



Standard Test Method for Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection¹

This standard is issued under the fixed designation D6920; 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 (mm²/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 **D6428**, as published in the U.S. Federal Register § 80.520(a)(1).

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.

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. Referenced Documents

2.1 ASTM Standards:²

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6428 Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection (Withdrawn 2006)³

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

2.2 U. S. Federal Register:

§ 80.520(a)(1) Vol. 68, No. 100⁴

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

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 The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

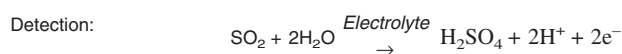
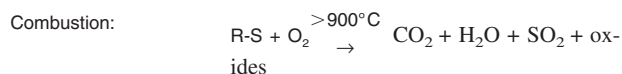
*A Summary of Changes section appears at the end of this standard

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 (SO₂). 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:



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 SO₂. 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 (O₂) 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.

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

7.4 *Electrochemical Detector*, capable of measuring SO₂ 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,⁵ 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(ClO₄)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

⁵ *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.