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## Standard Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils<sup>1</sup>

This standard is issued under the fixed designation D5705; 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.

### 1. Scope\*

1.1 This test method covers the field determination of hydrogen sulfide ( $H_2S$ ) in the vapor phase (equilibrium headspace) of a residual fuel oil sample.

1.2 The test method is applicable to liquids with a viscosity range of 5.5 mm<sup>2</sup>/s at 40°C to 50 mm<sup>2</sup>/s at 100°C. The test method is applicable to fuels conforming to Specification D396 Grade Nos. 4, 5 (Heavy), and 6.

1.3 The applicable range is from 5 to 4000 parts per million by volume (ppm v/v) (micro mole/mole).

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

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:*<sup>2</sup>

D396 [Specification for Fuel Oils](#)

~~D4057 Practice for Manual Sampling of Petroleum and Petroleum Products~~ [Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D6021 Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection](#)

[D7621 Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction](#)

### 3. Terminology

3.1 *Definitions:*

3.1.1 *equilibrium headspace, n*—the vapor space above the liquid in which all vapor components are in equilibrium with the liquid components.

3.1.2 *residual fuel oil, n*—a fuel oil comprising a blend of viscous long, short, or cracked residue from a petroleum refining process and lighter distillates blended to a fuel oil viscosity specification.

3.1.2.1 *Discussion*—Under the conditions of this test (1:1 liquid/vapor ratio, temperature, and agitation) the  $H_2S$  in the vapor phase (sample's headspace) will be in equilibrium with the  $H_2S$  in the liquid phase.

### 4. Summary of Test Method

4.1 A 1-L  $H_2S$ -inert test container (glass test bottle) is filled to 50 volume % with fuel oil from a filled  $H_2S$ -inert container (glass sample bottle) just prior to testing. In the test container, the vapor space above the fuel oil sample is purged with nitrogen to displace air. The test container with sample is heated in an oven to 60°C, and agitated on an orbital shaker at 220 rpm for 3 min.

4.2 A length-of-stain detector tube and hand-operated pump are used to measure the  $H_2S$  concentration in the vapor phase of the test container. The length-of-stain detector tube should be close to but not in contact with the liquid surface.

### 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 a health hazard, OSHA limits violation, and public complaints about odors. Control measures to maintain safe levels of H~~

<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 on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels.

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<sup>2</sup> 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.

5.1 Residual fuel oils can contain H<sub>2</sub>S in the tank atmosphere for those working in the vicinity require a consistent method for the assessment of potentially hazardous levels of H<sub>2</sub>S in the liquid phase and this can result in hazardous vapor phase levels of H<sub>2</sub>S in fuel oils (Warning—H<sub>2</sub>S in storage tank headspaces. The vapor phase levels can vary significantly according to the headspace volume, fuel temperature and agitation. Measurement of H<sub>2</sub>S is a highly toxic substance. Use extreme care in the sampling and handling of samples that are suspected of containing high levels of H<sub>2</sub>S 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<sub>2</sub>S.);

5.2 This test method has been developed to provide refineries, fuel terminals, and independent testing laboratories, which do not have access to analytical instruments such as a gas chromatograph, with a simple and consistent field test method for the rapid determination of H<sub>2</sub>S 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<sub>2</sub>S in the vapor phase of residual fuel oils. S.

5.1.1 The measurement of H<sub>2</sub>S in the liquid phase is appropriate for product quality control, while the measurement of H<sub>2</sub>S in the vapor phase is appropriate for health and safety purposes.

5.2 This test method was developed to provide refineries, fuel terminals and independent testing laboratories, which do not have access to analytical instruments such as a gas chromatograph, with a simple and consistent field test method for the rapid determination of H<sub>2</sub>S in the vapor phase above residual fuel oils.

NOTE 1—D5705 is one of three test methods for quantitatively measuring H<sub>2</sub>S in residual fuels:

1) Test Method D6021 is an analytical test method to determine H<sub>2</sub>S levels in the liquid phase.

2) Test Method D7621 is a rapid test method to determine H<sub>2</sub>S levels in the liquid phase.

NOTE 2—Because of the reactivity, absorptivity and volatility of H<sub>2</sub>S, any measurement method only provides an H<sub>2</sub>S concentration at a given moment in time.

5.3 This test method does not necessarily simulate the vapor phase H<sub>2</sub>S concentration of in a fuel storage tank. It does, however, provide a level of consistency so that the test result is only a function of the residual fuel oil sample and not the test method, operator, or location. No general correlation can be established between this field test and actual vapor phase concentrations of H<sub>2</sub>S in residual fuel oil storage or transports. However, a facility that produces fuel oil from the same crude source under essentially constant conditions might be able to develop a correlation for its individual case.

## 6. Interferences

6.1 Typically, sulfur dioxide and mercaptans may cause positive interferences. In some cases, nitrogen dioxide can cause a negative interference. Most detector tubes will have a *precleanse* layer designed to remove certain interferences up to some maximum interferant level. Consult the manufacturer's instructions for specific interference information.

## 7. Apparatus

7.1 *Shaker*, a bench-top orbital shaker and platform equipped with a four-prong clamp to hold 1-L Boston round-bottom glass bottles and capable of operation at 220 rpm.

7.2 *Timer*, capable of measuring from 1 s to 30 min at second intervals.

7.3 *Stopper with Temperature Measuring Device*, a No. 2 cork stopper with a temperature measuring devices inserted through it that is capable of accurately measuring the temperature of the sample at  $60 \pm 1^\circ\text{C}$  as required in the procedure and extending at least 25 mm into the residual fuel but no closer than 25 mm from the bottom of a test bottle (see Fig. 1(a)). A dial thermometer having a range of  $-18$  to  $82^\circ\text{C}$  and a 200-mm stem has been found suitable to use.

7.4 *Oven or Water Bath*, capable of heating the fuel oil samples to  $60 \pm 1^\circ\text{C}$ .

7.5 *Detector Tube Pump*, a hand-operated piston or bellows-type (Fig. 1(b)) pump with a capacity of  $100 \text{ cm}^3 \pm 5 \text{ cm}^3$  per stroke.<sup>3</sup> It must be specifically designed for use with detector tubes. (Warning—A detector tube and pump together form a unit and must be used as such. Each manufacturer calibrates detector tubes to match the flow characteristics of its specific pump. Crossing brands of pumps and tubes is not permitted, as considerable loss of system accuracy is likely to occur.)

## 8. Reagents and Materials

8.1 *Containers*—Both sample and test containers are composed of H<sub>2</sub>S-inert material such as 1-L size (clear Boston round-bottom) glass bottles with screw caps. The bottles are clean and dry. Mark test containers at the 50 % volume level by using a ruler. (Warning—Hydrogen sulfide reacts with metal surfaces and is easily oxidized, which depletes its concentration and gives false low test results. Containers such as epoxy-lacquered cans are suitable for sample collection. Alternative containers must give equivalent results to those obtained by using glass.)

8.2 *Length-of-Stain Detector Tube and Calibration Scale*, a sealed glass tube with breakoff tips sized to fit the tube holder of the detector tube pump. The reagent layer inside the tube, typically a silica gel substrate coated with the active chemicals, must be specific for hydrogen sulfide and must produce a distinct color change when exposed to a sample of gas containing hydrogen sulfide. Any substances known to interfere must be listed in the instructions accompanying the tubes. A calibration scale should be marked directly on the tube, or other markings that provide for easy interpretation (reading) of hydrogen sulfide content from a separate calibration scale should be supplied with the tubes. The calibration scale shall correlate H<sub>2</sub>S concentration to the length

<sup>3</sup> Direct Reading Colorimetric Indicator Tubes Manual, First Edition, American Industrial Hygiene Association, Akron, OH 44311, 1976.

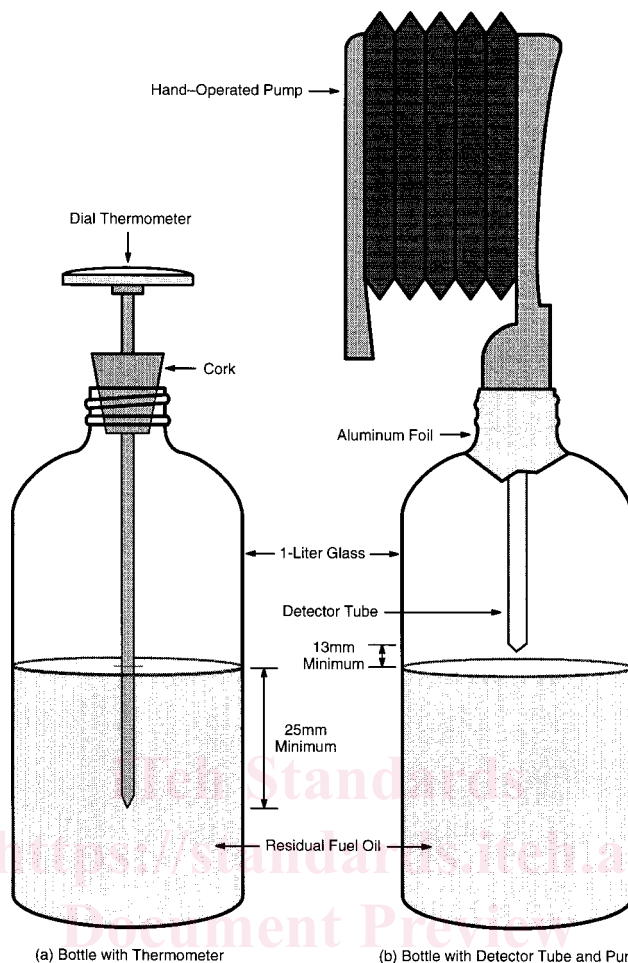


FIG. 1 Measurement of H<sub>2</sub>S in the Vapor Phase of Residual Fuel Oil

of the color stain. Annex A1 provides additional information. Shelf life of the detector tubes must be a minimum of two years from the date of manufacture, when stored according to the manufacturer's recommendations.

## 9. Sampling

9.1 The sampling of residual fuel oils is done according to Practice D4057 for the sampling of storage tanks, ships, or barges. Composite sampling or running samples can be taken; spot samples should be taken from the midpoint or below midpoint of the fuel oil in a storage tank by first sufficiently purging sample transfer lines and then taking single samples where each sample comprises one and only one test. (**Warning**—Samples taken for this test method shall be dedicated to a single H<sub>2</sub>S determination and not used for any other purpose, as any additional handling can lead to loss of H<sub>2</sub>S and thus low results.)

**NOTE 1—Liquid 3—Liquid** samples taken well into the fuel oil have had less H<sub>2</sub>S lost by degassing as compared with a fuel oil's surface. Samples taken from well within the fuel oil storage provide material that represents the greatest potential for H<sub>2</sub>S exposure during fuel oil movements. Hydrogen sulfide is lost by degassing (elevated temperature and mechanical agitation increases H<sub>2</sub>S degassing), oxidation, and absorption on water-wet surfaces.

9.2 Fill at least two 1-L size sample containers with fuel oil. Minimize the headspace of the sample container. Cap immediately and deliver to the testing facility. Test each sample within one to four hours from the time of sampling.

9.3 Sample integrity is extremely important; therefore, sample containers must be composed of inert materials, filled nearly completely with liquid, and capped tightly until tested. Sample handling should be minimized, and rapid testing for H<sub>2</sub>S is required. Samples can not be stored for later testing as H<sub>2</sub>S loss may occur by the mechanism described in **Note 1** and **Note 3**.

## 10. Procedure

10.1 Let each filled sample container sit at room temperature for at least 1 h, transfer part of its contents to an empty 1-L test bottle such that it is filled 50% ± 5 volume % with the sample. Discard the remaining contents of the sample container in compliance with applicable laws. A single test is to be performed on material from an individual sample container.

10.2 Insert a nitrogen purge line outlet to within about 13 mm above the fuel surface. Nitrogen purge at 2 L/min for 30 s the headspace above the test sample to displace air and water vapor. Minimize the time the bottle is open to avoid further loss of sample