



Designation: D4045 – 19

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

This standard is issued under the fixed designation D4045; 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 sulfur in petroleum products in the range from 0.02 mg/kg 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 °C and 371 °C (86 °F 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D1193 Specification for Reagent Water

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 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.

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 (H₂S). Readout is by the rateometric detection of the colorimetric reaction of H₂S 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

5.1 *Pyrolysis Furnace*—A furnace that can provide an adjustable temperature from 900 °C 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 H₂S Readout*—Hydrogenolysis products contain H₂S in proportion to sulfur in the sample. The H₂S 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

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