Designation: D6334 – 12

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*

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 mg/kg. Therefore, the practical range for this test method is from 15 to 940 mg/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 to 940 mg/kg; however, below 15 mg/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.

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 System in Petroleum Products 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 is measured. The intensity of a corrected background, measured at a recommended wavelength of 5.190 Å, or if a rhodium tube is used, 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 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.

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[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.

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

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 mg/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 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 polycarbonate, or 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 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 of thiophene and 0.767 g of 2-methylthiophene and record the masses to the nearest 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 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 + 0.010 g. This stock standard contains approximately 10 mg/g sulfur.

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	—

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:

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

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

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 of stock standard to 250 mL using the base material. This gives a standard of approximately 1000 mg/kg. Divide the standard concentration calculated in 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 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 mg/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:

$$S = aR + b \quad (3)$$

where:

S = sulfur concentration, mg/kg,
R = net intensity for the sulfur radiation,
a = slope of the calibration curve, and
b = intercept of the calibration curve.

9.6.3 Plot corrected net intensity in counts per second (cps) versus sulfur concentration. Plot data in two ranges listed in Table 1.

9.7 During collection of calibration data, measure the intensity of the drift monitor standards. Use the intensities from these standards to correct for day to day instrument sensitivity. This value corresponds to *A* in Eq 5, Section 11. Many instrument manufacturers have built drift correction procedures into their software.

9.8 At the completion of the calibration, measure one or more independent calibration check standards to verify the accuracy of the calibration curve. These standards (see 7.7) are independent of the calibration set. The measured value shall agree with the standard value within ±2 % relative or 2 ppm, whichever is greater.

NOTE 3—NIST traceable gasoline standards are available at the 1, 10, 40, and 300 mg/kg levels. Other concentrations may be prepared by dilution of these standards with a solvent of similar matrix to the standards previously prepared.

NOTE 4—NIST has suggested a "designer" method for the preparation of NIST traceable fossil fuel standards with concentrations intermediate to SRM values for sulfur. Laboratories can mix and prepare standards for distillate fuels oils, residual fuel oil in almost any desired concentrations with uncertainties that are calculable and traceable to NIST-certified values. This method enables the SRM user to create a customized series of calibration and quality control test samples.[3]

NOTE 5—A DVD available from NIST includes the above cited paper plus subsequent papers dealing with this subject as well as programmable spreadsheet to calculate blend concentrations and uncertainties. Some of the subsequent papers discuss the actual procedure to use when mixing rather than the proof of concept given in the first paper.[4]

10. Procedure

10.1 Measure the intensity of the drift correction monitor(s) used in 9.7. The value determined corresponds to *B* in Eq 5, Section 11. This measurement may not be required on high stability instrumentation. Determine the value of *F*′ in Eq 6, Section 11 at regular intervals by measuring the peak and background count rates on the solvent blank. This measurement may not be needed on some instruments.

10.2 Place the sample in an appropriate cell using techniques consistent with good practice for the particular instrument being used. Although sulfur radiation will penetrate only a small distance into the sample, scatter from the sample cup and the sample may vary to such an extent that a specific amount or a minimum amount of sample shall be used. Generally, filling the cup to one-half capacity is sufficient.

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[3] Kelly. W.R., MacDonald, B. S., and Leigh, S. D., "A Method for the Preparation of NIST Traceable Fossil Fuel Standards with Concentrations Intermediate to SRM Values", J. ASTM International, 4(2), # 1100748, (2007).

[4] Kelly, W. R., MacDonald, B. S., Molloy, J. L., Leigh, S. D., and Rukhin, A. L., "A Method for the Preparation of NIST Traceable Fossil Fuel Standards with Concentrations Intermediate to SRM Values", NIST Special Publication 260-167[2010].

Once this amount is established for each instrument, this volume of sample is used for each measurement.

10.3 Place the sample in the X-ray beam, and allow the X-ray optical atmosphere to come to equilibrium.

10.4 Determine the intensity of the sulfur K_α radiation at 5.373 Å by making counting rate measurements at the precise angular settings for this wavelength.

NOTE 6—Take a sufficient number of counts to satisfy at least a 1.0 % expected coefficient of variation when practical. When sensitivity or concentration, or both, make it impractical to collect a sufficient number of counts to achieve a 1.0 % coefficient of variation, accepted techniques, which will allow the greatest statistical precision in the time allotted for each analysis, should be used. Calculate the coefficient of variation as follows:

$$\textit{Coefficient of variation, \%} = \left(100\sqrt{N_s + N_b}\right)/(N_s - N_b) \quad (4)$$

where:

N_s = gross number of counts collected at sulfur line, and

N_b = gross number of counts collected at background wavelength (on the base material) in the same time interval taken to collect N_s counts.

10.5 Measure background count-rate at a previously selected, fixed, angular setting, adjacent to the sulfur K_α peak.

NOTE 7—Suitability of any background setting will depend on the X-ray tube anode employed. A wavelength of 5.190 Å is recommended where chromium or scandium is used, whereas 5.437 Å has been found suitable for rhodium. Twenty peak and background angles for various crystals are listed in Table 2.

10.6 Calculate the corrected net counting rate using Eq 6 in Section 11.

10.7 If, from the measurements made in accordance with 10.3 and 10.4, the counting rate is higher than that of the highest point on the calibration curve, dilute the sample with base material until the sulfur count rate is within the limits of the calibration curve and repeat the procedure described in 10.2 – 10.6.

10.8 *Quality Control*— For the purpose of establishing the statistical control status of the testing process since the last valid calibration, QC samples prepared from material(s) selected and stored as described in 7.7 are regularly tested as if they were production samples. Results are recorded and analyzed by control charts (see Note 8) or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. An immediate investigation for root cause(s) is triggered by any 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 samples 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 sample that is regularly tested be representative of samples routinely analyzed. Further guidance on quality control charting can be found in Practices D6299 and D6792 and MNL 7.[5]

TABLE 2 20 Angles for Various Crystals

Crystal	2d (Å)	SKα (5.373 Å)	Background (5.190Å)	(5.437 Å)
NaCl (200)	5.640	144.56	133.89	149.12
EDDT (020)	8.806	75.18	72.12	76.24
ADP (101)	10.64	60.65	58.39	61.46
Pentaerythritol (002)	8.742	75.85	72.84	76.92
Quartz (101)	6.587	106.93	101.81	106.97
Ge (111)	6.532	110.68	105.23	112.68
Graphite (002)	6.706	106.45	101.38	106.29
Graphite (002) (PG)	6.74	105.72	100.71	107.55

NOTE 8—The precise test 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.

11. Calculation

11.1 Calculate the correction factor for changes in daily instrument sensitivity as follows:

$$F = A/B \quad (5)$$

where:

A = counting rate of the calibration check standard as determined at the time of calibration, and

B = counting rate of the calibration check standard as determined at the time of analysis.

NOTE 9—Inclusion of F in Eq 6 may not be necessary or desirable with some highly stable instrumentation.

11.2 Determine the corrected net counting rate as follows:

$$R = [(C_K / S_1) - (C_B F' / S_2)]F \quad (6)$$

where:

C_K = total counts collected at 5.373 Å,

C_B = total counts collected at sulfur background,

S_1 and S_2 = seconds required to collect C counts,

R = corrected net counting rate, and

F' = (counts/s at 5.373 Å)/(counts/s at background wavelength) on a blank sample containing no sulfur.

NOTE 10—The F' factor is optional and is offered for use in the case that it has a significant value.

11.3 Apply the corrected net counting rate to the appropriate calibration curve and read and report the sulfur concentration in mg/kg.

11.4 Calculate the concentration of sulfur in a diluted sample as follows:

$$S\ mg/kg = S_b \times [(W_s + W_o)/W_s) \quad (7)$$

where:

S_b = mg/kg sulfur in diluted blend,

W_s = mass of original sample, g, and

W_o = mass of diluent, g.

12. Reporting

12.1 For samples analyzed without dilution, report the result calculated in 11.3. For samples that have been diluted, report the result calculated in 11.4. Report this result as the sulfur concentration in mg/kg to the nearest whole number. State that the results were obtained according to Test Method D6334.

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[5] MNL 7, *Manual on Presentation of Data Control Chart Analysis*, Section 3, "Control Charts for Individuals," 6th ed., ASTM International, W. Conshohocken.

13. Precision and Bias

13.1 The precision of the test method as obtained by statistical examination of interlaboratory test results is as follows:

NOTE 11—The precision on methanol-containing samples has not been determined.

13.1.1 *Repeatability*— The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in Table 3 only in one case in twenty.

13.1.2 *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 in Table 4 only in one case in twenty.

13.2 *Bias*—Studies done in conjunction with the Western States Petroleum Association and the California Air Resources Board as well as ASTM Round Robins have shown that there is no significant bias between this test method and others available for the analysis of sulfur in light fuels at the appropriate levels. These include Test Methods D2622, D3210, D4045, D4294, and D5453

14. Keywords

14.1 analysis; gasoline; gasoline-oxygenate blend; petroleum; spectrometry; sulfur; X-ray

TABLE 3 Method Repeatability

Sulfur Content, mg/kg	Repeatability, mg/kg
15 to 940	$0.0400\times(X+97.29)$
15 mg/kg	4.5 mg/kg
50 mg/kg	5.9 mg/kg
100 mg/kg	7.9 mg/kg
500 mg/kg	23.9 mg/kg
940 mg/kg	41.5 mg/kg

TABLE 4 Method Reproducibility

Sulfur Content, mg /kg	Reproducibility, mg/kg
15 to 940	0.1182×(X+54.69)
15 mg/kg	8.2 mg/kg
50 mg/kg	12.4 mg/kg
100 mg/kg	18.3 mg/kg
500 mg/kg	65.6 mg/kg
940 mg/kg	117.6 mg/kg

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D6334–07) that may impact the use of this standard.

(1) Added more information on preparing of NIST traceable standards to Note 3.

(2) Added a Footnote 3 to reference the NIST citation.

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