Designation: D7039 – 15a

# 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 Spectrometry[1]

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**

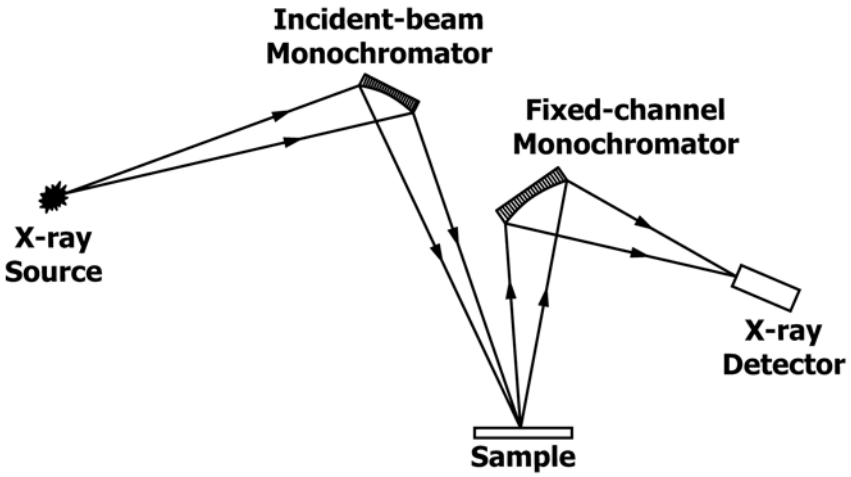


**FIG. 1 Schematic of the MWDXRF Analyzer**

## 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 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.[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 Kα 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.

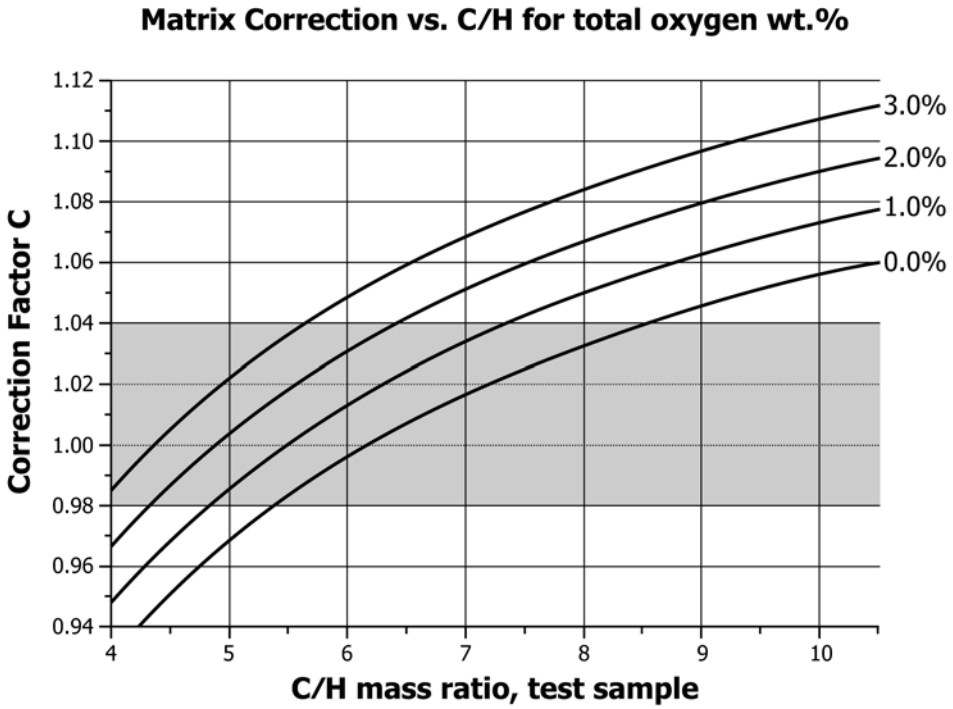


**FIG. 2 Matrix Correction for a Test Sample vs. C/H and Total Oxygen Content Using Chromium Kα for the Excitation Beam**

**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 (*iso*octane) 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 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.

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.

[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.

**TABLE 2 Correction Factors for Biodiesel Blends Measured on a Mineral Oil Calibration Curve**

NOTE 1—Determine the correction factor in the table below by finding the known oxygen content of the test specimen (for example, 11 wt %) as the sum of the value in the first column and the value in the first row (for example, 11 = 10+1). The intersection of these two values is the correction factor (for example, 1.1914). Apply the correction according to 12.5.

| Oxygen, wt % | 0 % | 1 % | 2 % | 3 % | 4 % | 5 % | 6 % | 7 % | 8 % | 9 % |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 % | 1.0000 | 1.0174 | 1.0348 | 1.0522 | 1.0696 | 1.0870 | 1.1044 | 1.1218 | 1.1392 | 1.1566 |
| 10 % | 1.1740 | 1.1914 | 1.2088 | 1.2262 | 1.2436 | 1.2610 | 1.2784 | 1.2958 | 1.3132 | 1.3306 |

**TABLE 3 Correction Factors for Gasoline-ethanol Blends Measured on a Mineral Oil Calibration Curve**

NOTE 1—Determine the correction factor in the table below by finding the known ethanol content of the test specimen (for example, 15 vol %) as the sum of the value in the first column and the value in the first row (for example, 15 = 10+5). The intersection of these two values is the correction factor (for example, 1.0881). Apply the correction according to 12.5.

| Ethanol, vol % | 0 % | 1 % | 2 % | 3 % | 4 % | 5 % | 6 % | 7 % | 8 % | 9 % |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 % | 0.9895 | 0.9962 | 1.0029 | 1.0095 | 1.0161 | 1.0228 | 1.0294 | 1.0360 | 1.0425 | 1.0491 |
| 10 % | 1.0556 | 1.0621 | 1.0686 | 1.0751 | 1.0816 | 1.0881 | 1.0945 | 1.1009 | 1.1073 | 1.1137 |
| 20 % | 1.1201 | 1.1265 | 1.1328 | 1.1391 | 1.1455 | 1.1518 | 1.1580 | 1.1643 | 1.1706 | 1.1768 |
| 30 % | 1.1830 | 1.1892 | 1.1954 | 1.2016 | 1.2077 | 1.2139 | 1.2200 | 1.2261 | 1.2322 | 1.2383 |
| 40 % | 1.2444 | 1.2504 | 1.2565 | 1.2625 | 1.2685 | 1.2745 | 1.2805 | 1.2865 | 1.2924 | 1.2984 |
| 50 % | 1.3043 | 1.3102 | 1.3161 | 1.3220 | 1.3279 | 1.3337 | 1.3396 | 1.3454 | 1.3512 | 1.3570 |
| 60 % | 1.3628 | 1.3686 | 1.3743 | 1.3801 | 1.3858 | 1.3915 | 1.3972 | 1.4029 | 1.4086 | 1.4143 |
| 70 % | 1.4199 | 1.4256 | 1.4312 | 1.4368 | 1.4424 | 1.4480 | 1.4536 | 1.4591 | 1.4647 | 1.4702 |
| 80 % | 1.4757 | 1.4813 | 1.4868 | 1.4922 | 1.4977 | 1.5032 | 1.5086 | 1.5141 | 1.5195 | 1.5249 |
| 90 % | 1.5303 | 1.5357 | 1.5410 | 1.5464 | 1.5518 | 1.5571 | 1.5624 | 1.5677 | 1.5730 | 1.5783 |

**TABLE 4 Correction Factors for Gasoline-ethanol Blends Measured on an Ethanol Calibration Curve**

NOTE 1—Determine the correction factor in the table below by finding the known ethanol content of the test specimen (for example, 85 vol %) as the sum of the value in the first column and the value in the first row (for example, 85 = 80+5). The intersection of these two values is the correction factor (for example, 0.9492). Apply the correction according to 12.5. Refer to 7.8 and 10.1 for ethanol calibration.

| Ethanol, vol % | 0 % | 1 % | 2 % | 3 % | 4 % | 5 % | 6 % | 7 % | 8 % | 9 % |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 % | 0.6248 | 0.6291 | 0.6333 | 0.6375 | 0.6417 | 0.6459 | 0.6500 | 0.6542 | 0.6583 | 0.6625 |
| 10 % | 0.6666 | 0.6707 | 0.6748 | 0.6789 | 0.6830 | 0.6871 | 0.6912 | 0.6952 | 0.6993 | 0.7033 |
| 20 % | 0.7073 | 0.7113 | 0.7153 | 0.7193 | 0.7233 | 0.7273 | 0.7313 | 0.7352 | 0.7392 | 0.7431 |
| 30 % | 0.7470 | 0.7510 | 0.7549 | 0.7588 | 0.7627 | 0.7665 | 0.7704 | 0.7743 | 0.7781 | 0.7820 |
| 40 % | 0.7858 | 0.7896 | 0.7934 | 0.7972 | 0.8010 | 0.8048 | 0.8086 | 0.8124 | 0.8161 | 0.8199 |
| 50 % | 0.8236 | 0.8274 | 0.8311 | 0.8348 | 0.8385 | 0.8422 | 0.8459 | 0.8496 | 0.8533 | 0.8569 |
| 60 % | 0.8606 | 0.8642 | 0.8679 | 0.8715 | 0.8751 | 0.8787 | 0.8823 | 0.8859 | 0.8895 | 0.8931 |
| 70 % | 0.8967 | 0.9002 | 0.9038 | 0.9073 | 0.9108 | 0.9144 | 0.9179 | 0.9214 | 0.9249 | 0.9284 |
| 80 % | 0.9319 | 0.9354 | 0.9388 | 0.9423 | 0.9458 | 0.9492 | 0.9527 | 0.9561 | 0.9595 | 0.9629 |
| 90 % | 0.9663 | 0.9697 | 0.9731 | 0.9765 | 0.9799 | 0.9833 | 0.9866 | 0.9900 | 0.9933 | 0.9967 |

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 5 mm. 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.[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 *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

[6] *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.

when calculating the exact concentrations of sulfur in calibration standards. (**Warning—**Di-n-butyl sulfide is flammable and toxic. Prepared solutions may not be stable several months after preparation.)

NOTE 2—It is essential to know the concentration of sulfur in the di-n-butyl sulfide, not only the purity, since impurities can also be sulfur-containing compounds. The sulfur content may be determined via mass dilution in sulfur-free white oil followed by a direct comparison analysis against NIST (or other primary standards body) reference materials.

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 3—Calibration standards may be used as drift-monitor samples. Because it is desirable to discard test specimens after each determination, a lower cost material is suggested for daily use. Any stable material can be used for daily monitoring of drift.

NOTE 4—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 5—Verification of system control through the use of QC samples and control charting is highly recommended.

NOTE 6—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.

7.8 *Ethanol,* use a high purity grade and account for its sulfur content when calculating the sulfur concentrations of the calibration standards. (**Warning—**Ethanol is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.9 *2,2,4-Trimethylpentane (Isooctane),* use a high purity grade and account for its sulfur content when calculating the sulfur concentration of the calibration standards. (**Warning—**Isooctane is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.10 *Toluene,* use a high purity grade and account for its sulfur content when calculating the sulfur concentration of the calibration standards. (**Warning—**Toluene is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.11 *Polysulfide Oil,* generally nonylpolysulfides containing a known percentage of sulfur diluted in a hydrocarbon matrix. (**Warning—**May cause allergic skin reactions.)

NOTE 7—Polysulfide oils are high molecular weight oils that contain high concentrations of sulfur, as high as 50 weight percent.

## 8. Sampling and Sample Handling

8.1 Sample fuel according to the procedures in Practices D4057 or D4177

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 °C to 4 °C until ready for analysis. If possible, maintain at this temperature throughout any transfer and handling processes. Allow specimens maintained at 0 °C to 4 °C to reach room temperature before testing, and expose these materials to ambient conditions only as long as necessary to obtain a sample for analysis. 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 on the film and wrinkles in the film 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

**TABLE 5 Recommended Sulfur Standard Concentration Ranges**

NOTE 1—Use the calibration range that brackets the expected sample concentration range. For example, it is not necessary to calibrate 0 to 3000 mg/kg unless the expected sample concentration range exceeds 500 mg/kg.

| 0 to 3000 mg/kg | 0 to 500 mg/kg |
|---|---|
| 0.0[A] | 0.0[A] |
| 25 | 5 |
| 100 | 15 |
| 500 | 50 |
| 1000 | 250 |
| 3000 | 500 |

[A] Base material.

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. When available, use the same batch of film for the analysis of test samples and the calibration standards used for constructing the calibration curve; otherwise follow 8.4 to verify the calibration integrity when switching to a new batch of film, and recalibrate using the new batch of film when results obtained on the calibration-check sample(s) fall outside acceptance criteria (see 10). 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 3000 mg/kg sulfur) in the samples by careful mass dilution of di-n-butyl sulfide (DBS) with a suitable base material (BM) (see Section 5). Two suitable base materials include mineral oil (see 7.6) for use with the correction factors in Table 3 and ethanol (see 7.8) for use with the correction factors in Table 4. All standards used in the analysis must be from a reliable and consistent source, which can include commercially available standards. Recommended nominal sulfur concentration standards are listed in Table 5.

10.1.1 Take into account any sulfur in the base materials when calculating the sulfur content (mg/kg) in each of the calibration standards as shown in Eq 1:

$$S = [(DBS \cdot S_{DBS}) + (BM \cdot S_{BM})] / (DBS + BM) \quad (1)$$

*where:*

$S$ = mass fraction of sulfur in the prepared standards, mg/kg,
$DBS$ = actual mass of di-n-butyl sulfide, g,
$S_{DBS}$ = mass fraction of sulfur in DBS, mg/kg, typically 21.91 %,
$BM$ = actual mass of base material, g, and
$S_{BM}$ = mass fraction of sulfur in the base material, mg/kg.

10.1.2 Alternatively, standards may be prepared by mass serial dilution of polysulfide oils (Note 7) with sulfur-free white oil. A freshly prepared polysulfide oil calibration curve should be verified using CRMs traceable to a national measurement institution that has demonstrated proficiency for measuring sulfur in the matrix of interest.

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 (N) to count rate ($R_S$) in counts per second by dividing N by the count time (T) using units of seconds (see 9.1.1, 9.1.2, and Eq 2).

$$R_s = N/T \quad (2)$$

*where:*

$R_s$ = measured total count rate of the sulfur fluorescence from 10.2, counts per second,
$N$ = total counts collected at 0.5373 nm, and
$T$ = seconds required to collect N counts.

10.3 Construct a linear calibration model by either:

10.3.1 Using the software supplied by the instrument manufacturer, or

10.3.2 Perform a linear regression of the calibration measurements. The following linear equation (Eq 3) describes the regression:

$$R_S = Y + (E \times S) \quad (3)$$

where:

$R_S$ = measured total count rate of the sulfur fluorescence from 10.2, counts per second,
$Y$ = y-intercept of the calibration curve, counts per second,
$E$ = slope of the calibration curve, counts kg $s^{-1}$ $mg^{-1}$, and
$S$ = sulfur concentration, mg/kg.

10.4 When using drift correction, measure the total counts of sulfur fluorescence from the drift-monitor sample during the calibration procedure. Determine $R_S$ by dividing the total counts by T. The factor, $R_S$, determined on the drift-monitor sample at the time of calibration, is factor A in Eq 4 in 12.1.

10.5 Immediately after analyzing the calibration standards, determine the sulfur concentration of one or more calibration-check samples (see 7.2). The determined value shall be in the range defined by the certified concentration plus or minus the repeatability of this test method. If this criterion is not met, the calibration process and calibration standards are suspect, corrective measures must be taken, and the calibration rerun. The degree of matrix mismatch between calibration check samples and standards should be considered when evaluating a calibration.

## 11. Procedure

11.1 When using drift correction, prior to analyzing samples on a given day, analyze the drift-monitor sample measured at the time of calibration. Divide the total counts measured on the drift-monitor sample by T to convert to $R_S$; this $R_S$ corresponds to factor B in Eq 4 in 12.1.

11.2 Analyze each sample of interest as follows:

11.2.1 Prepare a test specimen of the sample of interest according to section 9.2.

11.2.2 Place the sample cell containing the test specimen in the X-ray beam, as directed in the instrument manufacturer's instructions. Allow the X-ray optical path to come to equilibrium.

11.2.3 Measure the total counts of sulfur fluorescence (N), and divide the total counts by T to calculate $R_S$ (see Eq 2).

11.3 If $R_S$ for a test specimen is greater than the highest count rate in the calibration curve, quantitatively dilute a fresh portion of the sample with the base material used to prepare the calibration standards. Dilute the sample so the resultant count rate is within the limits of the calibration curve. Repeat the procedures described in 11.2 on a test specimen of the diluted sample.

11.4 Calculate the concentration of sulfur in the test specimen as instructed in Section 12.

## 12. Calculation

12.1 When using a drift monitor sample, calculate a drift correction factor (F) for changes in daily instrument sensitivity according to Eq 4. If a drift monitor is not used, F is set equal to 1.

$$F = A/B \tag{4}$$

where:

$A$ = $R_S$ for the drift monitor sample determined at the time of calibration (10.4), and
$B$ = $R_S$ for the drift monitor sample determined at the time of analysis (11.1).

12.2 Calculate the drift-corrected count rate ($R_{cor}$) for the test specimen as follows:

$$R_{cor} = F \times R_S \tag{5}$$

where:

$F$ = drift correction factor, calculated by Eq 4, and
$R_S$ = total count rate for test specimen.

12.3 Calculate the sulfur content (S) of the test specimen by using the drift-corrected count rate ($R_{cor}$) in place of $R_s$ in Eq 3 of 10.3.

12.4 If the test specimen was prepared from a quantitatively diluted sample, correct the measured concentration for sample dilution. The sulfur concentration ($S_o$) in the original, undiluted sample is calculated as follows:

$$S_o = [S_d \times (M_o + M_b)/M_o] - [S_b \times (M_b/M_o)] \tag{6}$$

where:

$S_d$ = concentration of sulfur in test specimen of the diluted sample (from 12.3), mg/kg,
$M_o$ = mass of original sample, g,
$M_b$ = mass of base material used to dilute sample, g, and
$S_b$ = concentration of sulfur in diluent, mg/kg.

12.5 If a correction factor was used to account for differences in the sample matrix versus the matrix of the calibration standards (see Section 5), multiply the sulfur concentration, S, obtained in Eq 3 by the correction factor.

## 13. Reporting

13.1 Report sulfur concentration of the test sample calculated from Section 12 using units of mg/kg, rounded to the nearest 0.1 mg/kg for concentrations <100 mg/kg, and rounded to the nearest 1 mg/kg for concentrations ≥100 mg/kg. Indicate that the results were obtained according to Test Method D7039.

## 14. Quality Control

14.1 Confirm the satisfactory performance of the instrument and the test procedure by analyzing a quality control sample (see 7.5) at least once each day the analyzer is used.

14.2 When quality control/quality assurance (QC/QA) protocols are already established in the testing facility, they can be used, provided they include procedures to monitor the reliability of the test results.

14.3 When there is no QC/QA protocol established in the testing facility, the system described in Appendix X2 can be used.

## 15. Precision and Bias

15.1 *Precision*—The precision of this test method was determined by statistical analysis of results obtained in an interlaboratory study[7] in accordance with Practice D6300. Precision was calculated by using data from nine analyzers at nine different laboratories. Each laboratory analyzed a sample set in blind duplicate. Precision was calculated by using data from 22 sulfur-containing materials, including five gasolines, seven diesel and biodiesel blends, three jet fuels, one kerosine, three biodiesels, and three gasoline-ethanol blends. The range of the measured average sulfur levels was 1.1 mg/kg to 2822 mg/kg. A pooled limit of quantitation (PLOQ) (calculated by procedures consistent with Practice D6259) of 3.2 mg/kg sulfur was determined.

15.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty. Repeatability (r) may be calculated as shown in Eq 7 for all materials covering the full scope of this method. See Table 6 for calculated values.

$$\text{Repeatability (r)} = 0.4998 \cdot X^{0.54} \tag{7}$$

where:

$X$ = the average sulfur concentration of two results in mg/kg.

[7] Supporting data are pending being filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1765.

**TABLE 6 Precision Values, All Sample Types**

| S, mg/kg | Repeatability r, mg/kg Eq 7 values | Reproducibility R, mg/kg Eq 8 values |
|---|---|---|
| 3.2 | 0.9 | 1.4 |
| 5.0 | 1.2 | 1.8 |
| 10.0 | 1.7 | 2.6 |
| 15.0 | 2.2 | 3.2 |
| 25.0 | 2.8 | 4.2 |
| 50.0 | 4.1 | 6.1 |
| 100 | 6 | 9 |
| 250 | 10 | 15 |
| 500 | 14 | 21 |
| 1000 | 21 | 31 |
| 2000 | 30 | 45 |
| 2822 | 36 | 54 |

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty. Reproducibility (R) may be calculated as shown in Eq 8 for all materials covering the full scope of this method. See Table 6 for calculated values.

$$\text{Reproducibility}\,(R) = 0.7384 \cdot X^{0.54} \quad (8)$$

where:

$X$ = the average sulfur concentration of two results in mg/kg.

15.2 *Bias*—No statistically significant bias was observed for this test method in gasoline and diesel fuel at the concentrations specified in Table 7 using NIST Standard Reference Materials (SRMs) SRM 2298, SRM 2723a, and SRM 2724b. Other biases were not determined; however, bias due to differences in the hydrogen, carbon, and oxygen content of the test samples and calibration standards may be corrected by following Section 5.

## 16. Keywords

16.1 analysis; biodiesel; diesel; fuel; gasoline; jet fuel; kerosine; monochromatic X ray; MWDXRF; spectrometry; sulfur; wavelength dispersive X-ray fluorescence; WDXRF; X-ray

**TABLE 7 Comparison of NIST SRM Data and ASTM Interlaboratory Study (ILS) Measured Results**

| NIST SRM Number | NIST Sulfur, mg/kg | NIST 95 % Lower Confidence Limit, Sulfur, mg/kg | NIST 95 % Upper Confidence Limit, Sulfur, mg/kg | Matrix | ILS Average Measured Sulfur, mg/kg | ILS Average Inside 95% Confidence Limit? |
|---|---|---|---|---|---|---|
| 2298 | 4.7 | 3.4 | 6.0 | Gasoline | 4.6 | Yes |
| 2723a | 10.90 | 10.59 | 11.21 | Diesel | 11.1 | Yes |
| 2724b | 426.5 | 420.8 | 432.2 | Diesel | 431 | Yes |

# ANNEX

## (Mandatory Information)

## A1. MATRIX CORRECTION

A1.1 Calculate a matrix-correction factor[8] (C) for differences in the carbon, hydrogen, and oxygen composition between a test sample and the calibration standards according to Eq A1.1 If an absorption correction is not used, C is set equal to 1. The subscript "cal" refers to the calibration samples, and the subscript "test" refers to the test sample. The variable, μ, is the average, mass absorption coefficient.

$$C = \left[{}^{\lambda 0}\mu_{test} + {}^{\lambda S}\mu_{test}\, G\right] / \left[{}^{\lambda 0}\mu_{cal} + {}^{\lambda S}\mu_{cal}\, G\right] \quad \text{(A1.1)}$$

where:

$$ {}^{\lambda\,0}\mu = {}^{\lambda 0}\mu_C\, X_C + {}^{\lambda 0}\mu_O\, X_O + {}^{\lambda\,0}\mu_H\, X_H \quad \text{(A1.2)}$$

$$ {}^{\lambda S}\mu = 198.3\, X_C + 468.3\, X_O + 0.58\, X_H \quad \text{(A1.3)}$$

$G$ = a constant determined by the angle between the sample surface and the incident and emitted beams. The instrument manufacturer provides G; 0.87 is a typical value for the analyzer shown in Fig. 1

${}^{\lambda\,0}\mu$ = average, mass absorption coefficient ($cm^2/g$) for the incident-beam wavelength (λ0),

${}^{\lambda\,S}\mu$ = average, mass absorption coefficient ($cm^2/g$) for sulfur radiation at λ = 0.5373 nm,

${}^{\lambda\,0}\mu_C$ = mass absorption coefficient ($cm^2/g$) of carbon for $\lambda_0$ (=14.8 for Cr Kα excitation),

${}^{\lambda 0}\mu_O$ = mass absorption coefficient ($cm^2/g$) of oxygen for $\lambda_0$ (=37.7 for Cr Kα excitation),

${}^{\lambda 0}\mu_H$ = mass absorption coefficient ($cm^2/g$) of hydrogen for $\lambda_0$ (=0.34 for Cr Kα excitation).

$X_C$ = mass fraction of carbon in calibrant or sample of interest,

$X_O$ = mass fraction of oxygen in calibrant or sample of interest,

$X_H$ = mass fraction of hydrogen in calibrant or sample of interest,

A1.2 Calculate the absorption-corrected count rate ($R_C$) for the test sample as follows:

$$R_C = C \times R_S \quad \text{(A1.4)}$$

where:

$R_C$ = corrected count rate for test sample,

$C$ = absorption-correction factor, calculated in Eq A1.1, and

$R_S$ = total count rate for test sample.

A1.3 Calculate the sulfur content (S) of the test sample by applying the absorption-corrected count rate (from Eq A1.4) to the calibration Eq 3 in 10.3.

A1.4 An example is provided in Fig. 2 to illustrate the absorption correction. The example uses a test sample with C/H ratios from 5 to 10 and total oxygen from 0 to 3.0 wt. %. The correction factor is calculated for chromium Kα excitation using Eq A1.1 for this test sample and a calibration sample with C/H = 6.2 and no oxygenate.

[8] Goldstein, J. I., *et al*., *Scanning Electron Microscopy and X-ray Microanalysis,* Plenum Press, New York, 1992, pp. 743-777.

# APPENDIXES

**(Nonmandatory Information)**

## X1. DETERMINING COUNT TIME

X1.1 The quality of X-ray fluorescence analyses is a function of count precision,[9] which can be improved by increasing the count time (T). It is recommended to accumulate a sufficient number of sulfur counts to achieve a 1.0 % expected relative standard deviation (% RSD) of the net sulfur signal, or better, when sensitivity and concentration make it practical (see X1.3).

X1.2 To determine the count time to achieve a desired RSD for a sample, analyze the sample using T = 100 s and determine $R_S$ and $R_B$. Calculate T for the desired percent RSD using the following equation:

$$\% \; RSD = 100 \; T^{-0.5} \left(R_S + R_B\right)^{0.5} / \left(R_S - R_B\right) \qquad \text{(X1.1)}$$

where:

$R_S$ = measured total count rate, counts per second, and
$R_B$ = background count rate measured on a blank sample (see X1.2.2) containing no sulfur.

X1.2.1 A current calibration equation can be used to estimate $R_s$ if the concentration of the test sample is approximately known. The background count rate can be estimated by substituting the y-intercept (Y) from the most recent linear regression calibration (see 10.3.2) for $R_B$ in Eq X1.1.

X1.2.2 The T required to attain the desired precision is applicable to samples with sulfur concentrations equal to or greater than the sample used to determine T.

X1.2.3 Because a single-channel analyzer is used to measure the sulfur signal, $R_B$ cannot be determined directly on samples containing sulfur. Therefore, $R_B$ can be obtained by measuring a blank sample containing no sulfur or by substituting the y-intercept from the most recent calibration curve for $R_b$ in Eq X1.1.

X1.3 As sulfur concentration decreases, the count time necessary to achieve the desired precision increases. If it is more practical to analyze all samples using the same count time, use the count time determined for the lowest expected sulfur concentration.

[9] Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis,* Plenum Press, New York, 1975, pp. 472-500.

## X2. QUALITY CONTROL PROTOCOL

X2.1 Monitor and control the stability and precision of the instrument by regularly analyzing a quality control (QC) sample.

X2.1.1 The type of QC sample used should be similar to the samples routinely analyzed by the instrument. An ample supply of QC material should be available for the intended period of quality control, and must be homogeneous and stable under the anticipated storage conditions.

X2.1.2 The frequency of QC testing is dependent on the criticality of the analysis, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each day of testing. The QC testing frequency should be increased if a large number of samples are routinely analyzed. However, when the testing process is demonstrated to be in statistical control, the QC testing frequency may be reduced.

X2.2 Record the QC sample results and analyze by control charts or other statistically equivalent techniques to immediately ascertain the statistical control status of the measurement process. See Practice D6299 and MNL-7A[10] for further guidance on QC and control charting techniques.

X2.2.1 Prior to using a QC sample control chart for assessing whether the measurement process is in statistical control, the user of the test method must have accumulated at least 15 suitable measurements and calculated an average value and control limits for the QC sample.

X2.2.2 Any QC sample result outside of control limits should trigger an investigation for root cause(s). The result of this investigation may indicate the need for instrument recalibration and other remedial action.

X2.2.3 Compare the site repeatability estimated from the QC sample with the published reproducibility of this test method. The site repeatability is expected to be less than or equal to the published reproducibility.

[10] *ASTM MNL 7A, Manual on Presentation of Data and Control Chart Analysis,* 7th ed., available from ASTM International Headquarters.

## X3. AIDS TO THE ANALYST

X3.1 Best practices for obtaining quality measurement results include: cleanliness steps to reduce contamination, correct sample preparation and measurement, and analyzer quality control. These steps become increasingly important when measuring low concentration values.

X3.1.1 See Practice D7343 for further guidance on optimization, sample handling, calibration, and validation of x-ray fluorescence spectrometry methods.

X3.2 Maintain a clean sample preparation area to minimize sample contamination. Ensure that removable sample cells, x-ray transparent film, and transfer pipettes are kept covered in a dust free area, such as a plastic bag, covered container, or drawer. If a vent tool is used (not needed for pre-vented sample cups), make sure it is also kept in a dust free environment, and clean reusable vent tools with an appropriate solvent after each use.

X3.3 Consult the manufacturer for instructions on cleaning the analyzer, including acceptable solvents for cleaning. Cleaning procedures for the sample area should be performed once daily or more often if necessary. If a suspicious measurement result is obtained, perform the cleaning procedures.

X3.3.1 Canned or compressed air, though not mandatory, is highly recommended in the cleaning and specimen preparation process. Canned air is used as a drying agent after cleaning and as a means to remove airborne contaminants such as dust. Do not shake the can before use as this may dislodge a visible propellant stream from the can that may form a contaminant coating. If this happens, perform the cleaning step again to remove the contamination or replace the disposable film as appropriate.

X3.3.2 Generally, it is acceptable to clean the sample chamber area with a clean, lint-free cloth wetted with isopropyl alcohol. This includes the inside of the lid, sample holder, and adjacent area, excluding any window films. Dry the area with canned air.

X3.3.3 Disposable secondary or primary windows should not be cleaned, they should be replaced instead. Blow the new film off with canned air before assembling, and make sure the completed window is wrinkle free. Make sure to verify calibration integrity after starting a new batch of film.

X3.3.4 Non-disposable primary windows should be cleaned carefully according to the manufacturer's instructions. Polyimide primary windows can be cleaned with a foam tipped (or lint-free) swab wetted with isopropyl alcohol. Shake the swab to remove excess alcohol, then hold the swab parallel to the top of the analyzer and carefully wipe the primary window with the swab. Polyimide primary windows are delicate and care should be taken when cleaning these primary windows to avoid breakage. Dry the primary window with canned air. If canned air propellant is visible when drying the window, repeat the primary window cleaning process.

X3.4 Follow Section 8 for Sampling and Sample Handling and Section 9 for Preparation of Apparatus and Specimens for Analysis instructions. Additional to these instructions, it is recommended to use canned air in sample preparation. Use canned air to blow out the sample cup before the sample is prepared (not necessary for preassembled, pre-vented sample cells).

X3.4.1 Use appropriate sample storage and mixing procedures. Make sure samples are homogenous before transferring a specimen to the sample cell. Filter the sample if necessary to remove water and particulate matter. Disposable transfer pipettes are recommended for filling the sample cup rather than pouring from the sample container. Do not reuse disposable pipettes.

X3.4.2 Before placing the film on the sample cup, use canned air to blow off the sample side of the film. When flipping the sample cell over for venting, make sure it rests on a sample stand or on a lint-free cloth to prevent film contamination. These steps are not necessary if using preassembled, pre-vented sample cells.

X3.4.3 Using canned air, blow off the sample cup film and then visually inspect film surface for leaks, wrinkles, or particulate matter before placing the specimen in the analyzer. Make sure to verify calibration integrity after starting a new batch of film. Measure the specimen promptly after preparation, and remove it promptly after analysis. Visually inspect the specimen after analysis for leaks. If the specimen has leaked, clean up the spill, change or clean any primary or secondary windows as necessary, and measure a new specimen.

X3.5 To ensure the analyzer is performing satisfactorily, follow Section 14 for Quality Control, unless quality control/quality assurance protocols are already established in the testing facility.

## SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7039 – 14) that may impact the use of this standard. (Approved July 1, 2015.)

*(1)* Added new Appendix X3; added Practice D7343 to Referenced Documents.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7039 – 13) that may impact the use of this standard. (Approved April 1, 2015.)

*(1)* Revised 9.2.2.