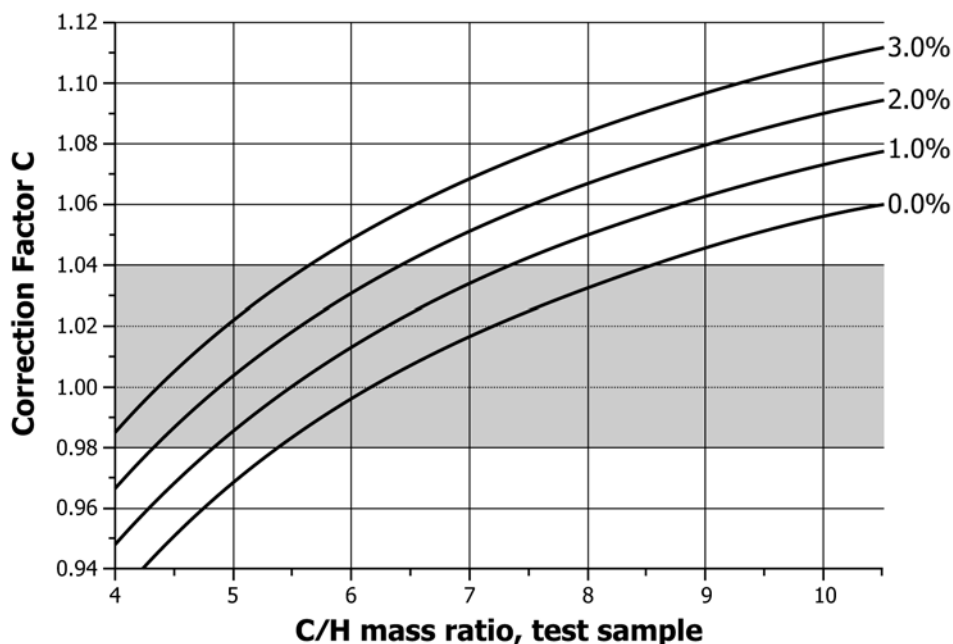


FIG. 2 Matrix Correction for a Test Sample vs. C/H and Total Oxygen Content Using Chromium $K\alpha$ for the Excitation Beam

TABLE 1 Methods for Interference Correction by Sample Type

Sample Type	Correction Tables (Table 2, Table 3, Table 4, or N/A)	Correction Calculation (Annex A1)	Matrix Matching
Biodiesel and Biodiesel Blends	2	Yes	Yes
Gasoline-ethanol Blends	3 or 4	Yes	Yes
All Other Sample Types	N/A	Yes	Yes

Annex A1), or obtained from the correction tables. Use Table 3 if the sample has been measured on a mineral oil calibration curve, or use Table 4 if the sample has been measured on an ethanol calibration curve. Ethanol-based calibrants can be used for gasoline-ethanol blends. Ethanol-based calibrants are recommended for gasoline-ethanol blends containing more than 50 % (by volume) ethanol.

5.3 Other samples having interferences as described in 5.1 may be analyzed using this test method by applying correction factors to the results or by using calibration standards that are matrix matched to the test sample (see Table 1). Correction factors may be calculated as described in Annex A1.

5.4 To minimize any bias in the results, use calibration standards prepared from sulfur-free base materials of the same or similar elemental composition as the test samples. When diluting samples, use a diluent with an elemental composition the same or similar to the base material used for preparing the calibration standards.

5.4.1 A base material for gasoline can be approximately simulated by mixing 2,2,4-trimethylpentane (*isooctane*) and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed.

6. Apparatus

6.1 *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*⁵, equipped for X-ray detection at 0.5373 nm (5.373Å). Any spectrometer of this type can be used if it includes the following features, and the precision and bias of test results are in accordance with the values described in Section 15.

6.1.1 *X-ray Source*, capable of producing X rays to excite sulfur. X-ray tubes with a power >25W capable of producing Rh $L\alpha$, Pd $L\alpha$, Ag $L\alpha$, Ti $K\alpha$, Sc $K\alpha$, and Cr $K\alpha$ radiation are recommended for this purpose.

6.1.2 *Incident-beam Monochromator*, capable of focusing and selecting a single wavelength of characteristic X rays from the source onto the specimen.

6.1.3 *Optical Path*, designed to minimize the absorption along the path of the excitation and fluorescent beams using a vacuum or a helium atmosphere. A vacuum of < 2.7 kPa (<20 Torr) is recommended. The calibration and test measurements must be done with identical optical paths, including vacuum or helium pressure.

6.1.4 *Fixed-channel Monochromator*, suitable for dispersing sulfur $K\alpha$ X rays.

6.1.5 *Detector*, designed for efficient detection of sulfur $K\alpha$ X rays.

6.1.6 *Single-Channel Analyzer*, an energy discriminator to monitor only sulfur radiation.

⁵ The sole source of this apparatus known to the committee at this time is X-ray Optical Systems, Inc., 15 Tech Valley Drive, East Greenbush, NY 12061. 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, which you may attend.