



Standard Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry¹

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1. Scope

1.1 This test method covers the determination of sulfur in petroleum products in the range from 0.02 to 10.00 mg/kg.

1.2 This test method may be extended to higher concentration by dilution.

1.3 This test method is applicable to liquids whose boiling points are between 30 and 371°C (86 and 700°F). Materials that can be analyzed include naphtha, kerosine, alcohol, steam condensate, various distillates, jet fuel, benzene, and toluene.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4.1 Certain specifications for the recorder (see 5.5) are excepted.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

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

3. Summary of Test Method

3.1 The sample is injected at a constant rate into a flowing hydrogen stream in a hydrogenolysis apparatus. The sample and hydrogen are pyrolyzed at a temperature of 1300°C, or above, to convert sulfur compounds to hydrogen sulfide (H_2S). Readout is by the rateometric detection of the colorimetric

reaction of H_2S with lead acetate. Condensable components are converted to gaseous products, such as methane, during hydrogenolysis.

4. Significance and Use

4.1 In many petroleum refining processes, low levels of sulfur in feed stocks may poison expensive catalysts. This test method can be used to monitor the amount of sulfur in such petroleum fractions.

4.2 This test method may also be used as a quality-control tool for sulfur determination in finished products.

5. Apparatus^{3,4}

5.1 *Pyrolysis Furnace*—A furnace that can provide an adjustable temperature from 900 to 1400°C in a 5-mm inside diameter or larger tube is required to pyrolyze the sample. The furnace entry temperature shall allow insertion of the hypodermic tip to a depth at which the temperature is 550°C to provide sample vaporization at the injection syringe tip. This temperature shall be above the boiling point of the sample and of the sulfur compounds in the sample (see Fig. 1). The pyrolyzer tube may be of quartz; however, the lifetime is limited above 1250°C. Ceramic may be used at any temperature.

5.2 *Rateometric H_2S Readout*—Hydrogenolysis products contain H_2S in proportion to sulfur in the sample. The H_2S is measured by measuring rate of change of reflectance caused by darkening when lead sulfide is formed. Rateometric electronics, adapted to provide a first derivative output, allows sufficient sensitivity to measure below 0.1 mg/L (see Fig. 2).

5.3 *Hypodermic Syringe*—A hypodermic having a needle long enough to reach the 550°C zone is required. A side port is convenient for vacuum filling and for flushing the syringe. A 100- μL syringe is satisfactory for injection rates down to 3 $\mu\text{L}/\text{min}$ and a 25- μL syringe for lower rates. (**Warning**—Exercise caution as hypodermics can cause accidental injury.)

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.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The apparatus described in 5.1–5.4 inclusive is similar in specification to the equipment available from Houston Atlas, Inc., 22001 North Park Dr., Kingswood, TX 77339-3804. For further information see Drushel, H. V., "Trace Sulfur Determination Petroleum Fractions," *Analytical Chemistry*, Vol 50, 1978, p. 76.

⁴ The sole source of supply of the apparatus known to the committee at this time is Houston Atlas, Inc. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.