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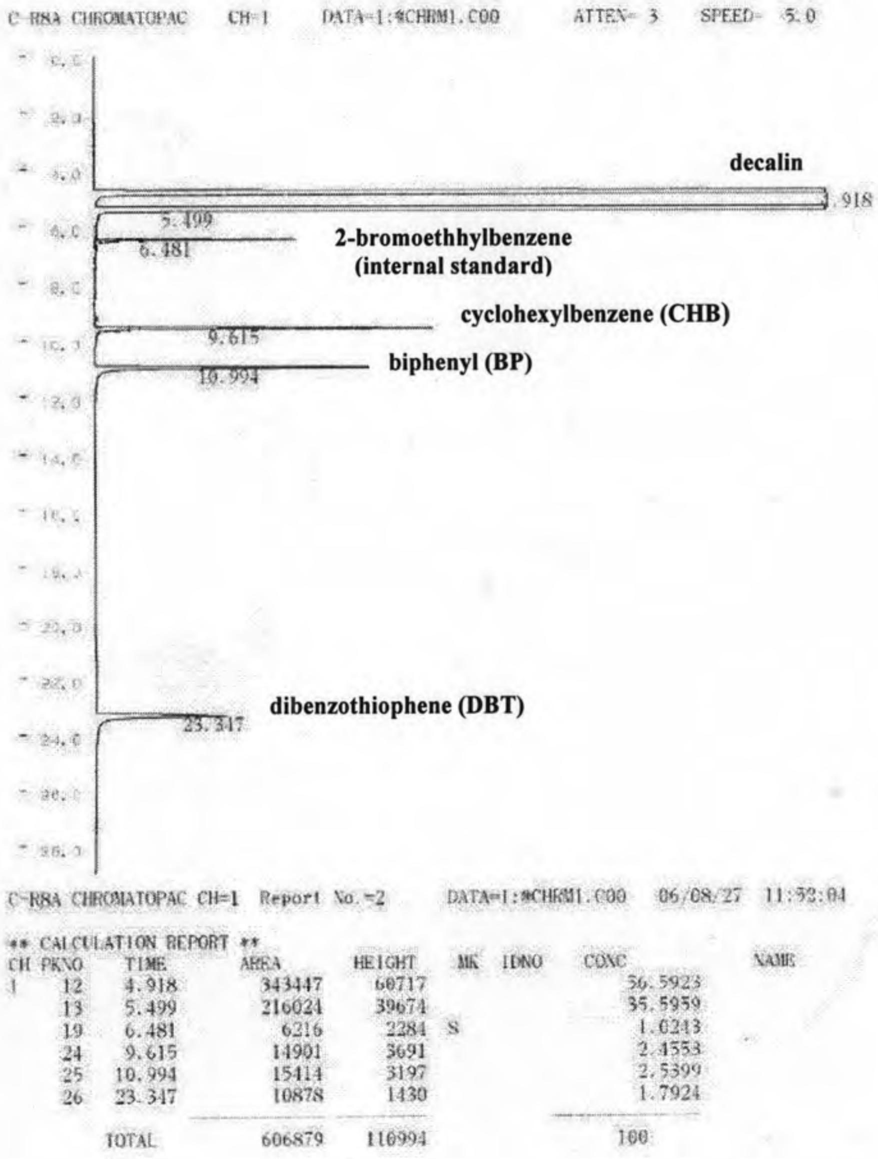
APPENDICES

APPENDIX A

Gas chromatography determined products of hydrodesulfurization of dibenzothiophene.

1. Hydrodesulfurization of dibenzothiophene

Cyclohexylbenzene (CHB) and biphenyl(BP) products were identified using standard addition method.



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** CALCULATION REPORT **
CH PKNO    TIME        AREA     HEIGHT   MK  IDNO    CONC          NAME
1    12    4.918     343447      60717                56.5923
     13    5.499     216024      39674                35.5959
     19    6.481       6216       2284   S             1.0243
     24    9.615      14901       3691                 2.4553
     25   10.994      15414       3197                 2.5399
     26   23.347      10878       1430                 1.7924
                    ----------  --------            ----------
          TOTAL      606879     110994                100
```

Figure A-1 Gas chromatography of liquid mixture for correction factor calculation.

Calculation of the correction factor

The correction factor was calculated based upon the results obtained from gas chromatography analysis (see also the experimental section). 2-bromoethylbenzene was use as internal standard.

A: exact amount of DBT prepared = 5.99×10^{-4} mol
B: exact amount of CHB prepared = 5.87×10^{-4} mol
C: exact amount of BP prepared = 7.19×10^{-4} mol
D: exact amount of internal standard = 7.32×10^{-4} mol
E: peak area of DBT prepared = 10878
F: peak area of CHB prepared = 14901
G: peak area of BP prepared = 15414
H: peak area of internal standard = 6216
I: total volume of the mixture = 5 mL

The calculation of the correction factor can be described as follows:

Correction factor of dibenzothiophene (DBT):

The amount of DBT from the reaction mixture

$= (D \times E/H) = J$
$= 7.32 \times 10^{-5} \times 10878/6216$
$= 1.28 \times 10^{-4}$

The amount of DBT in I mL (total volume of the mixture)

$= J \times I = K$
$= 1.28 \times 10^{-4} \times 5$
$= 6.40 \times 10^{-4}$

Thus, the correction factor of DBT can be calculated as:

$= A/K$
$= 5.99 \times 10^{-4} / 6.40 \times 10^{-4}$
$= 0.93$

Correction factor of cyclohexylbenzene (CHB):

The amount of CHB from the reaction mixture

$= (D \times F/H) \quad = L$

$= 7.32 \times 10^{-5} \times 14901/6216$

$= 1.75 \times 10^{-4}$

The amount of CHB in I mL (total volume of the mixture)

$= L \times I = M$

$= 1.75 \times 10^{-4} \times 5$

$= 8.77 \times 10^{-4}$

Thus, the correction factor of CHB can be calculated as:

$= B/M$

$= 5.87 \times 10^{-4} / 8.77 \times 10^{-4}$

$= 0.70$

Correction factor of biphenyl (BP):

The amount of BP from the reaction mixture

$= (D \times G/H) \quad = M$

$= 7.32 \times 10^{-5} \times 15414/6216$

$= 1.81 \times 10^{-4}$

The amount of BP in I mL (total volume of the mixture)

$= M \times I = N$

$= 1.81 \times 10^{-4} \times 5$

$= 9.07 \times 10^{-4}$

Thus, the correction factor of BP can be calculated as:

$= C/M$

$= 7.19 \times 10^{-4} / 9.07 \times 10^{-4}$

$= 0.79$

The correction factors of chemicals are listed as follows:

Dibenzothiophene (DBT) = 0.93
Cyclohexylbenzene (CHB) =0.70
Biphenyl (BP) = 0.79

2. Hydrodesulfurization of 4,6-dimethydibenzothiophene

GC-MS was used to detect the mass spectrum of each GC peak on GC chromatography that included substrated and products. Methylcyclohexyltoluene (MCHT) and dimethylbiphenyl (DMBP) were products of the reaction. All of mass spectra for hydrodesulfurization of 4,6-dimethyldibenzothiophene were shown as follows:

The substrate of hydrodesulfurization was 4,6-dimethyldibenzothiophene, which showed mass spectrum at m/z = 212

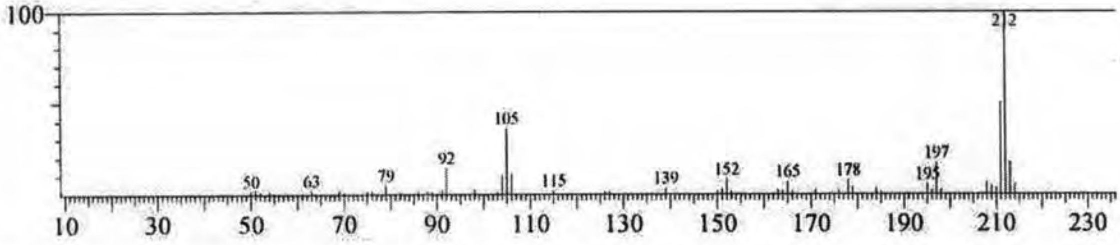


Figure A-2 Mass spectrum of 4,6-dimethyldibenzothiophene.

The hydrogenation product of hydrodesulfurization of 4,6-dimethyldibenzothiophene was methylcyclohexyltoluene (MCHT), which gave m/z = 188.

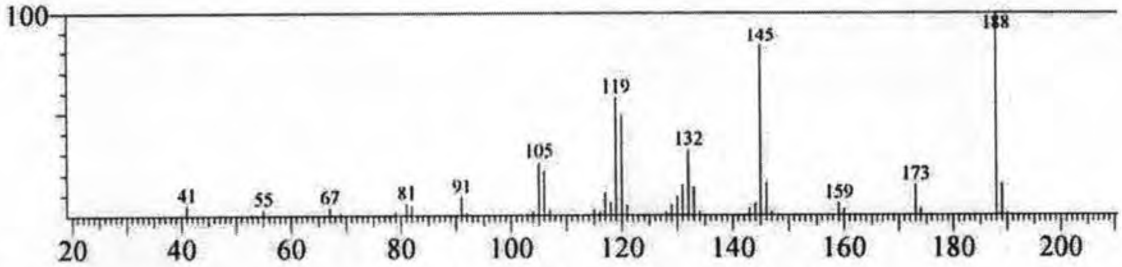


Figure A-3 Mass spectrum of methylcyclohexyltoluene (MCHT).

The hydrogenolysis product of hydrodesulfurization of 4,6-dimethyl-dibenzothiophene was dimethylbiphenyl (DMBP), which gave m/z = 182.

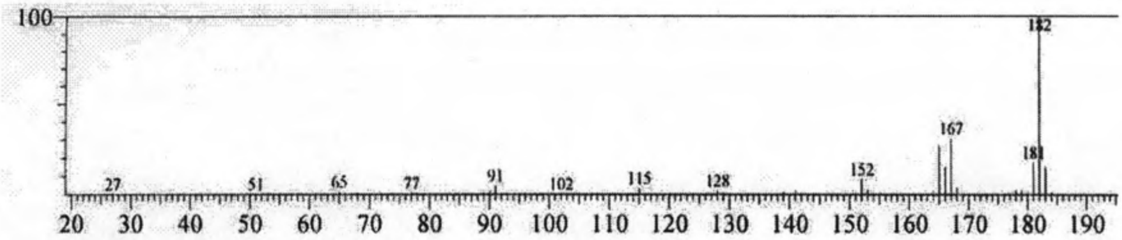
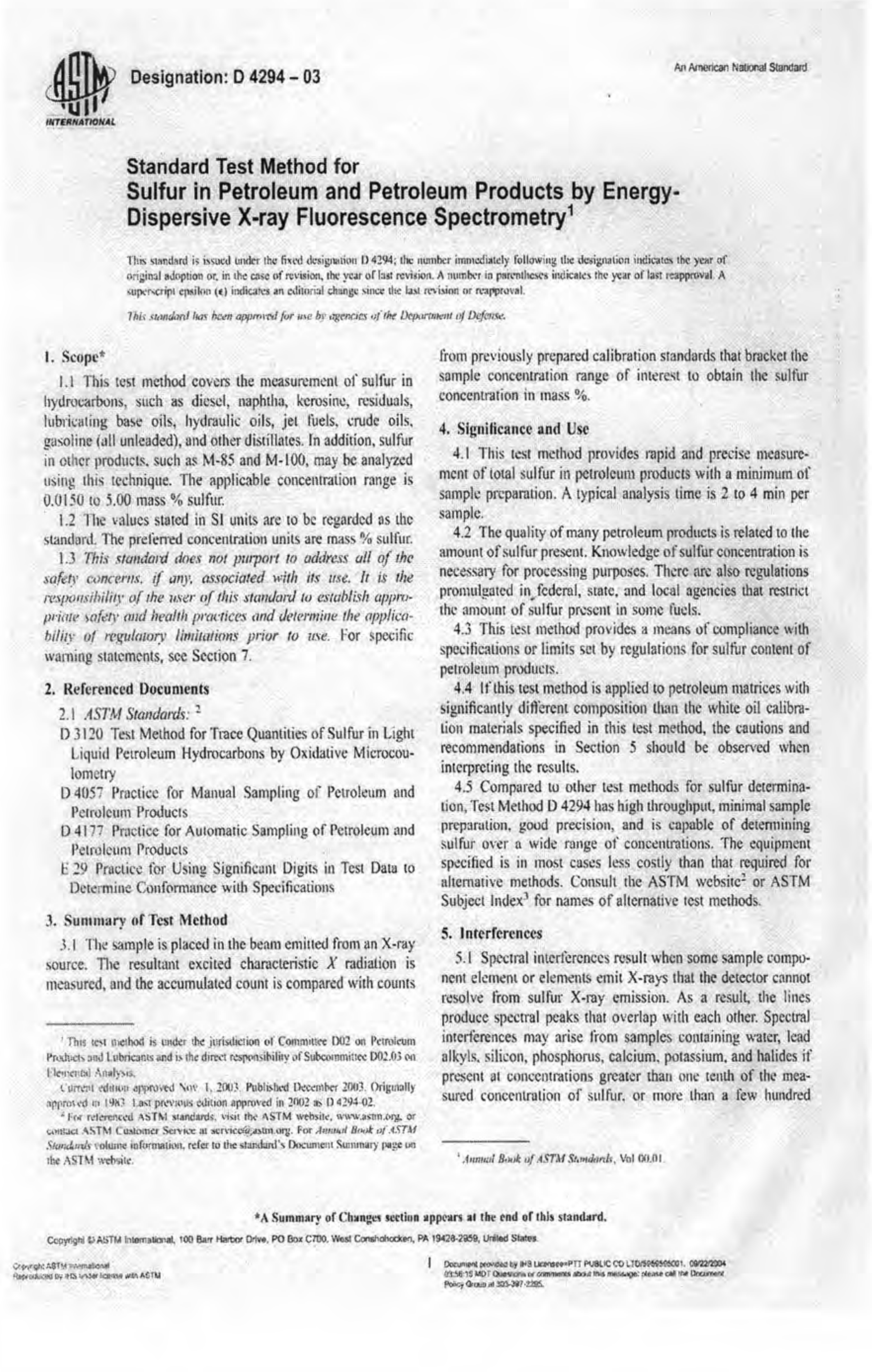


Figure A-4 Mass spectrum of dimethylbiphenyl (DMBP).

APPENDIX B



Designation: D 4294 – 03

An American National Standard

Standard Test Method for
Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 4294; 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.

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

1. Scope*

1.1 This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosine, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. In addition, sulfur in other products, such as M-85 and M-100, may be analyzed using this technique. The applicable concentration range is 0.0150 to 5.00 mass % sulfur.

1.2 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mass % 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.* For specific warning statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

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

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

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 that bracket the sample concentration range of interest to obtain the sulfur concentration in mass %.

4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation. A typical analysis time is 2 to 4 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 compliance with specifications or limits set by regulations for sulfur content of petroleum products.

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

4.5 Compared to other test methods for sulfur determination, Test Method D 4294 has high throughput, minimal sample preparation, good precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified is in most cases less costly than that required for alternative methods. Consult the ASTM website[2] or ASTM Subject Index[3] for names of alternative test methods.

5. Interferences

5.1 Spectral interferences result when some sample component element or elements emit X-rays that the detector cannot resolve from sulfur X-ray emission. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing water, lead alkyls, silicon, phosphorus, calcium, potassium, and halides if present at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred

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[1] This test method is under the jurisdiction of Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved Nov. 1, 2003. Published December 2003. Originally approved in 1983. Last previous edition approved in 2002 as D 4294-02.

[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.

[3] *Annual Book of ASTM Standards*, Vol 00.01.

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

milligrams/kilogram. Follow the manufacturer's operating-guide to compensate for the interferences.

5.2 Matrix effects are 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.

5.3 Both types of interferences are compensated for in contemporary instruments with the use of built-in software. It is recommended that these interferences be checked from time to time and that the software corrections offered by the manufacturer not be accepted at face value. Corrections should be verified for new formulations.

5.4 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. As such, they have a high oxygen content, hence, absorption of sulfur Kα radiation. Such fuels can, however, be analyzed using this test method provided that the calibration standards are prepared to match the matrix of the sample. There may be a loss of sensitivity and precision. The repeatability, reproducibility, and bias obtained in this test method did not include M-85 and M-100 samples.

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

NOTE 1—In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and immediately tested. The interference is greatest if the water creates a layer over the transparent film as it will attenuate the X-ray intensity for sulfur. One such method to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.

6. Apparatus

6.1 *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:

6.1.1 *Source of X-ray Excitation*, X-ray source with energy above 2.5 keV. (**Warning**—In addition to other precautions, if a radioactive source is used, it must be well shielded to international standard requirements and, therefore, not present any safety hazard. However, attention to the source is only to be carried out by a fully trained and competent person using the correct shielding techniques.)

NOTE 2—Operation of analyzers using X-ray tube sources is to be conducted in accordance with the manufacturer's safety instructions and local regulations.

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

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

6.1.4 *Filters*, or other means of discriminating between sulfur Kα radiation and other X-rays of higher energy.

6.1.5 Signal conditioning and data handling electronics that include the functions of X-ray intensity counting, a minimum of two energy regions (to correct for background X-rays), spectral overlap corrections, and conversion of sulfur X-ray intensity into percent sulfur concentration.

6.1.6 *Display or Printer*, that reads out in mass % sulfur.

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.[4] 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 (DBS)*, 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 (9.1.7). (**Warning**—Di-*n*-butyl sulfide is flammable and toxic.)

NOTE 3—It is essential to know the concentration of the sulfur in the di-*n*-butyl sulfide, not the purity, since impurities may also be sulfur containing compounds.

7.3 *Mineral Oil, White (MOW)*, ACS reagent grade or less than 2 mg/kg sulfur.

7.4 *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.

7.4.1 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 foil. Although polyimide foil 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.

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

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practice D 4057 or D 4177, where appropriate.

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[4] *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.

Samples should be analyzed immediately after pouring into a sample cell and allowing for the escape of the air bubbles caused by mixing.

8.2 If using reusable sample cells, clean and dry cells before use. Disposable sample cells are not to be reused. A new piece of X-ray film on a reused sample cell is required prior to analyzing the 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 film is changed.

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 verified after starting each new roll of film.

9. Calibration and Standardization

9.1 *Preparation of Calibration Standards*:

9.1.1 Although it is possible to make a single calibration to measure sulfur in a variety of matrices, it is strongly recommended that, whenever possible, the calibration is matrix specific, that is, a diesel calibration should be based on diesel standards. This is especially true for the analysis of sulfur at low levels. Hence, the matrix diluent should be as close to the form of the matrix being analyzed as possible. White mineral oil (see 7.3) is acceptable as an alternative matrix diluent.

9.1.2 Make primary standards independently at normal concentrations of 0.1 and 5 mass % sulfur and not by serial dilution from a single concentrate. The exact sulfur content in each standard is to be calculated to four decimal places.

9.1.3 Accurately weigh the nominal quantity of matrix diluent to the nearest 0.1 mg, as shown in Table 1, into a suitable, narrow-necked container and then accurately weigh in the nominal quantity of di-*n*-butyl sulfide. Mix thoroughly (a PTFE-coated magnetic stirrer is advisable) at room temperature.

9.1.4 Prepare calibration standards that will bracket the expected sulfur concentrations in samples, using the matrix diluent (9.1.1) and the primary standards (9.1.2) to prepare the blank and known standard concentrations, respectively, for each calibration range that is established. Consult the manufacturer's instructions for determining the number of standards and ranges to prepare. Table 2 provides an example of how two concentration ranges can be prepared by diluting each primary standard with the applicable matrix diluent.

TABLE 1 Nominal Composition of Primary Standards

Sulfur Content, mass %	Mass of Matrix Diluent, g	Mass of Di-*n*- Butyl Sulfide, g
5	48.6	14.4
0.1	43.6	0.200

TABLE 2 Nominal Calibration Standards

Range	1	2
Sulfur mass %	0.0020 to 0.1	0.1 to 5.0
Std 1	0.000	0.000
Std 2	0.0020	0.100
Std 3	0.0050	0.500
Std 4	0.0100	1.00
Std 5	0.0300	2.50
Std 6	0.0600	5.00
Std 7	0.100	

9.1.4.1 Standard 1 on Range 2 in Table 2 may not be required if the instrument is also calibrated on Range 1. Consult the manufacturer's calibration instructions for specific guidance.

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

9.1.6 If the matrix diluent being used for the preparation of standards contains sulfur, add this value to the calculated sulfur content of the prepared standards (consult your supplier for a certified sulfur concentration or test the mineral oil using Test Method D 3120 or any other equivalent low level sulfur analyzing method with an MDL no higher than 1 ppm).

9.1.7 Weigh the DBS and matrix diluent to the recommended mass to the nearest 0.1 mg. It is important that the actual mass is known; thus, the actual concentration of the prepared standards is calculated and entered into the instrument for calibration purposes. The concentration of sulfur can be calculated using the following equation:

$$S = [DBS \times S_{DBS}) + (MO \times S_{MO})]/(DBS + MO) \qquad (1)$$

where:

S = mass % sulfur of the prepared standards,
DBS = actual mass of DBS, g,
S_{DBS} = the mass % sulfur in DBS, typically 21.91 %,
MO = actual mass of mineral oil, g,
S_{MO} = mass % sulfur in the mineral oil.

9.2 *Certified Calibration Standards*—Calibration standards, which are certified by a national standards organization, may be used in place of some or all of the standards prescribed in 9.1 when of similar matrix to the sample of interest. Such standards include Standard Reference Materials (SRM) prepared and certified by the National Institute of Standards and Technology (NIST), that is, SRM 2724 for sulfur in diesel. The standards used must cover the nominal concentrations ranges identified in Table 2.

9.3 *Calibration Check Standards*—Several additional standards (calibration check standards) that were not used in generating the calibration curve can be used to check the validity of the calibration. Calibration check standards may be independently prepared according to 9.1, or certified standards according to 9.2. The concentration of the calibration check standards shall be near the expected concentration of the samples being analyzed.

9.4 *Quality Control Samples*—Stable petroleum or product samples (that is, quality control samples) representative of the samples of interest may be run on a regular basis to verify that the system is in statistical control (see Section 14).

9.5 *Storage of Standards and Quality Control Samples*—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 is observed, discard the standard.

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.

11. Procedure

11.1 Although X-radiation penetrates only a short distance into the sample, scatter from the sample cell and the sample may vary. Consequently, the analyst must 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-fourths the capacity of the sample cell will be sufficient. Prepare the sample cell by 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 for the appropriate range, 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. Obtain two readings on the standard using the recommended counting time for the instrument according to Table 3. With minimal delay, repeat the procedure using freshly prepared cells and fresh portions of the standard. Once all the standards have been analyzed, follow the manufacturer's instructions for generating the optimum calibration curve based on the net sulfur counts for each standard that has been analyzed four times. Immediately upon completion of the calibration, determine the sulfur concentration of one or more of the calibration check samples (see 9.3). The measured values should be within 3 % relative of the certified values. If 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.

11.3 *Analysis of Unknown Samples*—Fill the cell with the sample to be measured as described in 11.1. Before filling the cell, it may be necessary to heat viscous samples so that they are easy to pour into the cell. Ensure that no air bubbles are present between the cell window and the liquid sample. Measure each sample (see Table 3 for the recommended counting times for the specific concentration ranges). With minimal delay, repeat the measurement using a freshly prepared cell and a fresh portion of the sample. Obtain the average of the two readings for the sulfur content in the unknown sample. If the average reading is not within the concentration range for that calibration, repeat the sample measurement in duplicate using the range that brackets the sample average determined.

TABLE 3 Counting Times For Sulfur Content Analysis

Sulfur Content Range, mass %	Counting Time, s
0.000 to 0.100	200 to 300
0.100 to 5.00	100

12. Calculation

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

13. Report

13.1 The preferred concentration unit for reporting the total sulfur content is mass %, although results may also be reported in other SI units, such as mg/kg. Round results to three significant figures using Practice E 29, and state that the results were obtained according to Test Method D 4294.

14. Quality Control

14.1 The use of quality control programs, such as the one described in 14.1.1, can assist in maintaining statistical control of this test method.

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

14.1.1 For the purpose of establishing the statistical control status of the testing process since the last valid calibration, quality control samples prepared from material(s) selected and stored according to 9.3 and 9.4 are to be regularly tested as if they were unknown production samples. Results are recorded and immediately analyzed by control charts[5] or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. Any out of control data shall trigger investigation for root cause(s). The outcome of the investigation may result in instrument recalibration. Depending on the criticality of the quality being measured and the demonstrated stability of the testing process, the frequency of quality control sample testing can range from once each day the test apparatus is in use to twice per week. It is recommended that at least one type of quality control sample be analyzed that is representative of samples routinely analyzed (as in 9.4).

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

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

TABLE 4 Bias

NIST Standard	Sulfur mass %	Bias	Significant
SRM 1616a	0.0146	0.0009	No
SRM 2724a	0.0430	0.0008	No
SRM 1617a	0.173	0.0003	No
SRM 1623c	0.381	-0.0119	Yes
SRM 1621e	0.948	-0.0198	No
SRM 2717	3.02	0.0072	No

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

$$0.02894(X + 0.1691) \qquad (2)$$

where X is the sulfur concentration in mass %.

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 only in one case in twenty:

$$0.1215\,(X + 0.05555) \qquad (3)$$

where X is the sulfur concentration in mass %.

15.2 *Bias*—The interlaboratory study included eight NIST reference materials. The certified values and bias are given in Table 4.

16. Keywords

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

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 4294–02) that may impact the use of this standard.

(1) Updated Section 13, Report, to allow option of reporting results in units other than mass %.

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