Designation: D6021 – 22

# Standard Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection[1]

This standard is issued under the fixed designation D6021; 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 a method suitable for measuring the total amount of hydrogen sulfide ($H_2S$) in heavy distillates, heavy distillate/residual fuel blends, or residual fuels as defined in Specification D396 Grade 4, 5 (Light), 5 (Heavy), and 6, when the $H_2S$ concentration in the fuel is in the 0.01 µg/g (ppmw) to 100 µg/g (ppmw) range.

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

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see 7.5, 8.2, 9.2, 10.1.4, and 11.1.

1.4 *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]

D396 Specification for Fuel Oils
D1193 Specification for Reagent Water
D2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)
D3609 Practice for Calibration Techniques Using Permeation Tubes
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4323 Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance
D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
D5705 Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils
D7621 Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.1.2 *heavy distillate, n*—a fuel produced from the distillation of crude oil which has a kinematic viscosity at 40 °C between 5.5 $mm^2/s$ and 24.0 $mm^2/s$, inclusive.

3.1.3 *heavy distillate/residual fuel blend, n*—a blend of heavy distillate and residual fuel oil having a viscosity at 40 °C between 5.5 $mm^2/s$ and 24.0 $mm^2/s$, inclusive.

3.1.4 *multiple headspace extraction, n*—a technique to determine the total concentration of a gas trapped in a liquid by analysis of successive gas extractions from the vapor space of a closed vessel containing a known amount of the sample.

3.1.5 *residual fuel oil, n*—any liquid or liquefiable petroleum product having a kinematic viscosity at 100 °C between 5.0 $mm^2/s$ and 50.0 $mm^2/s$, inclusive, burned for the generation of heat in a furnace or firebox or for the generation of power in an engine.

## 4. Summary of Test Method

4.1 A representative sample of residual fuel oil is obtained in sufficient quantity to completely fill the sample container.

[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 D02.14 on Stability, Cleanliness and Compatibility of Liquid Fuels.

Current edition approved April 1, 2022. Published May 2022. Originally approved in 1996. Last previous edition approved in 2017 as D6021 – 12 (2017). DOI: 10.1520/D6021-22.

[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.

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

The sample is taken to the laboratory preferably within one to 4 h, within 24 h maximum and placed in a refrigerator until the hydrogen sulfide analysis can be run. At that time, the sample is removed from the refrigerator and allowed to sit at ambient temperature until it flows freely.

4.2 A 0.05 g to 5.0 g test specimen (aliquot) is placed in a headspace vial and heated in an oven at 60 °C for more than five but less than 15 min. The headspace gas is sampled and injected into either of two types of apparatus capable of measuring the hydrogen sulfide concentration in the gaseous sample.[3] The two types of apparatus are those using the reaction of lead acetate with $H_2S$ (see Test Method D4084 or Test Method D4323) and those based on chemiluminescence (see Test Method D5504).

4.3 The remaining contents of the headspace vial are cooled for 5 min, then again heated in the oven. The headspace contents are again transferred to the hydrogen sulfide measuring instrument. The procedure is repeated for a third time. This is known as multiple headspace extraction procedure (MHE).

4.4 A linear plot of the natural logarithm of the area or peak height difference of the instrument reading against the number of injections is indicative of the correctness of the extraction procedure. The difference in area or peak height of the first two injections is used to calculate a total area or total peak height difference. The total area or total peak height difference is multiplied by a response factor determined from a direct gas calibration mixture and divided by the weight of the test specimen to determine the concentration of $H_2S$ in the residual fuel in µg/g (ppmw).

## 5. Significance and Use

5.1 Residual fuel oils can contain $H_2S$ in the liquid phase, and this can result in hazardous vapor phase levels of $H_2S$ in storage tank headspaces. The vapor phase levels can vary significantly according to the headspace volume, fuel temperature, and agitation. Measurement of $H_2S$ levels in the liquid phase provides a useful indication of the residual fuel oil's propensity to form high vapor phase levels, and lower levels in the residual fuel oil will directly reduce risk of $H_2S$ exposure. It is critical, however, that anyone involved in handling fuel oil, such as vessel owners and operators, continue to maintain appropriate safety practices designed to protect the crew, tank farm operators and others who can be exposed to $H_2S$.

5.1.1 The measurement of $H_2S$ in the liquid phase is appropriate for product quality control, while the measurement of $H_2S$ in the vapor phase is appropriate for health and safety purposes.

5.2 This test method was developed so refiners, fuel terminal operators and independent testing laboratory personnel can analytically measure the amount of $H_2S$ in the liquid phase of residual fuel oils.

NOTE 1—Test Method D6021 is one of three test methods for quantitatively measuring $H_2S$ in residual fuels:
1) Test Method D5705 is a simple field test method for determining $H_2S$ levels in the vapor phase.
2) Test Method D7621 is a rapid test method to determine $H_2S$ levels in the liquid phase.

5.3 $H_2S$ concentrations in the liquid and vapor phase attempt to reach equilibrium in a static system. However, this equilibrium and the related liquid and vapor concentrations can vary greatly depending on temperature and the chemical composition of the liquid phase. A concentration of 1 mg/kg (µg/g) (ppmw) of $H_2S$ in the liquid phase of a residual fuel can typically generate an actual gas concentration of >50 µL/L(ppmv) to 100 µL/L(ppmv) of $H_2S$ in the vapor phase, but the equilibrium of the vapor phase is disrupted the moment a vent or access point is opened to collect a sample.

NOTE 2—Because of the reactivity, absorptivity, and volatility of $H_2S$ any measurement method only provides an $H_2S$ concentration at a given moment in time.

## 6. Apparatus

6.1 A schematic of the headspace sampling system required for this analysis is shown in Fig. 1. It consists of:

6.1.1 *Sampling On/Off Valve,* with 3.2 mm o.d. connector (Valve 1).

6.1.2 *Six-Port External Loop Injection Valve,* made with 316 stainless steel, resistant to attack by sulfur compounds and having 3.2 mm o.d. tubing from each port (Valve 2).

6.1.3 *Polytetrafluoroethylene (PTFE) Sample Loops,* of 0.5 mL, 2.5 mL, and 10 mL are used for $H_2S$ content of 1 ppmw to 100 ppmw, 0.1 ppmw to 50 ppmw, and 0.01 ppmw to 10 ppmw, respectively.

6.1.4 *Pressure/Vacuum Gauge,* 6.3 mm diameter dial type with range of −100 kPag to 200 kPag, 5 kPa divisions from −100 kPag to 0 kPag and 10 kPa divisions from 0 kPag to 200 kPag.

6.1.5 *Vacuum On/Off Valve,* 3.2 mm o.d. connector (Valve 3).

6.1.6 *Sulfur Selective Detector,* any $H_2S$ specific detector capable of measuring $H_2S$ in the gas from 1 ppmv to 10 000 ppmv with a repeatability of ±2 % of full scale.

NOTE 3—Good performance has been obtained with a lead acetate tape detector and a sulfur chemiluminescence detector.

6.1.7 *Fluorocarbon Tubing,* 0.6 m long by 3.2 mm o.d. to connect components together.

6.2 *Vacuum pump,* 3.2 mm o.d. outlet, capable of achieving a 0.2 kPa vacuum and with a capacity of 100 mL/min.

6.3 *Headspace Oven,* capable of operating at 60 °C ± 0.5 °C with internal dimensions of 30 cm by 30 cm by 30 cm. An optional vent line is recommended in case a vial leaks.

6.4 *Analytical Balance,* sensitivity of 0.01 mg, maximum weight of 250 g.

6.5 *Data Handling System,* such as electronic integrator or any computer unit that can work with a chromatographic signal.

6.6 If sulfur specific detectors are used instead of an $H_2S$ analyzer then a chromatographic system equipped with a

[3] Determination of $H_2S$ in Residual Fuel Oils by Multiple Headspace Extraction: A Critical Evaluation of Available Analytical Methods. Silva, B., Carvajal, N., Gonzalez, A., Eastern Analytical Symposium, sponsored by American Chemical Society and the American Microchemical Society, November 16–20, 1992, Somerset, N.J.