Standard Test Method for
Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection[1]

This standard is issued under the fixed designation D 6920; 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 determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 to 400°C, with viscosities between approximately 0.2 and 10 cSt (mm/S) at room temperature. This test method is applicable to naphthas, distillates, and motor fuels such as gasolines, reformulated gasolines, gasohols, diesels and biodiesels containing approximately 1 to 100 mg/kg total sulfur in gasoline type products, and approximately 1 to 40 mg/kg sulfur in diesel type products.

1.2 The detector response for this technique within the scope of this test method is linear with sulfur concentration.

1.3 Based on interlaboratory study, the pooled limit of quantitation of this test method is 3 mg/kg for gasoline and <0.5 mg/kg for diesel samples.

1.4 This test method meets the U.S. EPA requirements for measuring sulfur in ultra low sulfur diesel fuels by the designated Test Method D 6428, as published in the U.S. Federal Register § 80.520(a)(1).

1.5 *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 hazard statements, see Sections 8 and 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[2]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[2]

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance[3]

D 6428 Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection[4]

2.2 *U. S. Federal Register:*

§ 80.520(a)(1) Vol. 68, No. 100[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *oxidative combustion, n*—process in which a sample undergoes combustion in an oxygen rich environment at temperatures greater than 650°C and compounds decompose to carbon dioxide, water, and elemental oxides.

3.1.2 *quartz combustion tube devitrification, n*—process in which samples containing alkali-metals (that is, elements from the Periodic Table Group IA, for example, sodium, potassium, etc.) or alkaline earth (that is, elements from the Periodic Table Group IIA, for example, calcium, magnesium, etc.) will cause quartz to devitrify (that is, become milky white and brittle) at elevated temperatures.

3.1.2.1 *Discussion*—It is suggested that the quartz combustion tube temperature be kept <1200°C in order to minimize or eliminate the possibility of quartz combustion tube devitrification from occurring.

4. Summary of Test Method

4.1 The sample is injected at a controlled rate into a stream of inert gas (helium or argon) or inert gas mixed with oxygen. The sample is vaporized and carried into a high temperature zone (>900°C) where oxygen is introduced. Sulfur compounds, present in the specimen are converted to sulfur dioxide (SO_2). Sulfur dioxide is reacted with the sensing electrode in a 3-electrode electrochemical cell. This reaction produces a measurable current that is directly proportional to the amount of sulfur in the original sample material. The reactions that occur are as follows:

Combustion: $\qquad R\text{-}S + O_2 \xrightarrow{>900°C} CO_2 + H_2O + SO_2 + \text{oxides}$

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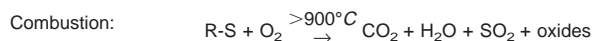
[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.
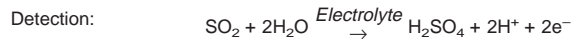
Current edition approved Sept. 10, 2003. Published September 2003.

[2] *Annual Book of ASTM Standards*, Vol 05.02.

[3] *Annual Book of ASTM Standards*, Vol 05.03.

[4] *Annual Book of ASTM Standards*, Vol 06.04.

[5] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

Detection: $SO_2 + 2H_2O \xrightarrow{Electrolyte} H_2SO_4 + 2H^+ + 2e^-$

TABLE 1 Dilutions for Working Standards

Desired µg S/mL	mL to pipet	From µg/mL	Dilution volume, mL
100.0	10.0	1000.0	100.0
10.0	10.0	100.0	100.0
1.0	10.0	10.0	100.0
0.5	5.0	10.0	100.0
0.05	5.0	1.0	100.0

5. Significance and Use

5.1 All sulfur present in petroleum products is converted to sulfur oxides upon combustion, which is a significant pollutant of the atmosphere. This test method can be used to monitor the total sulfur levels in these fuels.

NOTE 1—Virtually all sulfur compounds will be detected by this technique.

6. Interferences

6.1 Moisture produced during the combustion step can interfere if not removed prior to the detector.

6.2 Equivalent amounts of nitrogen in the sample may also interfere.

7. Apparatus

7.1 *Pyrolysis Furnace*, a furnace capable of maintaining a temperature sufficient to volatilize and combust all of the sample and oxidize the sulfur to SO_2. The furnace temperatures for petroleum substances shall be as recommended by the manufacturer.

7.2 *Quartz Combustion Tube*, capable of withstanding 900 to 1200°C. The inlet end of the tube holds a septum for syringe entry of the sample and has inlet fittings or side arms for the introduction of oxygen (O_2) and inert gas. The construction is such that the inert gas (or inert gas and oxygen mixture) sweeps the inlet zone transporting all of the volatilized sample into a high temperature oxidation zone. The oxidation section shall be large enough to ensure complete oxidation of the sample.

7.3 *Drier Tube*—The reaction products include water vapor that must be removed prior to measurement by the electrochemical detector. This can be accomplished with a magnesium perchlorate scrubber or a membrane drying tube (permeation drier), or both.

7.4 *Electrochemical Detector*, capable of measuring SO_2 in the combustion gas stream.

7.5 *Data Reduction System*, having the capability of measuring, amplifying, and integrating the current from the electrochemical detector. The amplified or integrated output signal shall be applied to a digital display or some other data reporting device.

7.6 *Microlitre Syringe*, of 5, 10, 25, 50, or 100 µL capacity capable of accurately delivering microlitre quantities is required. The needle should be long enough to reach the hottest portion of the inlet section of the furnace when injecting the sample.

7.7 *Recorder (Optional)*.

7.8 *Constant Rate Injector or Automatic Sampler System(s) (Optional)*, capable of delivering a sample at a precisely controlled rate.

8. Reagents

8.1 *Purity of Chemicals*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[6] where such specifications are available. 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.

8.2 *Magnesium Perchlorate,* $Mg(ClO_4)_2$—(**Warning—** Magnesium perchlorate is a strong oxidizer, and is an irritant) for drying products of the combustion (if a permeation drier is not used).

8.3 *Inert Gas*—Either argon (Ar) or helium (He) may be used. The purity should be no less than 99.99 mol %.

8.4 *Oxygen*—The purity should be no less than 99.99 mol % (**Warning—**Oxygen of this purity will vigorously accelerate combustion).

8.5 *Solvent*—The solvent chosen should be capable of dissolving the sulfur-containing compound used to prepare the standard and, if necessary, the samples. The solvent of choice should have a boiling point similar to the samples being analyzed and it should contain less sulfur than is in the lowest sample to be analyzed. Suggested possibilities include, but are not limited to: toluene, *iso*-octane, methanol, cetane, or other solvent similar to the compound present in the sample to be analyzed (**Warning—**Flammable solvents).

NOTE 2—A quick screening can be conducted by injecting the solvent and sample once or twice and comparing relative integral response.

8.6 *Sulfur Stock Solution,* 1000 µg S/mL—Prepare a stock solution by accurately weighing to the nearest 0.1 mg, 0.576 g of dibenzothiophene into a tared 100-mL volumetric flask. Dilute to volume with selected solvent. This stock may be further diluted to desired sulfur concentrations.

$$\mu g\ S/mL = \tag{1}$$
$$\frac{\text{exact weight of dibenzothiophene (mg)} \times 32.06 \times 1000\ (\mu g/mg)}{100\ mL \times 184.27}$$

NOTE 3—Dibenzothiophene may be used for calibration throughout the boiling range of this test method.

8.7 *Dibenzothiophene* ($C_{12}H_8S$), CAS 132650—(**Warning—**Dibenzothiophene is an irritant) molecular weight 184.27, purity >99.8 %.

8.8 *Sulfur Working Standard Solutions*, 0.5, 1.0, 10.0, and 100.0 µg S/mL—The working standards are prepared by accurately pipetting and diluting each to volume with solvent. To obtain the following concentrations 100.0, 10.0, 1.0, and 0.5 µg S/mL see Table 1.

NOTE 4—Working standards should be prepared fresh on a regular basis, depending upon frequency of use and age.

9. Hazards

9.1 Consult current OSHA regulations, suppliers' Materials Safety Data Sheets, and local regulations for all materials used in this test method.

9.2 High temperature is employed in this test method. Extra care must be exercised when using flammable materials near the high temperature furnace.

10. Sample Handling

10.1 Collect the samples in accordance with Practice D 4057 or Practice D 4177 as appropriate.

10.2 To preserve sample integrity (consistency) and prevent the loss of volatile components, which may be present in some samples, do not uncover samples any longer than necessary. Analyze samples as soon as possible after taking from the bulk supplies to prevent loss of sulfur or contamination.

10.3 Since this procedure is intended for trace levels, care must be taken to ensure the containers used for the sample, the specimen, and the working standards do not alter the sample result.

11. Preparation of Apparatus

11.1 Assemble the apparatus in accordance with manufacturer's instructions.

11.2 Adjust the gas flows and the combustion temperature to the desired operating conditions.

12. Calibration and Standardization

12.1 Prepare a series of calibration standards using a stock solution covering the range of operation as described in 8.6-8.8, and consisting of sulfur type and matrix similar to samples to be analyzed.

12.2 Volumetric measurement of the injected sample can be obtained by filling the syringe to the 80 % level, retracting the plunger so that the lower liquid meniscus falls on the 10 % scale mark, and recording volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 10 % scale mark, and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

12.3 Alternatively, the sample injection device may be weighed before and after injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ± 0.01 mg is used.

12.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at a uniform rate of 0.2 to 1.0 µL/s. Rate of injection is dependent on such factors as viscosity, sample type, and sulfur concentration. Each user must adopt a method whereby a consistent and uniform injection rate is ensured.

NOTE 5—For the most consistent injection rate and best analytical results, a constant rate injection system or automatic sampling system may be helpful. Consult manufacturer for recommendations.

NOTE 6—With direct injection below 2 mg/kg of sulfur, the needle-

TABLE 2 Concentrations for Suggested Sample Sizes

Sulfur, mg/kg	Sample Size, µL
1 and less	up to 20
10	up to 10
100	up to 5

septum blank may become increasingly important. Error due to this can be avoided by inserting the syringe needle into the hot inlet and allowing the needle-septum blank to dissipate before injecting the sample.

12.5 For the method blank, rinse the syringe thoroughly with the solvent blank, Then inject the same amount of solvent blank as utilized with standards and obtain the reading. Measure the blank a second time and average the results. The solvent blank should contain less than 0.05 mg/kg of sulfur.

12.6 If the system features an automatic calibration procedure, repeat the measurement of each calibration standard three times. All calibration points shall be used to construct a calibration curve. System performance shall be checked with a suitable calibration standard each day and when changing concentration ranges.

12.7 For those analyzers not equipped with an automatic calibration procedure, construct a standard curve as follows: Repeat the determination of each calibration standard and the blank three times to determine the average net response for each standard. Construct a curve plotting mg/kg of sulfur injected versus detector response (integration count). The response curve should be linear and shall be checked at least once per week.

13. Procedure

13.1 Sample sizes ranging from 3 to 40 µL are acceptable. It is advisable that the size of injected sample shall be similar to the size of injected standard.

13.2 Experience dictates the best sample size. Typical sample sizes are shown in Table 2.

13.3 Flush the microlitre syringe several times with the unknown sample. Determine the sample size as described in 13.2 and inject it at an even rate as described in 12.4.

14. Calculation

14.1 For analyzers equipped with an automatic calibration, calculate the sulfur content of the sample in parts per million by weight (mg/kg) by either of the following equations:

$$\text{Sulfur, mg/kg} = (I - B) \times K / (V \times D) \qquad (2)$$

$$\text{Sulfur, mg/kg} = (I - B) \times K / M \qquad (3)$$

where:
D = density of sample, g/mL,
K = dilution factor,
V = volume of sample, µL,
M = mass of sample, mg,
I = visual display reading of sample, and
B = average of visual display readings of blank.

14.2 For analyzers not equipped with automatic calibration, calculate the sulfur content of the sample in parts per million by weight (mg/kg) as follows:

$$\text{Sulfur, mg/kg} = I \times S \times K / (V \times D) \qquad (4)$$

TABLE 3 Repeatability[A, B]

	Gasoline	Diesel
Total S, mg/kg	3 to 100 $0.3395\ X^{0.7739}$	1 to 40 $0.1960\ (X + 0.61789)^{0.9022}$

[A] X = the average of two results in mg/kg.

[B] APS	$0.2395\ X^{0.5242}$	$0.002246\ (X + 160.55)$
Antek	$0.3302\ (X + 0.0001)^{0.8743}$	$0.1826\ (X + 1.3086)$

TABLE 4 Reproducibility[A, B]

	Gasoline	Diesel
Total S, mg/kg	3 to 100 $1.6384\ X^{0.7739}$	1 to 40 $1.3028\ (X + 0.61789)^{0.9022}$

[A] X = the average of two results in mg/kg.

[B] APS	$2.2331\ X^{0.5242}$	$0.6128\ (X + 3.6168)$
Antek	$1.2542\ (X + 0.0001)^{0.8743}$	$0.7642\ (X + 3.2734)$

where:
D = density of sample, g/mL,
S = slope of standard curve, mg S/count,
V = volume of sample, μL,
I = detector response, integration counts, and
K = dilution factor (when applicable).

15. Precision and Bias [7]

15.1 *Precision*—The precision of this test method as determined by the statistical examination of the interlaboratory test results is as follows. These data were produced from an interlaboratory study involving 16 laboratories that analyzed a total of 16 samples for gasoline and 16 samples for diesel. Two instruments were used in this interlaboratory study, one from APS Technologies and one from Antek Instruments. Since the results from these instruments were statistically different, precision statements are provided for each of the instruments.

15.1.1 *Repeatability*—The difference between successive results obtained on the same day 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.

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 values in Table 4 only in one case in twenty.

15.2 *Bias*—Based on the analysis of NIST Standard Reference Materials (SRM), there was no significant bias for the test method on either instrument between the results by this test method and the certified values by NIST for diesel SRM 2723a. For gasoline SRMs, there was no bias for SRM 2299 containing 13.6 mg/kg sulfur. However, for gasoline SRM 2298 containing 4.6 mg/kg total sulfur there was a bias of –0.78 mg/kg for the test method on both instruments.

16. Quality Control

16.1 Confirm the performance of the instrument or the test procedure by regularly analyzing QC samples.

16.1.1 When QC/QA protocols are already established in the testing facility, these may be used so long as they can properly confirm the reliability of this test method's test results.

16.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as a guide for acceptable QC/QA practices for this test method.

17. Keywords

17.1 diesel; diesel fuel; diesel fuel additives; electrochemical detection; gasoline; motor fuels; oxidative combustion; petroleum; sulfur

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[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1547.

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

X1.2 Prior to monitoring the measuring process, determine the average value and control limits for the QC sample (see Practice D 6299 and MNL 7[8]).

X1.3 Record QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process (see Practice D 6299 and MNL 7[8]). Investigate and out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements.

Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it has been demonstrated that the testing is under statistical control, The QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM test method precision to ensure data quality (see Practice D 6299 and MNL 7[8]).

Note X1.1—In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

X1.6 See Practice D 6299 and MNL 7[8] for further guidance on Test Method QC and Control Charting techniques.

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[8] *ASTM MNL7*, *Manual on Presentation of Data Control Chart Analysis*, 6th edition, Section 3, ASTM International, W. Conshohocken, PA 19428.