Designation: ~~D6334 – 12~~ D6334 – 12 (Reapproved 2017)

Standard Test Method for
Sulfur in Gasoline by Wavelength Dispersive X-Ray Fluorescence[1]

This standard is issued under the fixed designation D6334; 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*~~Scope

1.1 This test method covers the quantitative determination of total sulfur in gasoline and gasoline-oxygenate blends. The Pooled Limit of Quantitation (PLOQ) was determined to be ~~15~~15 mg ~~mg/kg.~~/kg. Therefore, the practical range for this test method is from ~~15~~15 mg/kg to ~~940~~940 mg ~~mg/kg.~~/kg.

NOTE 1—This concentration range is based on that used in the interlaboratory round robin, which shows that the range of sulfur in the round robin samples was from ~~1.5~~1.5 mg/kg to ~~940~~940 mg ~~mg/kg;~~/kg; however, below ~~15~~15 mg ~~mg/kg,~~/kg, the reproducibility approaches 100 % of the concentration.

1.2 *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 limitation prior to use.*

1.3 The values stated in SI units are to be regarded as the standard. The preferred units are mg/kg sulfur.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
D3210 Test Method for Comparing Colors of Films from Water-Emulsion Floor Polishes
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
D4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

3. Summary of Test Method

3.1 The sample is placed in the X-ray beam, and the intensity of the sulfur Kα line at ~~5.373 Å~~5.373 Å is measured. The intensity of a corrected background, measured at a recommended wavelength of ~~5.190 Å,~~5.190 Å, or if a rhodium tube is used, ~~5.437 Å,~~ 5.437 Å, is subtracted from this intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mg/kg. (**Warning**—Exposure to excessive quantities of X radiation is

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

injurious to health. Therefore, it is imperative that the operator avoid exposing any part of his or her person, 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 of recommendations governing the use of ionizing radiation.)

4. Significance and Use

4.1 Knowledge of the presence of sulfur in petroleum products, especially fuels, helps predict performance characteristics, potential corrosion problems, and vehicle emission levels. In addition, some regulatory agencies mandate reduced levels of sulfur in reformulated type gasolines.

5. Interferences

5.1 Fuels with compositions that vary from those specified in 9.1 may be analyzed with standards made from base materials that are of similar composition to minimize matrix effects.

5.1.1 Fuels containing oxygenates may be analyzed using standards prepared with similar amounts of the same oxygenate added to the standard dilution matrix. However, round robin studies done by the Western States Petroleum Association have shown no significant bias in determining sulfur in gasolines with and without oxygenates at regulatory levels (0 to 2.7 weight percent oxygen).

5.1.2 Methanol fuels (M85 and M100) exhibit interferences at this level of detection (<100(<100 mg mg/kg). /kg). They can be analyzed using a calibration curve produced by diluting the standards in a similar matrix of M85 or M100 or by Test Method D2622.

6. Apparatus

6.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF),* equipped for soft ray detection in the 5.37 Å 5.37 Å range. For optimum sensitivity to sulfur, equip the instrument with the following:

6.1.1 *Optical Path,* of helium.

6.1.2 *Pulse-Height Analyzer,* or other means of energy discrimination.

6.1.3 *Detector,* designed for the detection of long wavelength X-rays.

6.1.4 *Analyzing Crystal,* suitable for the dispersion of sulfur Kα X-rays within the angular range of the spectrometer employed. Pentaerythritol and germanium are the most popular, although materials, such as EDDT, ADP, graphite, and quartz, may be used.

6.1.5 *X-Ray Tube,* capable of exciting sulfur K_α radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular, although other anodes may be suitable.

7. Reagents

7.1 *Di-n-Butyl Sulfide* (MW – 146.30),a high-purity grade standard with a certified sulfur analysis.

7.2 *Thiophene* MW– 84.14),a high-purity (98+ %) grade standard with a certified sulfur analysis.

7.3 *2-Methylthiophene* MW – 98.17),a high purity (98+ %) grade standard with a standard sulfur analysis.

7.4 *2,2,4-Trimethylpentane,* (*iso*octane), reagent grade, MW-114.23.

7.5 *Methylbenzene,* (Toluene), reagent grade, MW-92.14.

7.6 *Drift Correction Monitor(s), (Optional),* several different materials have been found to be suitable for use as drift correction monitors. Examples of sulfur containing materials that meet these requirements are renewable liquid petroleum materials, semipermanent solids, pressed powder pellets, metal alloys, or fused glass disks. Bracket the calibration range with concentrations of monitor samples. The counting rate for each monitor is determined during calibration (see 9.7) and again at the time of analysis (see 10.1). These counting rates are used to calculate a drift correction factor (see 11.1).

7.7 *Calibration Check Standards,* one or more liquid petroleum or product standards of known sulfur content (which do not represent one of the samples prepared in Section 9) are used to verify the accuracy of the calibration curve.

7.8 *Quality Control (QC) Sample,* one or more stable liquid petroleum or product samples, which are used to verify that the measurement system is in control. Preferably the QC sample(s) should be representative of the samples typically analyzed. In cases where volatility of the QC sample(s) may affect the sample integrity, precautions need to be taken to minimize or eliminate sample losses prior to analysis to ensure that a stable and representative sample can be taken and analyzed over the period of intended use. It is permissible to use calibration standards for this purpose. Since standard samples are discarded after each determination, it is recommended that a lower cost material be used for daily calibration checks.

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practice D4057, D4177, D5842, or D5854, where appropriate.

8.2 Clean and dry reusable cells before use. Disposable sample cups are not to be reused. Window material usually is 8 μm polyester, 8 μm 8 μm polycarbonate, or 6 μm 6 μm polypropylene film. Renewal of the window of the sample cup is essential for the measurement of each sample. Avoid touching the inside of the sample cup, the portion of the window film in the cup, or 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 number of sulfur X-rays transmitted. Therefore, the importance of the film's tautness and cleanliness cannot be over stressed. Recalibrate the analyzer when you change the type or thickness of the window film.

8.3 Polyester films often contain impurities that may affect the measurement of low levels of sulfur and may vary from lot to lot. Therefore, if using a polyester film, check the calibration with the start of each new roll.

8.4 X-ray films may vary in thickness from batch to batch. Check the calibration when starting a new roll of any film.

8.5 Samples of high aromatic count 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 that can adversely affect the results obtained by this test method.

9. Calibration

9.1 Prepare calibration standards by the careful preparation by mass of a 50:50 mixture (based on sulfur content) of the certified thiophene and 2-methylthiophene or *n*-butyl sulfide with ~~2020 %~~20 % to 80 % mixture of toluene–*iso*octane or other suitable base material (see 5.1). Exact standards of the nominal sulfur concentrations listed in Table 1 are recommended.

9.2 *Preparation of Stock Standard:* Weigh approximately ~~0.657 g~~ 0.657 g of thiophene and ~~0.767 g~~ 0.767 g of 2-methylthiophene and record the masses to the nearest ~~0.1 mg,~~ 0.1 mg, or weigh 2.286 of *n*-butyl sulfide to the nearest 0.1 mg. Add the standard materials to a tared ~~100 mL~~ 100 mL volumetric flask. Add mixed solvent of 20 % toluene and 80 % *iso*octane (by volume) or other base material (see 5.1) to a net mass of ~~50.000~~50.000 g + ~~0.010 g.~~ 0.010 g. This stock standard contains approximately ~~10~~10 mg ~~mg/g~~/g sulfur. Correct the concentration by multiplying the measured masses by the sulfur equivalency in each of the standards, that is thiophene grams × 0.3803 × purity plus 2-methylthiophene grams × 0.3260 × purity (or *n*-butyl sulfide grams × 0.2191 × purity) = weight of sulfur in the standard solution. Divide this number by the total mass of the standards and base material added to them, multiply by 1000 mg/g and the result is the actual sulfur concentration in mg/g. This calculation is as follows:

$$S, \text{mg/g} = 1000 \times \frac{T \times 0.3803 \times P + M \times 0.3260 \times P}{F} \tag{1}$$

$$S, \text{mg/g} = 1000 \times \frac{DB \times 0.2187 \times P}{F} \tag{2}$$

~~*where:*~~
where:

S	=	final sulfur concentration,
T	=	mass of thiophene added,
M	=	mass of 2-methylthiophene added,
DB	=	mass of di-*n*-butyl sulfide added,
P	=	purity of the standard material, and
F	=	final mass of mixture.

9.3 *Preparation of Diluted Standard:* Dilute ~~25.0 mL~~25.0 mL of stock standard to ~~250 mL~~250 mL using the base material. This gives a standard of approximately ~~1000~~1000 mg ~~mg/kg.~~/kg. Divide the standard concentration calculated in ~~9.2~~9.2 by 10 to determine the actual concentration.

9.4 *Serial Dilutions:* Prepare serial dilutions of the diluted standard by diluting the following volumes to ~~100 mL~~100 mL using the base material:

0.5 mL	=	5 mg/kg
1.0 mL	=	10 mg/kg
5.0 mL	=	50 mg/kg
10.0 mL	=	100 mg/kg
25.0 mL	=	250 mg/kg
50.0 mL	=	500 mg/kg
Diluted Standard	=	1000 mg/kg

NOTE 2—Prepare calibrations up to ~~1000~~1000 mg ~~mg/kg~~/kg sulfur, and dilute samples with higher concentrations of sulfur to within this concentration range.

9.5 Establish calibration curve data by carefully measuring the net intensity of the emitted sulfur radiation from each of the standards by the procedure described in Sections 10 and 11.

9.6 Construct a calibration model by:

9.6.1 Using the software and algorithms supplied by the instrument manufacturer.

9.6.2 Fitting the data to an equation of the type:

$$S = aR + b \tag{3}$$

TABLE 1 Nominal Sulfur Standards

Range 1 Sulfur Concentration, mg/kg	Range 2 Sulfur Concentration, mg/kg
0	100
5	250
10	500
50	1000
100	—