



# Standard Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection<sup>1</sup>

This standard is issued under the fixed designation D 6021; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Warning notes were placed in the text editorially in May 2001.

## 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 D 396 Grade 4, 5 (Light), 5 (Heavy), and 6, when the  $H_2S$  concentration in the fuel is in the 0.01 to 100  $\mu\text{g/g}$  (ppmw) range.

1.2 The values stated in SI units are to be regarded as the 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 and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 5.1, 7.5, 8.2, 9.2, 10.1.4, and 11.1.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 396 Specification for Fuel Oils<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum (LP) Gases (Lead Acetate Method)<sup>2</sup>
- D 3609 Practice for Calibration Techniques Using Permeation Tubes<sup>4</sup>
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>5</sup>
- D 4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)<sup>6</sup>
- D 4323 Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance<sup>4</sup>

D 5504 Test Method for the Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence Detection<sup>6</sup>

D 5705 Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils<sup>7</sup>

## 3. Terminology

### 3.1 Definitions:

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

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

3.1.3 *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.

3.1.4 *residual fuel oil, n*—any liquid or liquefiable petroleum product having a kinematic viscosity at 100°C between 5.0 and 50.0  $\text{mm}^2/\text{s}$ , 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. 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 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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.E0.01 on Burner Fuels.

Current edition approved Dec. 10, 1996. Published February 1997.

<sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 11.03.

<sup>5</sup> Annual Book of ASTM Standards, Vol 05.02.

<sup>6</sup> Annual Book of ASTM Standards, Vol 05.06.

<sup>7</sup> Annual Book of ASTM Standards, Vol 05.03.

measuring the hydrogen sulfide concentration in the gaseous sample.<sup>8</sup> The two types of apparatus are those using the reaction of lead acetate with H<sub>2</sub>S (see Test Method D 4084 or Test Method D 4323) and those based on chemiluminescence (see Test Method D 5504).

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<sub>2</sub>S in the residual fuel in µg/g (ppmw).

## 5. Significance and Use

5.1 Excessive levels of hydrogen sulfide in the vapor phase above residual fuel oils in storage tanks may result in health hazard, OSHA limits violation, and public complaint. An additional concern is corrosion that can be caused by the presence of H<sub>2</sub>S during refining and other production activities. Control measures to maintain safe levels of H<sub>2</sub>S require a consistent method for the assessment of potentially hazardous levels of H<sub>2</sub>S in fuel oils. (**Warning**— H<sub>2</sub>S is a highly toxic substance. Extreme care must be used in the sampling and handling of samples that are suspected of containing high levels of H<sub>2</sub>S.)

5.2 A concentration of 0.1 µg/g (ppmw) of H<sub>2</sub>S in the liquid phase of a No. 4, 5, or 6 residual fuel oil can generate an actual gas concentration of 10 to 100 µL/L (ppmv) of H<sub>2</sub>S in the vapor phase; therefore an accurate analytical method is required to determine the total H<sub>2</sub>S concentration of these residual fuel oils. This test method was developed so refiners, fuel terminal operators, and independent testing laboratory personnel can analytically measure the amount of H<sub>2</sub>S in residual fuel oils.

5.3 Test Method D 5705 provides a simple and consistent field test method for the rapid determination of H<sub>2</sub>S in the residual fuel oils storage tank vapor phase. However, it does not necessarily simulate the vapor phase H<sub>2</sub>S concentration of a fuel storage tank nor does it provide any indication of the liquid phase H<sub>2</sub>S concentration. This test method provides a quantitative measure of a residual fuel oils liquid phase H<sub>2</sub>S concentration. It requires a laboratory and a skilled operator to perform the test but gives a more quantitative indication of potential H<sub>2</sub>S exposure than Test Method D 5705.

NOTE 1—Because of the reactivity, absorptivity, and volatility of H<sub>2</sub>S

<sup>8</sup> Determination of H<sub>2</sub>S 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.

any measurement method only provides an H<sub>2</sub>S concentration at a given moment in time.

## 6. Apparatus

6.1 A schematic of the headspace sampling system<sup>9</sup> 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, 2.5, and 10 mL are used for H<sub>2</sub>S content of 1 to 100, 0.1 to 50, and 0.01 to 10 ppmw, respectively.

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

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

6.1.6 *Sulfur Selective Detector*,<sup>10</sup> any H<sub>2</sub>S specific detector capable of measuring H<sub>2</sub>S in the gas from 1 to 10 000 ppmv with a repeatability of ±2 % of full scale.

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 ± 0.5°C with internal dimensions of 30 by 30 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<sub>2</sub>S analyzer then a chromatographic system equipped with a suitable column and oven is required to separate H<sub>2</sub>S from other sulfur compounds (see Test Method D 5504).

6.7 *Hand Crimper*, to crimp 20 mm diameter aluminum seals.

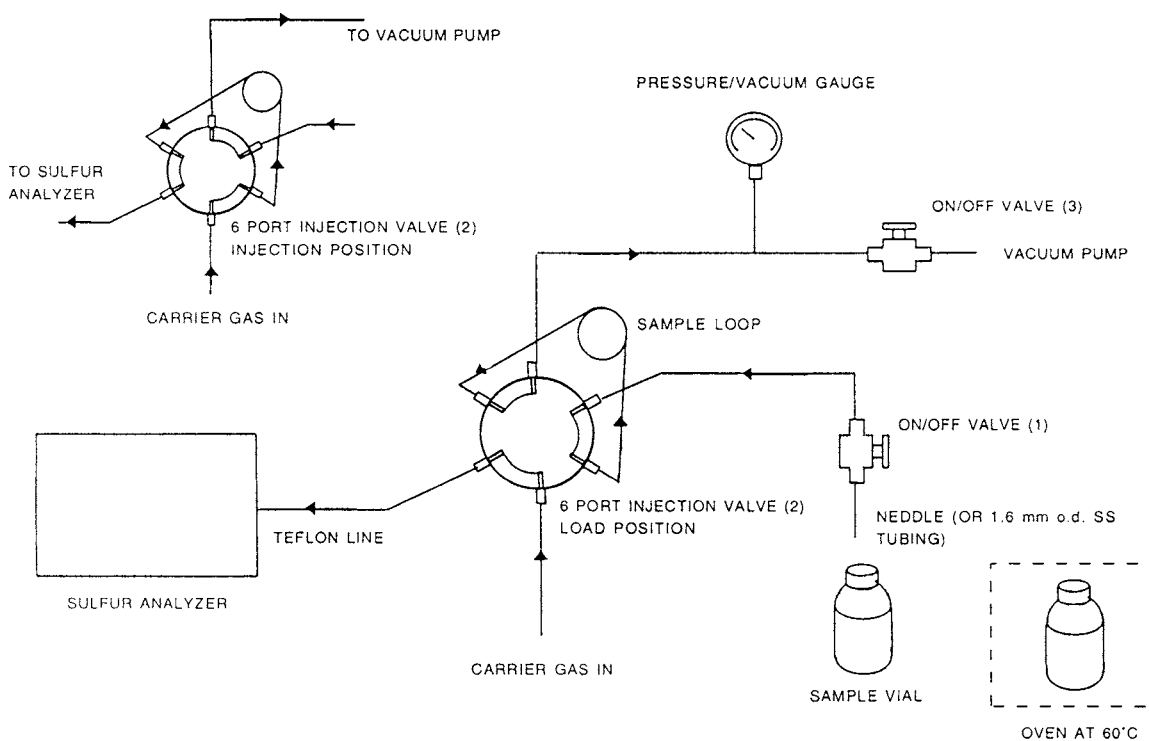
## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>11</sup> 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.

<sup>9</sup> The Model 695 may be a suitable apparatus. It is available from Houston Atlas Company.

<sup>10</sup> Good performance has been obtained with a lead acetate tape detector and a sulfur chemiluminescence detector.

<sup>11</sup> *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 *Analar 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.



DETAILED VIEW OF INJECTION SYSTEM  
**FIG. 1 Schematic of Headspace Analysis System**

7.2 *Acetic Acid Solution*—Add 50 mL of glacial acetic acid (CH<sub>3</sub>COOH) to a 1-L volumetric flask and then add Type II distilled water, as specified in Specification D 1193, to the 1-L mark to make a 5 % acetic acid solution.

7.3 *Aluminum Seals*, 20 mm diameter to seal septas to headspace sample vials.

7.4 *Headspace Vials*, 30-, 60-, or 120-mL borosilicate glass vials with 20 mm mouth diameter.

7.5 *Hydrogen Sulfide Gas Calibration Standard*, 1, 10, and 100 µL/L H<sub>2</sub>S in helium or nitrogen high pressure cylinders (obtain from gas supply company).<sup>12</sup> (**Warning**—Hydrogen sulfide is an extremely toxic gas.)

7.6 *Gases*, helium or nitrogen (H<sub>2</sub>S free), chemically pure grade or purified, as carrier gas to sweep sample into the detector.

7.7 *Lead Acetate Sensing Paper*—Prepare in accordance with Test Method D 2420, using appropriate size strips and drying in an H<sub>2</sub>S-free environment. Commercially available test paper has been found satisfactory.<sup>13</sup>

NOTE 2—Reagents from 7.2 and 7.7 are only needed if using an H<sub>2</sub>S lead acetate tape detector.

7.8 *Nuts and Ferrules*, Polytetrafluoroethylene (PTFE) and stainless steel (3.2 mm).

7.9 *Septas*, 20 mm diameter PTFE silicone/fluorocarbon to seal headspace sample vials.

7.10 *Side Port Needles*, for pressure lock, A-gas series (with reduction union 3.2 mm to 1.6 mm).

7.11 *Syringe Needles*, common dischargeable (dosing needle).

## 8. Sampling

8.1 Using a suitable H<sub>2</sub>S inert container of 250 to 500 mL, collect a representative sample by Practice D 4057. Suitable containers can be made of borosilicate glass or aluminum. If the sample temperature is below 60°C then a high density polyethylene bottle can be used.

8.2 Fill the container completely to the top so that there is no headspace in the container. Cap immediately. (**Warning**—At no time should the container temperature be allowed to exceed the temperature of the sample at the time.)

8.3 Take the samples to the laboratory preferably within one to four hours, within 24 h maximum. Place the samples in refrigerated storage. Store samples until analysis time but not more than three days.

## 9. Preparation of Apparatus

9.1 Assemble the headspace sampling system as shown in Fig. 1.

9.2 Because of the chemical activity and adsorptive properties of H<sub>2</sub>S, it is highly desirable to connect the components of the test apparatus together using minimum lengths of aluminum or fluorocarbon sample lines. (**Warning**—To preclude the formation of mercaptide gels and to reduce problems associated with corrosion do not use brass or copper flow system parts.)

<sup>12</sup> H<sub>2</sub>S gas calibration standard supplied by Airco has been found to be suitable (stable concentration over time).

<sup>13</sup> Lead acetate sensing paper is available from Houston Atlas.