



# Standard Test Method for Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 6445; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Warning notes were editorially moved into the standard text in July 2004.

## 1. Scope

1.1 This test method covers the measurement of sulfur in nonleaded gasoline and gasoline-oxygenate blends. The applicable concentration range is 48 to 1000 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 may involve hazardous materials, operations, and equipment. *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 warning statements, see Sections 5 and 7.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

## 3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards to obtain the

sulfur concentration in mg/kg. One group of calibration standards is required to span the concentration 5 to 1000 mg/kg sulfur.

## 4. Significance and Use

4.1 This test method provides a means of quantifying sulfur content in gasoline. It can be referenced in specification documents as a means to determine if the material meets the desired sulfur content. It is a rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation.

4.2 The quality of gasoline is related to the amount of sulfur present. Knowledge of sulfur concentration is necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in gasoline as it affects performance characteristics and potential corrosion problems and emission levels. During combustion, the sulfur content in fuel affects SO<sub>x</sub> emissions, which degrade air quality. Certain jurisdictions may restrict the amount of sulfur in gasoline to prevent or limit pollution to the environment.

## 5. Apparatus

5.1 *Energy-dispersive X-ray Fluorescence Analyzer*—The analyzer needs to have sufficient sensitivity to measure the concentration of sulfur at 500 mg/kg with a one standard deviation value due to counting statistics no greater than 10 mg/kg under optimized conditions. Any energy dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum, the following features:

5.1.1 *Source of X-ray Excitation*—X-ray tube with energy above 2.5 keV.

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.

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

<sup>1</sup>This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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<sup>2</sup>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.

5.1.3 *X-ray Detector*, with a resolution value not to exceed 800 eV at 2.3 keV. A gas filled proportional counter has been found suitable to use.

5.1.4 *Filters*, or other means of discriminating between sulfur  $K_{\alpha}$  radiation and other X rays.

5.1.5 Signal conditioning and data handling electronics that include the functions of X-ray intensity counting, spectral overlap corrections, and conversion of sulfur X-ray intensity into mg/kg sulfur concentration. It is also imperative that the instrument has the capability to monitor counts for at least one energy region distinct from the sulfur region to allow compensation for variations in spectral background (that is, calculation of net intensities).

5.1.6 *Display or Printer*, that reads or prints out in mg/kg or mass percent sulfur.

## 6. Matrix Effects

6.1 Matrix effects refer to changes in measured intensity of sulfur caused by concentration variations of the elements in a sample. These variations directly influence X-ray absorption and change the measured intensity of each element. For example, performance enhancing additives, such as oxygenates in gasoline, can affect the apparent sulfur reading. These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

6.2 Many modern instruments have the capability to correct for matrix effects by ratioing measured sulfur intensities to that of X-ray radiation scattered from the sample (for example, scattered X-ray tube lines). This can be an effective method for compensating for matrix differences between samples and standards, although it can result in some degradation of the measurement precision. It is the user's responsibility, however, to ensure that the matrix corrections applied are accurate. It is recommended that these are checked by analyzing standard reference materials and that the software corrections offered by the manufacturer not be accepted at face value. In addition, corrections should be verified for new formulations.

## 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.<sup>3</sup> 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. The concentration should be known to at least three significant figures or nearest 1 mg/kg, whichever is higher.

7.2 *Di-n-Butyl Sulfide (DBS)*, (**Warning**—Di-n-butyl sulfide is flammable and toxic.) A high purity standard, minimum 96 % purity, with a certified analysis for sulfur content. Use the

certified sulfur content when calculating the exact concentrations of the calibration standards (see 10.1).

7.3 *Thiophene*, sulfur content 37.72 mass %, 99 % purity.

7.4 *2-Methylthiophene*, 32.00 % sulfur, 98 % purity.

NOTE 2—Purity on the label for di-n-butyl sulfide, thiophene, and 2-methylthiophene is only a nominal value. It is essential to know the concentration of sulfur in the sulfur standard, not the purity, since impurities may also be sulfur containing compounds.

7.5 *Isooctane (2,2,4-trimethylpentane)*, with a certified analysis for sulfur content or checked by Test Method D 3120 or equivalent test method as containing less than 3 mg/kg sulfur.

7.6 *Toluene*, with a certified analysis for sulfur content or checked by Test Method D 3120 or equivalent test method as containing less than 3 mg/kg sulfur.

7.7 *X-ray Transparent Film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent may be used. Films found to be suitable are polyester, polypropylene, polycarbonate, and polyimide films. Typical film thicknesses range from 1.5 to 8  $\mu\text{m}$ . Film thickness will affect the transmission of X rays and the films resistance to chemical attack.

7.7.1 Samples of high aromatic content may dissolve polyester and polycarbonate films. In these cases, other materials besides these films may be used for X-ray windows, provided that they do not contain any elemental impurities. An optional window material is polyimide film. While polyimide film absorbs sulfur X rays more than other films, it may be a preferred window material as it is much more resistant to chemical attack by aromatics and exhibits higher mechanical strength.

7.8 *Sample Cells*, resistant to sample attack and meeting geometry requirements of spectrometer. Disposable cells are preferred.

## 8. Sampling and Specimen Preparation

8.1 Take samples in accordance with the instructions in Practice D 4057 or D 4177 where appropriate. Thoroughly mix and analyze samples immediately after pouring into a sample cell. Inspect the sample for any air bubbles or sediment. Allow air bubbles to escape or resample if necessary.

NOTE 3—The measured sulfur concentration may vary with the time that the sample/standard contacts the film covering the sample cell. By consistently minimizing the length of time the film comes into contact with the sample or standards, possible variations can be reduced.

8.2 If using reusable sample cells, clean and dry cells before use. Do not reuse disposable sample cells. Replacement of the X-ray film of a reused sample cell is essential for the measurement of each sample. 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 can affect the reading when analyzing for low levels of sulfur. 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. The analyzer will need recalibration if the type or thickness of the window material is changed.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.3 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in window materials films and may vary from lot to lot. Therefore, check the calibration after starting each new package of film.

### 9. Preparation of Apparatus

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

### 10. Calibration and Standardization

#### 10.1 Preparation of Calibration Standards:

10.1.1 Prepare diluent by blending 20 % toluene and 80 % *isooctane* by volume.

10.1.2 Use either di-*n*-butyl sulfide or a blend of thiophene/2-methylthiophene as a source of sulfur in the primary standards. If using di-*n*-butyl sulfide as the source of sulfur, proceed to 10.1.3.

10.1.2.1 To prepare the thiophene/2-methylthiophene (TM) blend, mix 9.90 g thiophene with 9.55 g 2-methylthiophene. Weigh the materials into a tared volumetric flask and record the mass to four significant digits. Calculate the exact sulfur content of the stock sulfur solution to the nearest mg/kg. Mix thoroughly (a polytetrafluoroethylene (PTFE)-coated magnetic stirrer is suitable) at room temperature.

10.1.3 Make primary standards independently at 100 and 2000 mg/kg sulfur and not by serial dilutions from a single concentrate. Refer to 10.1.3.1 if using di-*n*-butyl sulfide and 10.1.3.2 if using the thiophene/2-methylthiophene blend for the source of sulfur.

10.1.3.1 Weigh the diluent and the di-*n*-butyl sulfide (DBS) into a tared volumetric flask, using the indicated mass in Table 1 (but record the mass to four significant digits). Mix thoroughly (a PTFE-coated magnetic stirrer is suitable) at room temperature.

10.1.3.2 Weigh the diluent and the thiophene/2-methylthiophene (TM) blend into a tared volumetric flask using the indicated mass in Table 2 (but record the mass to four significant digits). Mix thoroughly (a PTFE-coated magnetic stirrer is advisable) at room temperature.

10.1.3.3 If the *isooctane*/toluene diluent being used for the preparation of standards contains sulfur, incorporate this value into the calculated sulfur content of the prepared standards (consult your supplier for a certified sulfur concentration or test the *isooctane*/toluene using Test Method D 3120 or any other equivalent low level sulfur analyzing method).

10.1.3.4 It is important that the actual mass is known and thus the actual concentration of the prepared standards is calculated and entered into the instrument for calibration purposes. Calculate the exact sulfur content in each of the

**TABLE 1 Composition of Primary Standards When Using Di-*n*-Butyl Sulfide (DBS)**

Sulfur (mg/kg)	Mass of Diluent (g)	Mass of DBS (g)
100	540	0.25
2000	200.8	1.85

**TABLE 2 Composition of Primary Standards When Using Thiophene/2-Methylthiophene Blend (TM)**

Sulfur (mg/kg)	Mass of Diluent (g)	Mass of TM (g)
100	540	0.15
2000	200.8	1.15

prepared standards to the nearest 1 mg/kg. Calculate the concentration of sulfur in the primary standard using the following equations. Use Eq 1 if using di-*n*-butyl sulfide and Eq 2 if using the thiophene/2-methylthiophene blend as a source of sulfur:

$$S = \frac{10,000(DBS \times S_{DBS} + Diluent \times S_{DILUENT})}{DBS + Diluent} \quad (1)$$

$$S = \frac{10,000(TM \times S_{TM} + Diluent \times S_{DILUENT})}{TM + Diluent} \quad (2)$$

where:

- S* = mg/kg sulfur of the primary standards,
- DBS* = if using the di-*n*-butyl sulfide, this is the actual mass in grams of di-*n*-butyl sulfide used,
- TM* = if using the thiophene/2-methylthiophene blend, this is the actual mass of the sulfur blend in grams,
- S<sub>DBS</sub>* = if using di-*n*-butyl sulfide, this is the mass % sulfur of the di-*n*-butyl sulfide, typically 21.91 %. For example, 21.91 % would be expressed as 21.91 in the formula (see Note 2),
- S<sub>TM</sub>* = if using the thiophene/2-methylthiophene blend, this is the mass % sulfur in the this blend, typically 34.9 mass %. For example, 34.9 % would be expressed as 34.9 in the formula (see Note 2),
- Diluent* = actual mass of *isooctane*/toluene diluent (g), and
- S<sub>Diluent</sub>* = mass % sulfur in the *isooctane*/toluene blend. For example, 0.0001 % would be expressed as 0.0001 in the formula.

10.1.4 Prepare calibration standards with the nominal concentration ranges identified in Table 3 for the two ranges by

**TABLE 3 Calibration Standards**

Standard Number	Nominal Concentration (mg/kg)	Mass of Primary Standard (g)	Mass of Diluent (g)
Use 100 mg/kg primary standard for Standards 1 through 6.			
Std 1	0	0	100
Std 2	10	10	90
Std 3	30	30	70
Std 4	50	50	50
Std 5	75	75	25
Std 6	100	100	0
Use 2000 mg/kg primary standard for Standards 7 through 9.			
Std 7	300	15	85
Std 8	500	25	75
Std 9	1000	50	50

diluting the appropriate primary standard with diluent. Adjust masses as needed if preparing more or less than 100 g of standard solutions.

10.1.4.1 Calculate the exact sulfur content in each of the calibration standards to the nearest mg/kg. Calculate the concentration of sulfur using the following equation:

$$S_{CAL} = \frac{(PM \times S_{PM} + Diluent \times S_{2DILUENT})}{PM + Diluent} \quad (3)$$

where:

- $S_{CAL}$  = mg/kg sulfur of the calibration standards,  
 $PM$  = this is the actual mass in grams of the primary standard used,  
 $S_{PM}$  = this is the mg/kg sulfur of the primary standard. For example, 100 mg/kg would be expressed as 100 in the formula,  
 $Diluent$  = actual mass in grams of the *isooctane/toluene* diluent, and  
 $S_{2Diluent}$  = mg/kg sulfur in the *isooctane/toluene* blend. For example, 0.5 mg/kg would be expressed as 0.5 in the formula.

10.1.5 Alternatively, nationally traceable certified standards, such as National Institute of Science and Technology (NIST), prepared as described above or composed of the matrix to be analyzed can be used.

10.2 *Certified Calibration Standards*—Calibration standards, which are certified by an organization in accordance with a protocol that is technically equivalent to that used by NIST for certification of standard reference materials organization, may be used when they cover the nominal concentrations in Table 2 and are applicable to the sample of interest.

10.3 *Quality Control (QC) Standards*—Use several additional standards (QC standards) that were not used in generating the calibration curve to check the validity of the calibration. QC standards may be independently prepared as per 10.1 or certified standards as per 10.2. The concentration and matrices of the QC standards shall be near the expected concentration of the samples being analyzed.

10.4 *Storage of Standards and QC Standards*: Store all standards in glass bottles, either dark or wrapped in opaque material, closed with glass stoppers, inert plastic lined screw caps, or other equally inert, impermeable closures, in a cool, dark place until required. As soon as any sediment or change of concentration or stratification is observed, discard the standard.

## 11. Procedure

11.1 Although sulfur radiation will penetrate through only a small distance in the sample, scatter from the sample cell and the sample may vary. As such, ensure that the sample cell is filled with sample above a minimum depth, at which point, further filling causes an insignificant change in the counting rate. Generally speaking, filling the sample cup to at least three quarters of the capacity of the sample cell will be sufficient. Prepare the sample cell, providing adequate head space. Provide a vent hole in the top to prevent bowing of the X-ray film during measurement of volatile samples. (**Warning**—Avoid spilling flammable liquids inside the analyzer.)

11.2 *Instrument Calibration*—Calibrate the instrument with the standards listed in Table 3, following manufacturer's

instructions. Typically, the calibration procedure involves setting up the instrument for recording of net sulfur X-ray intensity, followed by the measurement of known standards. Analyze each standard two times, using a freshly prepared cell for each analysis and an analysis time of 200 to 300 s. Once all the standards have been analyzed, follow manufacturer's instructions for generating the optimum calibration curve based on the net sulfur counts for each standard.

11.3 *Analysis of Unknown Samples*—Fill the cell with the sample to be measured, as described in 11.1. Ensure that no air bubbles are present between the cell window and the liquid sample. Analyze each sample two times, using a freshly prepared sample, and analyze each sample, using the same analysis time as in the calibration. Obtain the average of the readings for the sulfur content in the unknown sample.

## 12. Calculation

12.1 The concentration of sulfur in the sample is automatically calculated from the calibration curve.

## 13. Report

13.1 Report the result as the total sulfur content to the nearest 1 mg/kg, and state that the results were obtained in accordance with Test Method D 6445.

## 14. Quality Control

14.1 For the purpose of establishing the in statistical control status of the testing process since the last valid calibration, QC standards prepared from material(s) selected and stored according to 10.3 and 10.4 are regularly tested as if they were production samples. Results are recorded and analyzed by control charts (see Note 4) or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. An investigation for root cause(s) shall be conducted when there are out of control data. The outcome of this investigation may, but not necessarily, result in instrument recalibration. In absence of other explicit requirements, the frequency of QC standards testing is dependent on the criticality of the quality being measured and the demonstrated stability of the testing process. It is recommended that at least one type of QC standard that is regularly tested be representative of samples routinely analyzed.

NOTE 4—The precise method of control charting, chart interpretation, and corrective action is left to the individual laboratory since the topic is outside the scope of this test method. One resource, however, that may be useful is Manual 7.<sup>4</sup>

## 15. Precision and Bias

15.1 *Precision*—The precision of this test method as obtained by statistical analysis of interlaboratory test results is as follows:

15.1.1 *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

<sup>4</sup> Manual 7, *Manual on Presentation of Data Control Chart Analysis*, 6<sup>th</sup> Edition, ASTM International, W. Conshohocken, PA.

operation of the test method, exceed the following values in only one case in twenty:

$$r = 12.30 (X+10)^{0.1}$$

where:

X is the sulfur concentration in mg/kg.

Repeatability values for some typical sulfur concentrations are shown in Table 4.

**TABLE 4 Repeatability (r) & Reproducibility (R)**

X (mg/kg)	r (mg/kg)	R (mg/kg)
50	19	55
100	20	58
300	22	64
500	23	68
700	24	70
1000	25	72

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, exceed the following values in only one case in twenty:

$$R = 36.26 (X+10)^{0.1}$$

where:

X is the sulfur concentration in mg/kg.

Reproducibility values for some typical sulfur concentrations are shown in Table 4.

15.2 *Bias*—Since no accepted reference materials were used in the interlaboratory test, no statement on bias is being made.

## 16. Keywords

16.1 analysis; energy dispersive; petroleum; spectrometry; sulfur; X ray

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