Standard Test Method for
Low Sulfur in Automotive Fuels by Energy-Dispersive X-ray Fluorescence Spectrometry Using a Low-Background Proportional Counter[1]

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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

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 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 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.

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.

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

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.

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 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 study[6] 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.

NOTE 3—One laboratory has shown that polycarbonate resists a mixture of 25 mass % isooctane and 75 mass % toluene for 80 min.

8.4.2 In these cases high purity polyester is acceptable, but overall, polycarbonate offers the best combination of spectral purity and resistance to stretching. Other materials may be used for X-ray windows, provided that they do not contain any elemental impurities and match the listed films for X-ray transmission.

8.5 *Sample Cells*, resistant to sample attack and meet the geometry requirements of spectrometer.

8.6 *Calibration Check Samples*, portions of one or more automotive fuel standards of known sulfur content and not used in the generation of the calibration line. The check samples shall be used to determine the accuracy of the initial calibration (see 11.3).

8.7 *Quality Control (QC) Samples*, preferably portions of one or more automotive fuel materials that are stable and representative of the samples of interest.

[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.

[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.

9. Sampling

9.1 A sample shall be taken in accordance with the instructions in Practice D4057 or D4177, where appropriate. Do not shake samples, thus avoiding entrained air. Analyze samples immediately after pouring into a sample cell and allowing the escape of the air bubbles caused by mixing.

9.2 For the measurement of low sulfur contents disposable cells are recommended. Preparation of sample cells must be done with care and by following any advice from the supplier. A freshly prepared sample cell including film is required prior to analyzing the samples. Avoid touching the inside of the sample cell or portion of the window film in the cell or in the instrument window that is exposed to X rays. Oil from fingerprints affects the reading when analyzing for low level of sulfur. Ensure that the film is not scratched, especially by the tear-off bar as it is withdrawn from the container. Wrinkles in the film will affect the intensity of sulfur X rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. Film may become electrostatically charged during handling so it is important that the cell window does not attract any dust, fiber, and hair. The analyzer will need recalibration if the type or thickness of the window film is changed.

9.3 If the instrument has a replaceable secondary/safety window, it must be changed for every sample to ensure there is no cross-contamination. When changing it, follow the precautions given in 9.2.

9.4 Impurities that may affect the measurement of low levels of sulfur have been found in polyester films. All films may vary in thickness from roll to roll. Therefore, the calibration shall be verified after starting each new roll of film.

9.5 Where laboratories use more than one XRF spectrometer or analyze different types of sample, a variety of cell window materials may be used. Always ensure that the correct film is clearly distinguished.

10. Preparation of Apparatus

10.1 Set up the apparatus in accordance with the manufacturer's instructions. Whenever possible, the instrument should remain energized to maintain optimum stability.

10.2 When changing the helium gas cylinder or after a system has been idle for a day or more ensure that the helium pipes are purged of air by performing a dummy measurement.

11. Calibration and Standardization

11.1 *Preparation of Calibration Standards*:

11.1.1 *Preparation of Stock Calibration Standard*— Accurately weigh the nominal quantity of white mineral oil to the nearest 0.1 mg, as shown in Table 1, into a suitable narrow-necked container, then accurately weigh in the nominal quantity of di-*n*-butyl sulfide. Mix thoroughly (a PTFE-coated magnetic stirrer is advisable) at room temperature. Calculate

the concentration of sulfur in the stock standard to 1 mg/kg using the following equation:

$$S_{Stock} = [DBS \times S_{DBS} / (DBS + MO)] \times 10\ 000 \tag{1}$$

where:
S_{Stock} = mg/kg of sulfur in the stock standard,
DBS = actual mass of DBS, g,
S_{DBS} = the mass % of sulfur in DBS, typically 21.91 %, and
MO = actual mass of white mineral oil, g.

11.1.2 *Preparation of Calibration Standards*—Accurately weigh the nominal quantity of white mineral oil to the nearest 0.1 mg, as shown in Table 2, into a suitable narrow-necked container, then accurately weigh in the nominal quantity of stock standard. Mix thoroughly (a PTFE-coated magnetic stirrer is advisable) at room temperature. Calculate the concentration of sulfur in the each standard to 0.1 mg/kg using the following equation:

$$S_{Std} = STK \times S_{Stock} / (STK + MO) \tag{2}$$

where:
S_{Std} = mg/kg of sulfur in the calibration standard, and
STK = actual mass of stock standard, g.

11.2 *Storage of Standards and Calibration Check Samples*—Store all standards and check samples in glass bottles in a cool, dark place until required. The glass bottles shall be either dark or wrapped in opaque material and closed with glass stoppers, inert plastic lined screw caps, or other equally inert, impermeable enclosures. As soon as any sediment or change of concentration is observed, discard the standard.

11.3 *Instrument Calibration*—Calibrate the instrument following the manufacturer's instructions. Typically, the calibration procedure involves setting up the instrument for recording of fluorescent sulfur K series intensity, argon K series intensity, and two intensities to determine spectral overlap from chlorine. In effect, sulfur is measured simultaneously with three different regions of interest, which are the normal setting and two others, one narrower, and one wider. All three regions have the same lower limit. The normal setting is approximately symmetrical around the center of the sulfur peak (1.92 to 2.51 keV), the narrower setting has its upper limit in the center of the sulfur peak (1.92 to 2.31 keV), and the wider region has its upper limit in the center of the chlorine peak (1.92 to 2.62 keV). Obtain readings on a portion (see Section 9) of every standard, then repeat the procedure on freshly prepared sample cells and fresh portion of every standard. Once all the standards have been measured twice, follow the manufacturer's instructions

TABLE 2 Nominal Calibration Standards

Sulfur Content, mg/kg	Mass of White Mineral Oil, g	Mass of Stock Standard, g
0	100.0	0.0
5	99.8	0.2
10	99.6	0.4
30	98.8	1.2
50	98.0	2.0
70	97.2	2.8
100	96.0	4.0
150	94.0	6.0

TABLE 1 Nominal Composition of Stock Standard

Sulfur Content, mg/kg	Mass of White Mineral Oil, g	Mass of Di-*n*-butyl Sulfide, g
2498	98.86	1.14

for generating the optimum calibration line based on the sulfur and argon intensities with a correction for residual air.

11.3.1 There is no chlorine present in the calibration standards, and therefore there is no need to apply a correction for spectral overlap by chlorine during the calibration procedure. However, it is necessary to generate calibration lines for the narrower and wider regions of interest as well as the normal one. The normal region of interest is used for determination of sulfur content whereas the other two are used to test for the presence of chlorine and where necessary apply a correction (see 12.3).

11.3.2 Immediately on completion of the calibration, measure one or more calibration check samples (see 8.6). The measured values must be within with 3 % relative of the certified value, or within 2 mg/kg, whichever is the greater.

12. Procedure

12.1 Prepare and fill the sample cup with the test portion as described in Section 9.

12.1.1 When using an autosampler, follow the manufacturer's advice on the number of samples than can be measured in one batch.

12.2 Take measurements for fluorescent sulfur K series intensity, argon K series intensity and two intensities to determine spectral overlap from chlorine (see 11.3) using the same counting time as used for calibration. With minimal delay, repeat the measurement on a freshly prepared sample cell and a fresh portion of the sample. Calculate the average of the two results.

12.3 When there is significant chlorine present in a sample (see 6.1), then identify it at this point and apply the necessary correction.

12.3.1 Compare the three sulfur results from the three calibration lines (see 11.3). Normally, the three measurements agree and no correction is necessary, but when chlorine is present, they differ. When the result from the wider region exceeds that from the narrower wider region by greater than 1.5 mg/kg then a correction is applied by using the following equation:

$$S_{coor} = S_{meas} - 1.47 \times (S_{wide} - S_{narrow}) \qquad (3)$$

where:

S_{coor} = result corrected for spectral overlap by chlorine,
S_{meas} = result calculated from the calibration line using the normal region of interest,
S_{wide} = result calculated from the calibration line using the wide region of interest, and
S_{narrow} = result calculated from the calibration line using the narrow region of interest.

12.4 Use the difference between the results on the two portions of sample to indicate possible problems. If the figures differ by more than 3 mg/kg then there may be an error in the measurement. Possible causes are contaminated cell window, leaking cell window, wrinkled or slack cell window, and use of the wrong window material.

12.5 After running a tray of samples, always remove them to ensure no leakage of sample into the spectrometer.

TABLE 3 Calculated Precision

S, mg/kg	r, mg/kg	R, mg/kg
8	2.0	4.6
10	2.0	4.7
15	2.1	4.9
20	2.2	5.1
25	2.2	5.2
30	2.3	5.3
35	2.3	5.4
40	2.3	5.4
45	2.4	5.5

13. Calculation of Results

13.1 The concentration of sulfur in the sample is automatically calculated from the calibration line (see 11.3).

14. Quality Control

14.1 Confirm the performance of the instrument or test procedure by analyzing a quality control (QC) sample (see 8.6) after each calibration and at least each day of use thereafter (see 12.2).

14.1.1 When QC/quality assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

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

15. Report

15.1 Report the result as the total sulfur content in mg/kg rounding to one decimal place using Practice E29, and state that the results were obtained in accordance with Test Method D7212.

16. Precision and Bias

16.1 The precision and bias were obtained by statistical analysis of results from an interlaboratory study[6] involving nine laboratories using six gasoline samples and six diesel fuel samples. An additional sample, a certified reference material of diesel fuel ERML-EF6736[7] with 52.4 mg/kg sulfur, was supplied as a calibration check sample (see 11.3.2).

16.2 *Precision*—The precision of this test method is as follows:

16.2.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty, where X equals the test result:

$$1.6196X^{0.1}$$

16.2.2 *Reproducibility*—The difference between two single and independent test 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

[7] Supplied by LGC Promochem, Queens Road, Teddington, Middlesex, TW11 0LY, United Kingdom.

the test method, exceed the following value only in one case in twenty, where *X* equals the test result:

$$3.7668X^{0.1}$$

16.2.3 Calculated examples of repeatability (r) and reproducibility (R) are given in Table 3.

16.3 *Bias*—A certified reference material of diesel fuel, ERML-EF674[7] with 11.0 mg/kg sulfur was included as a test sample in the interlaboratory test results. There was no significant bias.

17. Keywords

17.1 analysis; automotive fuels; energy dispersive; low background; low sulfur; spectrometry; X-ray

APPENDIXES

(Nonmandatory Information)

X1. PRECISION FOR INSTRUMENTS QUALIFIED FOR US EPA DOCUMENT 40 CFR 80.584

X1.1 Precision

X1.1.1 The precision was obtained by statistical analysis of results obtained from an interlaboratory study which included the measurement of ten diesel fuel samples with sulfur concentrations between 7 and 21 mg/kg. The study was conducted by Southwest Research Institute for the US EPA, and included six laboratories using Test Method D7212. Each participating laboratory qualified their measurement method per 40 CFR 80.584[8] by demonstrating precision and accuracy as follows:

"I. Precision demonstration for motor vehicle diesel fuel and diesel fuel additives subject to the 15 mg/kg sulfur standard.

Precision Criteria, § 80.584(a)(1) - a standard deviation less than 0.72 mg/kg, computed from the results of a minimum of 20 repeat tests made over 20 days on samples taken from a single homogeneous commercially available diesel fuel with a sulfur content in the range of 5-15 mg/kg. The 20 results must be a series of tests with a sequential record of analyses and no omissions.

II. Accuracy demonstration for motor vehicle diesel fuel and diesel fuel additives subject to the 15 mg/kg sulfur standard.

Accuracy Criterion –

1. The arithmetic average of a continuous series of at least 10 tests performed on a commercially available gravimetric sulfur standard (CAGSS) in the range of 1-10 mg/kg sulfur shall not differ from the accepted reference value of that standard by more than 0.54 mg/kg sulfur.

2. The arithmetic average of a continuous series of at least 10 tests performed on a CAGSS in the range of 10-20 mg/kg sulfur shall not differ from the accepted reference value of that standard by more than 0.54 mg/kg sulfur."

TABLE X1.1 Calculated Repeatability (r) and Reproducibility (R)

S, mg/kg	r, mg/kg	R, mg/kg
7	1.2	1.6
8	1.2	1.6
10	1.3	1.7
12	1.4	1.8
15	1.4	1.9
18	1.5	1.9
20	1.5	2.0
21	1.5	2.0

X1.1.2 The repeatability and reproducibility were calculated using Practice D6300.[9]

X1.2 Repeatability

X1.2.1 The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty, where X equals the test result:

$$0.8220 * X^{0.2} \qquad \text{(X1.1)}$$

Calculated examples of repeatability (r) are given in Table X1.1.

X1.3 Reproducibility

X1.3.1 The difference between two single and independent test 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 value only in one case in twenty, where X equals the test result:

$$1.0767 * X^{0.2} \qquad \text{(X1.2)}$$

Calculated examples of reproducibility (R) are given in Table X1.1.

X2. QUALITY CONTROL MONITORING

X2.1 Confirm the performance of the instrument or test procedure by analyzing quality control (QC) samples.

X2.1.1 The white mineral oil used to make the standards can usefully be measured as one of the QC check samples to confirm that the instrument blank reading has not changed.

X2.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See Practice D6299 and MNL 7.[10]

X2.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice D6299 and MNL 7.[10]

Note X2.1—In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

X2.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM test method precision to ensure data quality. See Practice D6299 and MNL 7.[10]

X2.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X2.6 See Practice D6299 and MNL 7[10] for further guidance on QC and control charting techniques.

[10] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., Section 3, ASTM International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7212–06) that may impact the use of this standard.

(1) Updated Referenced Documents to include Practice D6300.

(2) Added new Appendix X1. Renumbered original Appendix X1 as Appendix X2.