Designation: D 7039 – 04

An American National Standard

Standard Test Method for
Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 7039; 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 gasolines, diesel fuels, and refinery process streams used to blend gasoline and diesel, at concentrations from 2 mg/kg to 500 mg/kg. The precision of this test method was determined by an interlaboratory study using representative samples of the liquids described in 1.1 and 1.2. The pooled limit of quantitation (PLOQ) was estimated to be 4 mg/kg.

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 Gasoline samples containing oxygenates may 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 Annex A1 is applied to the results. The conditions for matrix matching and matrix correction are provided in the Interferences section (Section 5).

1.3 Gasolines and diesels with sulfur contents above 500 mg/kg can be analyzed after dilution with appropriate solvent (see 5.2). 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).

1.4 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.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *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]
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance
D 6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

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 Kα 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.[3] (**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 gasolines and diesels with minimal
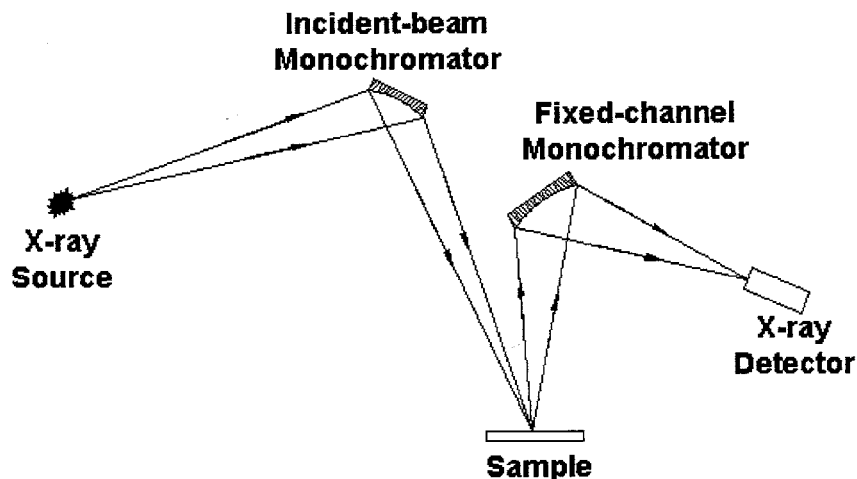

FIG. 1 Schematic of the MWDXRF Analyzer

sample preparation and analyst involvement. The typical time for each analysis is two to three 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 diesels and gasolines within the scope of this test method, the only important 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. Samples used in the 2002 interlaboratory study fall within this category. 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 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.

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

5.2.2 Fuels containing oxygenates may be analyzed using calibration standards containing the same amount of the same oxygenate in the test fuel.

6. Apparatus

6.1 *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*[4], 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 Lα, Pd Lα, Ag Lα, Ti Kα, Sc Kα, and Cr Kα 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 Kα X rays.

---

[4] 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.

2

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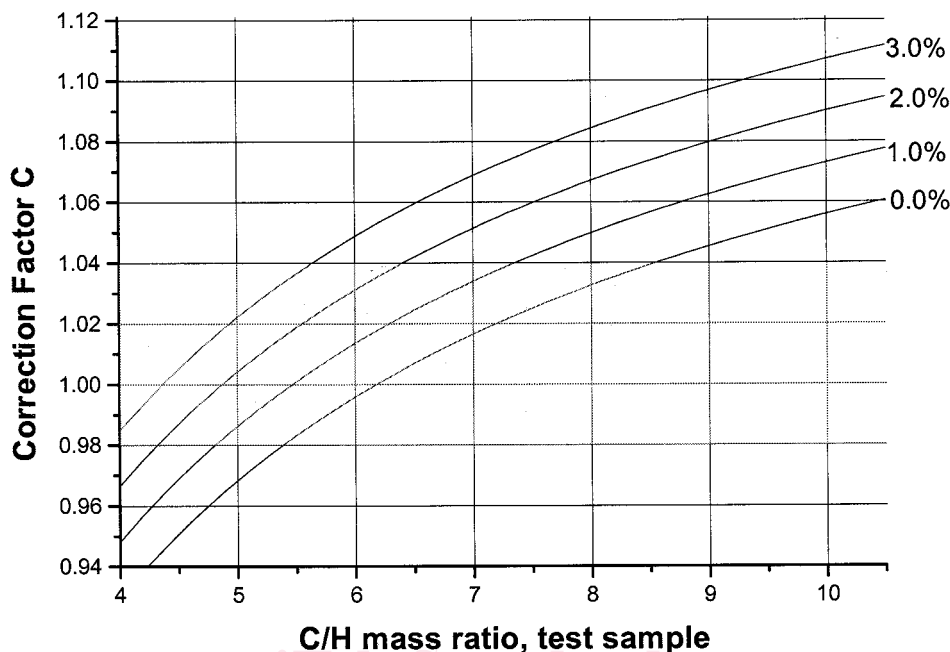

FIG. 2 Matrix Correction for a Test Sample vs. C/H and Total Oxygen Content Using Chromium Kα for the Excitation Beam

6.1.5 *Detector*, designed for efficient detection of sulfur Kα X rays.

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

6.1.7 *Removable Sample Cell*, an open-ended specimen holder compatible with the geometry of the MWDXRF spectrometer and designed to use replaceable X-ray transparent film (see 6.1.8) to hold a liquid specimen with a minimum depth of 5mm. The sample cell must not leak when fitted with X-ray transparent film. A disposable cell is recommended.

6.1.8 *X-Ray Transparent Film*, for containing and supporting the test specimen in the sample cell (see 6.1.7) while providing a low-absorption window for X rays to pass to and from the sample. Any film resistant to chemical attack by the sample, free of sulfur, and X-ray transparent can be used, for example, polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

7. Reagents and Materials

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.[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.

7.2 *Calibration-Check Samples*, for verifying the accuracy of a calibration. The check samples shall have known sulfur content and not be used in determining the calibration curve. A standard from the same reliable and consistent source of calibration standards used to determine the calibration curve is convenient to check the calibration.

7.3 *Di-n-butyl Sulfide*, a high-purity liquid with a certified sulfur concentration. Use the certified sulfur concentration when calculating the exact concentrations of sulfur in calibration standards.

7.4 *Drift-Monitor Sample (Optional)*, to determine and correct instrument drift over time (see 10.4, 11.1, and 12.1). Various forms of stable sulfur-containing materials are suitable drift-correction samples, for example, liquid petroleum, solid, pressed powder, metal alloy, and fused glass. The count rate displayed by the monitor sample, in combination with a convenient count time (T), shall be sufficient to give a relative standard deviation (RSD) of < 1 % (see Appendix X1).

NOTE 2—Calibration standards may be used as drift-monitor samples. Because it is desirable to discard test specimens after each determination,

---

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

a lower cost material is suggested for daily use. Any stable material can be used for daily monitoring of drift.

NOTE 3—The effect of drift correction on the precision and bias of this test method has not been studied.

7.4.1 Drift correction can be done automatically if the instrument embodies this option, although the calculation can be readily done by conventional methods of data reduction and processing.

7.5 *Quality-Control (QC) Samples* , for use in establishing and monitoring the stability and precision of an analytical measurement system (see Section 14). Use homogeneous materials, similar to samples of interest and available in sufficient quantity to be analyzed regularly for a long period of time

NOTE 4—Verification of system control through the use of QC samples and control charting is highly recommended.

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

7.6 *White Oil*, use a high purity mineral oil and account for its sulfur content when calculating the sulfur concentrations of the calibration standards.

7.7 *Helium*, minimum purity 99.9 %, for use as an optical path.

8. Sampling and Sample Handling

8.1 Sample fuel according to the procedures in Practices D 4057 or D 4177

8.2 Use the utmost care in sampling and handling gasoline to prevent evaporation of light ends which could change the concentration of sulfur in the sample. Store gasoline in a leak tight container at 0 to 4°C until ready for analysis. If possible, maintain at this temperature throughout any transfer and handling processes. Analyze test specimens as soon as possible after sub-sampling from bulk container. Do not allow bulk container to remain uncovered any longer than is needed to obtain desired sub-samples.

8.3 For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, any portion of the film exposed to the liquid or the X-ray beam, and also avoid touching the instrument window. (It is highly recommended that clean, disposable rubber or plastic gloves be used when preparing test specimens.) Oil from fingerprints and wrinkles can generate errors in the analysis of sulfur. Therefore, make sure the film is taut and clean to ensure reliable results. Use calibration-check samples (see 7.2) to verify calibration integrity if the type and thickness of the window film is changed. After the sample cell is filled, provide a vent above the sample to prevent bowing of the film by accumulating vapors. When reusable sample cells are used, thoroughly clean and dry cells before each use. Disposable sample cells shall not be reused.

8.4 Because impurities and thickness variations can occur in commercially available transparent films and vary from lot to lot, use calibration-check samples (see 7.2) to verify calibration integrity after starting each new batch of film.

9. Preparation of Apparatus and Specimens for Analysis

9.1 *Analyzer Preparation*—Ensure that the MWDXRF analyzer has been installed and put into operation according to

manufacturer's instructions. Allow sufficient time for instrument electronics to stabilize. Perform any instrument checkout procedures required. When possible, the instrument should be run continuously to maintain optimum stability.

9.1.1 Use the count time (T) recommended by the instrument manufacturer for the lowest sulfur concentration expected. The typical time for each measurement is two to three minutes.

9.1.2 Alternatively, determine T expected for a desired count precision by following the procedure in Appendix X1.

9.2 *Specimen Preparation*—Prepare a specimen of a test sample or a calibration standard as follows:

9.2.1 Carefully transfer a sufficient portion of the liquid to fill an open-ended sample cell above a minimum depth of 5 mm, beyond which additional liquid does not affect the count rate. Filling the sample cell to three-fourths of the cell's depth is generally adequate.

9.2.2 Fit an unused piece of X-ray-transparent film over the sample-cell opening and attach securely. Use the same batch of film for the analysis of test samples and the calibration standards used for constructing the calibration curve. Avoid touching the inside of the sample cell, any portion of the film exposed to the liquid or the X-ray beam, and also avoid touching the instrument window. (It is highly recommended that clean, disposable rubber or plastic gloves be used when preparing test specimens.) Ensure the film is taut, wrinkle-free, and not leaking.

9.2.3 Provide a small vent to prevent bowing of the window film caused by the accumulating vapor. Many commercially available sample cells provide a means to vent the space above the liquid.

9.2.4 Perform the analysis of the specimen promptly after preparing the specimen. Do not let the specimen remain in the sample cell any longer than necessary before collecting the data.

10. Calibration

10.1 Obtain or prepare a set of calibration standards bracketing the expected concentration range (up to 500 mg/kg sulfur) in the samples by careful mass dilution of di-n-butyl sulfide with a suitable base material (see 5.2). All standards used in the analysis must be from a reliable and consistent source, which can include commercially available standards. Calculate the sulfur content (mg/kg) in each of the calibration standards, accounting for the amount of sulfur in the base material.

10.2 Following instrument manufacturer's instructions and the instructions in 11.2, measure the sulfur fluorescence intensity (total sulfur count rate) for each of the calibration standards. Convert total counts to count rate (R_S) in counts per second by dividing by the count time (T) using units of seconds (see 9.1.1 and 9.1.2).

10.3 Construct a linear calibration model by either:

10.3.1 Using the software supplied by the instrument manufacturer, or

10.3.2 Do a linear regression of the calibration measurements. The following linear equation describes the regression:

$$R_S = Y + (E \times S) \qquad (1)$$