



Designation: ~~D5705~~—~~15~~ D5705 – 20

Standard Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils¹

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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 mm²/s at 40°C to 50 mm²/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 $\mu\text{mol/mol}$ to 4000 $\mu\text{mol/mol}$ (micromoles per mole) (5 ppm v/v to 4000 ppm v/v (parts per million by volume)).

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

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

D396 Specification for Fuel Oils

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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:*

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 Cleanliness Compatibility of Liquid Fuels.

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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.

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

3.1.1 For definitions of terms used in this test method, see Terminology [D4175](#).

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

3.1.3 *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.

3.1.3.1 *Discussion*—

Under the conditions of this test (1:1 liquid/vapor ratio, temperature, and agitation) the H₂S in the vapor phase (sample's headspace) will be in equilibrium with the H₂S in the liquid phase.

4. Summary of Test Method

4.1 A 1 L H₂S-inert test container (glass test bottle) is filled to 50 % by volume with fuel oil from a filled H₂S-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 3.67 s⁻¹ ± 0.08 s⁻¹ (220 r/min ± 5 r/min (revolutions per minute)) for 3 min.

4.2 A length-of-stain detector tube and hand-operated pump are used to measure the H₂S 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 Residual fuel oils can contain H₂S in the liquid phase and this can result in hazardous vapor phase levels of H₂S in storage tank headspaces. The vapor phase levels can vary significantly according to the headspace volume, fuel temperature and agitation. Measurement of H₂S 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 H₂S 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 H₂S.

5.1.1 The measurement of H₂S in the liquid phase is appropriate for product quality control, while the measurement of H₂S 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 H₂S in the vapor phase above residual fuel oils.

NOTE 1—D5705 is one of three test methods for quantitatively measuring H₂S in residual fuels:

- 1) Test Method [D6021](#) is an analytical test method to determine H₂S levels in the liquid phase.
- 2) Test Method [D7621](#) is a rapid test method to determine H₂S levels in the liquid phase.

NOTE 2—Because of the reactivity, absorptivity and volatility of H₂S, any measurement method only provides an H₂S concentration at a given moment in time.

5.3 This test method does not necessarily simulate the vapor phase H₂S concentration 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 H₂S 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 $3.67 \text{ s}^{-1} \pm 0.08 \text{ s}^{-1}$ ($220 \text{ r/min} \pm 5 \text{ r/min}$ (revolutions per minute)).

NOTE 3—An orbital shaker with an orbit of 19 mm has been found to be suitable.

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 $60 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ 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 $-18 \text{ }^\circ\text{C}$ to $82 \text{ }^\circ\text{C}$ 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 $60 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$.

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.³ 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.)

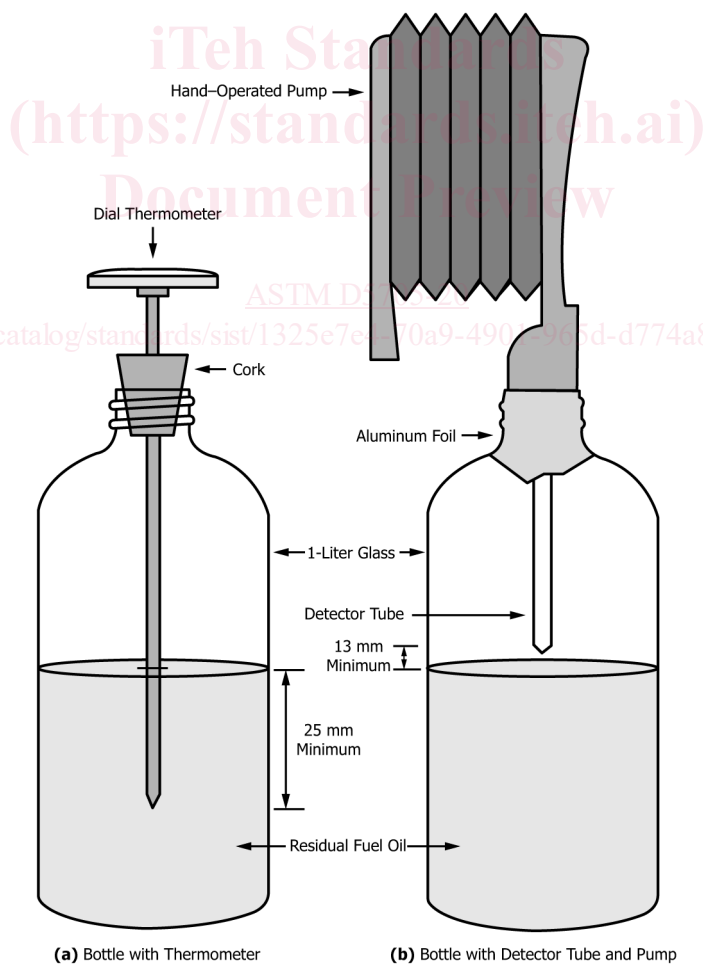


FIG. 1 Measurement of H_2S in the Vapor Phase of Residual Fuel Oil

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

8. Reagents and Materials

8.1 *Containers*—Both sample and test containers are composed of H₂S-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 H₂S concentration to the length 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 H₂S determination and not used for any other purpose, as any additional handling can lead to loss of H₂S and thus low results.)

NOTE 4—Liquid samples taken well into the fuel oil have had less H₂S 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 H₂S exposure during fuel oil movements. Hydrogen sulfide is lost by degassing (elevated temperature and mechanical agitation increases H₂S 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 H₂S is required. Samples can not be stored for later testing as H₂S loss may occur by the mechanism described in **Note 4**.

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 $50\% \pm 5\%$ by 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 vapors. Close the test bottle opening (gas tight) with a cork stopper fitted with a dial thermometer (**Fig. 1(a)**) *immediately* after nitrogen purging.

10.3 Place each test bottle with sample in an oven or a water bath, set at $60\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$, until the sample temperature reaches $60\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. Keep the sample in the oven or bath for a *minimum of 30 min*, which includes the time for the sample to reach $60\text{ }^{\circ}\text{C}$.

NOTE 5—If the sample temperature does not reach $60\text{ }^{\circ}\text{C}$, low results will be obtained for the H₂S concentration. If the temperature exceeds $60\text{ }^{\circ}\text{C}$, high results will be obtained for the H₂S concentration.

10.4 While the sample is heating, place an unbroken length-of-stain detector tube in the hand-operated pump and test the pump for leaks. Consult the manufacturer's instructions for leak check procedure details and for maintenance instructions if leaks are detected. The leak check typically takes 1 min.