



# Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 2622; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope\*

1.1 This test method covers the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquefiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, M-85 and M-100.

1.2 Interlaboratory studies on precision covered a variety of materials with sulfur concentrations ranging from approximately 3 mg/kg to 5.3 mass %. For a subset of these samples, with sulfur concentrations below 60 mg/kg, the repeatability standard deviation ( $S_r$ ) was 1.5 mg/kg. An estimate of the limit of detection is  $3 \times S_r$ , and an estimate of the limit of quantitation<sup>2</sup> is  $10 \times S_r$ . However, because instrumentation covered by this test method can vary in sensitivity, the applicability of the test method at sulfur concentrations below approximately 20 mg/kg must be determined on an individual basis.

1.3 Samples containing more than 5.0 mass % sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method.

1.4 Volatile samples (such as high vapor pressure gasolines or light hydrocarbons) may not meet the stated precision because of selective loss of light materials during the analysis.

1.5 A fundamental assumption in this test method is that the standard and sample matrix are well matched. Matrix mismatch can be caused by C/H ratio differences between samples and standards (see Tables 1 and 2) or by the presence of other heteroatoms (see Table 3).

1.6 The values stated in either SI units or angstrom units are to be regarded as standard.

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 appro-*

TABLE 1 Comparison of NIST and ASTM Interlaboratory Study (RR) Results

NIST SRM	Sulfur, mass %, NIST	Sulfur, mass %, ASTM RR Average	C/H mass ratio	Apparent Bias, % Sulfur	Relative Bias, %	Significant
1616a	0.0146	0.0148	5.205	0.0002	1.37	No
1617a	0.1731	0.1776	5.205	0.0045	2.60	Yes
2724a	0.0430	0.0417	5.986	-0.0013	-3.02	Yes
1623c	0.3806	0.3661	7.504	-0.0145	-3.81	Yes
2717	3.0220	2.948	8.229	-0.0736	-2.44	Yes
1621e	0.948	0.8973	8.553	-0.0507	-5.35	Yes
1624c		0.3918	6.511			
2723		0.0299	5.937			

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

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4294 Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy<sup>3</sup>

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy<sup>3</sup>

E 29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>4</sup>

## 3. Summary of Test Method

3.1 The sample is placed in the X-ray beam, and the peak intensity of the sulfur  $K\alpha$  line at 5.373 Å is measured. The background intensity, measured at a recommended wavelength of 5.190 Å (5.437 Å for a Rh target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain

<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> *Analytical Chemistry*, Vol 55, 1983, pp. 2210-2218.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>4</sup> *Annual Index of ASTM Standards*, Vol 14.02.

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

**TABLE 2 Comparison of NIST and ASTM Interlaboratory Study (RR) Corrected Results, Mass % Sulfur**

NOTE—The correction factors were calculated from data determined with XRF-11.<sup>7</sup> Application of these correction factors requires separate determination of the C/H mass ratio. The significance was determined based on a *t* test using a function of the NIST uncertainty at 1 sigma and the round robin reproducibility standard deviation. The correction formula, which is applicable when the base material used for the calibration standards is white oil, is:

$$S_{\text{corrected}} = S_{\text{uncorrected}} / (1.086 - 0.01511 \times C/H)$$

where:

*C/H* = mass ratio of carbon to hydrogen for the sample.

SRM	RR ID	NIST	RR Corrected	Apparent Bias	Relative Bias, %	Significant
1616a	K2	0.0146	0.0147	0.0001	0.68	No
1617a	K1	0.1731	0.1763	0.0032	1.85	No
2724a	D2	0.0430	0.0419	-0.0011	-2.56	No
1623c	R1	0.3806	0.3763	-0.0043	-1.13	No
2717	R4	3.0220	3.065	0.0430	1.42	No
1621e	R3	0.948	0.9382	-0.0098	-1.03	No
1624c	D3		0.397			
2723	D4		0.0300			

**TABLE 3 Concentration of Interfering Elements**

Element	Mass % Tolerated
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Ethanol (Note 14)	8.6
Methanol (Note 14)	6

the concentration of sulfur in mass %. (**Warning**—Exposure to excessive quantities of X-radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their 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 rapid and precise measurement of total sulfur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1 to 2 min per sample.

4.2 The quality of many petroleum products 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 some fuels.

4.3 This test method provides a means of determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

4.4 When this test method is applied to petroleum materials with matrices significantly different from the white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting results.

NOTE 1—Compared to other test methods for sulfur determination, Test Method D 2622 has high throughput, minimal sample preparation, and excellent precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified for Test Method D 2622 tends to be more expensive than that required for alternative test methods, such as Test Method D 4294. Consult the Index to ASTM Standards<sup>5</sup> for alternative test methods.

#### 5. Interferences

5.1 When the elemental composition (excluding sulfur) of samples differs significantly from the standards, errors in the sulfur determination can result. For example, differences in the carbon-hydrogen ratio of sample and calibration standards introduce errors in the determination. Some other interferences and action levels are listed in Table 3.

5.2 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. They have a high oxygen content leading to significant absorption of sulfur K $\alpha$  radiation. Such fuels can, however, be analyzed using this test method provided either that correction factors are applied to the results (when calibrating with white oils) or that the calibration standards are prepared to match the matrix of the sample.

5.3 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 can be analyzed with standards made from base materials that are of the same or similar composition. Thus a gasoline may be simulated by mixing *isooctane* and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

5.4 Test Method D 4927 is the recommended test method for determination of sulfur in lubricating oils and lubricating oil additives because Test Methods D 4927 implements inter-element correction factors.

#### 6. Apparatus

6.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF)*, equipped for X-ray detection in the 5.37 Å range. For optimum sensitivity to sulfur, the instrument should be equipped 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 K $\alpha$  X-rays within the angular range of the spectrometer employed. Pentaerythritol and germanium are popular although other materials, such as EDDT, ADP, graphite, and quartz can be used.

6.1.5 *X-ray Tube*, capable of exciting sulfur K $\alpha$  radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

#### 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 00.01.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>6</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.

7.2 *Di-n-butyl Sulfide*, a high-purity standard with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (see 9.1).

NOTE 2—It is essential to know the concentration of sulfur in the di-n-butyl sulfide, not the purity, since impurities may also be sulfur containing compounds.

7.3 *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 have been found to be suitable include a renewable liquid petroleum material, a semipermanent solid, a pressed powder sample, a metal alloy, or a fused glass disk. The monitor's count rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The count rate for the monitor sample is determined during calibration (see 9.4) and again at the time of analysis (see 10.1). These counting rates are used to calculate a drift correction factor (see 11.1).

7.3.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

NOTE 3—Calibration standards may be used for this purpose. Because it is desirable to discard standards after each determination, a lower cost material is suggested for daily use.

7.4 *White Oil*, containing less than 2 mg/kg sulfur or other suitable base material containing less than 2 mg/kg sulfur. When low level (<200 mg/kg) measurements are anticipated, then the sulfur content, if any, of the base material needs to be included in the calculation of calibration standard concentration (see 9.1).

7.5 *X-ray Transparent Film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent can be used. Films can include polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

7.6 *Helium Gas*, minimum purity 99.9 %.

7.7 *Counting Gas*, for instruments equipped with flow proportional counters.

7.8 *Sample Cells*, compatible with the sample and the geometry requirements of the spectrometer. Disposable cells are preferred.

<sup>6</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.

**TABLE 4 Sulfur Standards**

Sulfur Concentration, mass %	Sulfur Concentration, mass %	Sulfur Concentration, mass %
0.0000 <sup>A</sup>	0.100	1.0
0.001	0.250	2.0
0.010	0.500	3.0
0.025		4.0
0.050		5.0
0.075		

<sup>A</sup> Base material.

7.9 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known sulfur content and not used in the generation of the calibration curve. The check samples shall be used to determine the accuracy of the initial calibration (see 9.5).

7.10 *Quality Control Samples*, stable petroleum or product samples representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (Section 13).

NOTE 4—Verification of system control through the use of QC samples and control charting is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

NOTE 5—Suitable QC samples can often be prepared by combining retains of typical samples.

## 8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practices D 4057 or D 4177 when applicable.

8.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, 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 intensity of the sulfur X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer may need recalibration if the type or thickness of the window film is changed. After the sample cell is filled, a small vent hole is provided.

8.3 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in polyester films and may vary from lot to lot. Therefore, the calibration shall be checked after starting each new roll or batch of film.

## 9. Calibration

9.1 Prepare calibration standards by careful mass dilution of the certified di-n-butyl sulfide with white oil or other suitable base material (see 5.3). The standards, with accurately known sulfur concentrations, shall approximate the nominal sulfur concentrations listed in Table 4 for the sulfur concentration ranges of interest. Take into account any sulfur in the base material when calculating the concentration of standards below 0.02 mass %.

NOTE 6—If desired, additional standards can be analyzed with concentrations between those listed in Table 4.

NOTE 7—Commercially available standards can be used provided their sulfur concentrations are accurately known and they approximate the nominal concentrations listed in Table 4.

9.2 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.

9.3 Construct a calibration model by either:

9.3.1 Using the software and algorithms supplied by instrument manufacturer,

9.3.2 Fitting the data to one of the following equations:

$$S \% = (D + ER)(1 + \alpha S) \text{ or} \quad (1)$$

$$S \% = aR + bR^2 + c \quad (2)$$

where:

$S$  = sulfur concentration in mass %,

$D$  = intercept of the calibration curve,

$E$  = slope of the calibration curve,

$R$  = net intensity for the sulfur radiation, and

$\alpha$  = correction factor for the effect of sulfur on the sulfur result and  $a$ ,  $b$ , and  $c$  are fitted constants.

NOTE 8—The factor  $\alpha$  in Eq 1 can be determined empirically or theoretically. Equipment vendors can often supply theoretical alphas.

9.3.3 Plotting corrected net intensity in counts per second versus sulfur concentration. Plot the data in several small ranges to minimize non-linear effects.

NOTE 9—Calibration plots are linear to a minimum concentration of 0.10 mass % sulfur. The analyst should choose the other plotting ranges to match the testing requirements. Deviation from linearity can increase as sulfur concentration increases.

9.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s) during the calibration procedure. The value determined corresponds to the factor  $A$  in Eq 4 in 11.1.

9.5 Immediately after completing the calibration, determine the sulfur concentration of one or more of the calibration check samples (7.9). The measured value shall be in the range defined by the certified concentration  $\pm$  the repeatability of this test method. When this is not the case, the calibration or calibration standards are suspect and corrective measures should be taken and the calibration rerun. The degree of matrix mismatch between samples and standards should also be considered when evaluating a calibration.

## 10. Procedure

10.1 When using drift correction monitors, prior to analyzing samples on a given day, analyze the drift correction monitor(s) and determine the counting rate, using the same material as used at the time of calibration. The value determined corresponds to the factor  $B$  in Eq 4 in 11.1.

10.1.1 When the factor  $F'$  is used in Eq 5 (Section 11), regularly analyze a blank sample to determine the factor  $F'$  in Eq 5. On a sulfur free sample, such as the base material, determine the count rate at the appropriate sulfur peak and background angles.

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

**TABLE 5 2 $\theta$  Angles for Various Crystals**

Crystal	2d (Å)	S K $\alpha$ (5.373 Å)	Background	
			(5.190 Å)	(5.437 Å)
NaCl (200)	5.6406	144.56	133.89	149.12
EDDT (020)	8.806	75.18	72.21	76.24
ADP (101)	10.640	60.65	58.39	61.46
Pentaerythritol (002)	8.742	75.85	72.84	76.92
Quartz (101)	6.5872	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

a small distance into the sample, scatter from the sample cell and the sample can vary. Laboratory personnel shall ensure that the sample cell is filled above a minimum depth, beyond which additional sample does not significantly affect the count rate. Generally, fill the sample cell to a minimum of three-fourths of the cell's capacity. Provide a small vent hole in the sample cell.

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

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

NOTE 10—It is suggested that a sufficient number of counts be taken to satisfy an expected coefficient of variation (% rsd) of 1.0 % or less 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. The coefficient of variation is calculated as follows:

$$\text{coefficient of variation, \%} = (100\sqrt{Ns + Nb}) / (Ns - Nb) \quad (3)$$

where

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

$N_b$  = number of counts collected at background wavelength 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 $\alpha$  peak.

NOTE 11—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, 2 $\theta$ , peak and background, angles for various crystals are listed in Table 5.

10.6 Determine the corrected counting rate and calculate the concentration of the sample as described in Section 11.

10.7 When, from the measurements made in accordance with 10.2-10.6, the counting rate is higher than that of the highest point of the calibration curve, dilute the sample with the base material used to prepare the calibration standards until the sulfur counting rate is within the limits of the calibration curve and repeat the procedure described in 10.3-10.6.

10.8 When the sample is known or believed to contain concentrations of interfering substances higher than those listed in Table 3, dilute the sample by mass with base material to concentrations below those listed.

NOTE 12—The concentrations of substances in Table 3 were determined by the calculation of the sum of the mass absorption coefficients times mass fraction of each element present. This calculation was made for



dilutions of representative samples containing approximately 3 % of interfering substances and 0.5 % sulfur.

10.8.1 The data collected showed reasonable X-ray results when the calculated sum of mass absorption coefficients times mass fractions for samples was not greater than 4 to 5 % above the sum of mass absorption coefficients times mass fractions for the calibration standards. Absorption interferences are additive, and they are only minimized by dilution, not completely eliminated. Table 3 is therefore to be used as a guide to concentrations that can be tolerated without significant error, not as an absolute quantity.

NOTE 13—The effect of matrix interferences can also be corrected on an empirical or theoretical basis. Except for gasohol, these corrections are not within the scope of this test method.

NOTE 14—The concentrations of ethanol and methanol were calculated using a theoretical mixture of hydrocarbons and di-butyl sulfide to which ethanol (or methanol) was added until the sum of the mass coefficients times mass fractions increased by 5 %. In other words, the amount of ethanol (or methanol) that caused a negative 5 % error in the sulfur measurement was calculated. This information is included in Table 3 to inform those who wish to use Test Method D 2622 for determining sulfur in gasohol (or M-85 and M-100) of the nature of the error involved.

10.8.2 Thoroughly mix the blend to ensure homogeneity, and transfer it to the instrument for measurement.

10.8.3 Determine the sulfur content of the blend in the normal manner as described in 10.2-10.6, and calculate the sulfur content of the original sample as described in Section 11.

## 11. Calculation

11.1 When using the drift correction monitor described in 7.3, calculate a correction factor for changes in daily instrument sensitivity as follows:

$$F = A/B \quad (4)$$

where:

$A$  = counting rate of the drift correction monitor as determined at the time of calibration (see 9.4), and

$B$  = counting rate of the drift correction monitor as determined at the time of analysis (see 10.1).

NOTE 15—The inclusion of this factor in Eq 5 may not be necessary or desirable with some instrumentation. In this case  $F$  is set to unity. It is recommended that the user chart the  $F$  factor and develop criteria for its application based on the stability of the instrumentation and standard SQC principles.

11.2 Determine the corrected net counting rate as follows:

$$R = [(C_K/S_1) - (C_B F'/S_2)]F \quad (5)$$

where:

$C_K$  = total counts collected at 5.373 Å,

$C_B$  = total counts collected at the background location chosen in 10.5,

$S_1$  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 chosen in 10.5 on a sample containing no sulfur.

11.2.1 The use of the factor  $F$  in Eq 5 is optional (Note 15).

11.2.2 The inclusion of the factor  $F'$  in Eq 5 is optional. In general it is needed for multichannel spectrometers, which use different spectrometer channels to measure peak and background intensities.

NOTE 16—Charting the  $F'$  factor, even if it is not used in Eq 5, will alert the user to changes in instrument operation due to contamination of system elements, such as crystals, collimators, and fixed windows.

11.3 Calculate the sulfur content of the sample by inserting the corrected net counting rate from Eq 5 in the chosen calibration model from Section 9. In many cases the instrument vendor will provide software or the required calculations.

11.4 Calculate the concentration of sulfur in samples, which have been diluted, as follows:

$$S, \text{ mass \%} = S_b \times [(W_s + W_o)/W_s] \quad (6)$$

where:

$S_b$  = mass % sulfur in diluted blend,

$W_s$  = mass of original sample, g, and

$W_o$  = mass of diluent, g.

The instrument vendor may have provided software to perform this calculation when required masses are input.

## 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 the result as the total sulfur content, mass %, to three significant figures for concentrations greater than 0.0100 %, to two significant figures between 0.0010 % and 0.0099 % and to one significant figure below 0.0010 %. For guidance in properly rounding significant figures, refer to the rounding method in Practice E 29. State that the results were obtained according to Test Method D 2622.

12.2 When analyzing M-85 or M-100 fuels with a calibration determined with white oil based standards, divide the result obtained in 11.3 as follows (Note 14):

$$S \text{ (in M-85), mass \%} = S, \text{ mass \%} / 0.59 \quad (7)$$

$$S \text{ (in M-100), mass \%} = S, \text{ mass \%} / 0.55 \quad (8)$$

This correction is not required if the standards are prepared in the same matrix as the samples, as described in 5.2.

NOTE 17—One laboratory compared the sulfur sensitivity for M-85 and M-100 fuels to the sulfur sensitivity for paraffin oils (Test Method D 2622) by theoretical calculation.<sup>7</sup> This laboratory and one other found excellent agreement between the theoretical and measured factors, therefore creating these correction factors.

## 13. Quality Control

13.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in this test method is in statistical control. One part of such a program might be the regular use and charting<sup>8</sup> of quality control samples (see 7.10). It is recommended that at least one

<sup>7</sup> XRF-11, Criss Software, Largo, MD.

<sup>8</sup> ASTM MNL 7, *Manual on Presentation of Data and Control Chart Analysis*, Section 3, Control Chart for Individuals, ASTM International, W. Conshohocken, PA.

type of quality control sample be analyzed that is representative of typical laboratory samples.

**14. Precision and Bias**

14.1 The precision of the test method was determined by statistical analysis of results obtained in three separate interlaboratory studies. The first interlaboratory study (Case I)<sup>9</sup> covered distillates, kerosines, residual oils, and crude oils. The second interlaboratory study (Case II)<sup>9</sup> covered a set of 21 gasolines. Neither M-85 nor M-100 was included. The third interlaboratory study (Case III)<sup>10</sup> involved 16 samples each of low level sulfur gasoline and diesel sample types analyzed by 28 laboratories. A practical limit of quantitation (PLOQ) of ≈20 μg/g S, was determined for the gasoline sample types. The precision for the diesel samples could not be calculated since the PLOQ of ≈14 μg/g S was above the average values determined for most of the samples analyzed in this study. The ranges of sulfur concentrations represented by the sample sets, together with the precisions, are listed in 14.1.1 and 14.1.2.

NOTE 18—The gasoline sulfur concentration range covered in the interlaboratory study associated with Case III falls within the expanded sulfur concentration range for gasoline determined in the Case II interlaboratory study. For gasoline concentrations determined between 0.0024 and 0.0080 mass %, it is recommended that the Case III precision values be applied.

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation 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:

Case	Range, Mass %	Repeatability
I	0.006–5.3	0.02651 X <sup>0.9</sup>
II	0.0003–0.093	0.00736 (X + 0.0002) <sup>0.4</sup>
III	0.0024–0.0080	0.02438 (X + 0.012469)

where: X is the sulfur concentration, mass %.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in

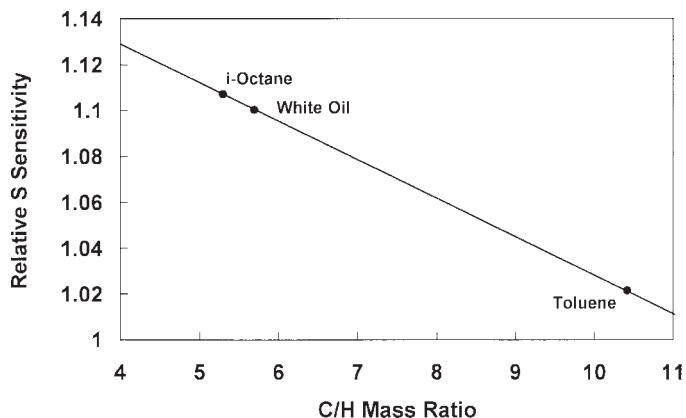


FIG. 1 Relative Sulfur Sensitivity

the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Case	Range, Mass %	Reproducibility
I	0.006–5.3	0.0913 X <sup>0.9</sup>
II	0.0003–0.093	0.0105 (X + 0.0002) <sup>0.4</sup>
III	0.0024–0.0080	0.04795 (X + 0.012469)

where: X is the sulfur concentration, mass %.

14.2 *Bias*—One interlaboratory study (Case I) included eight NIST reference materials. The certified sulfur value, interlaboratory round robin (RR) value, measured C/H, apparent bias, and relative bias are given in Table 1. Table 2 compares NIST value with sulfur concentrations corrected for C/H ratio. The white oil was assumed to have a C/H mass ratio of 5.698 (C<sub>22</sub>H<sub>46</sub>).

14.2.1 The variation in relative sulfur sensitivity as a function of C/H mass ratio is shown graphically in Fig. 1.

14.2.2 For Case III, based on the analysis of 3 NIST Standard Reference Materials (SRMs), there was no significant bias between the certified values and the results obtained in this interlaboratory study, although all three samples had means <PLOQ values determined for each sample type. The gasoline SRMs analyzed were SRM 2298 (4.7 μg/g S) and SRM 2299 (13.6 μg/g S). SRM 2723a (10 μg/g S) was analyzed with the diesel samples.<sup>10</sup>

**15. Keywords**

15.1 analysis; diesel; gasoline; jet fuel; kerosine; petroleum; spectrometry; sulfur; X-ray

<sup>9</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1428.

<sup>10</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1547.

## SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 2622-98) that may impact the use of this standard.

(1) Updated Section 14, Precision and Bias, to incorporate results obtained in a low level sulfur interlaboratory study.

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