



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

This standard is issued under the fixed designation D 5705; 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 field determination of hydrogen sulfide (H₂S) 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 D 396 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 the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 396 Specification for Fuel Oils

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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 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 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 220 rpm 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 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 H₂S in the tank atmosphere for those working in the vicinity require a consistent method for the assessment of potentially hazardous levels of H₂S in fuel oils (**Warning**—H₂S is a highly toxic substance. Use extreme care in the sampling and handling of samples that are suspected of containing high levels of H₂S.).

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 H₂S in the vapor phase of residual fuel oils.

5.3 This test method does not necessarily simulate the vapor phase H₂S concentration of 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

¹ 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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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.

concentrations of H_2S 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.³

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 device 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°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.⁴ 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_2S -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,

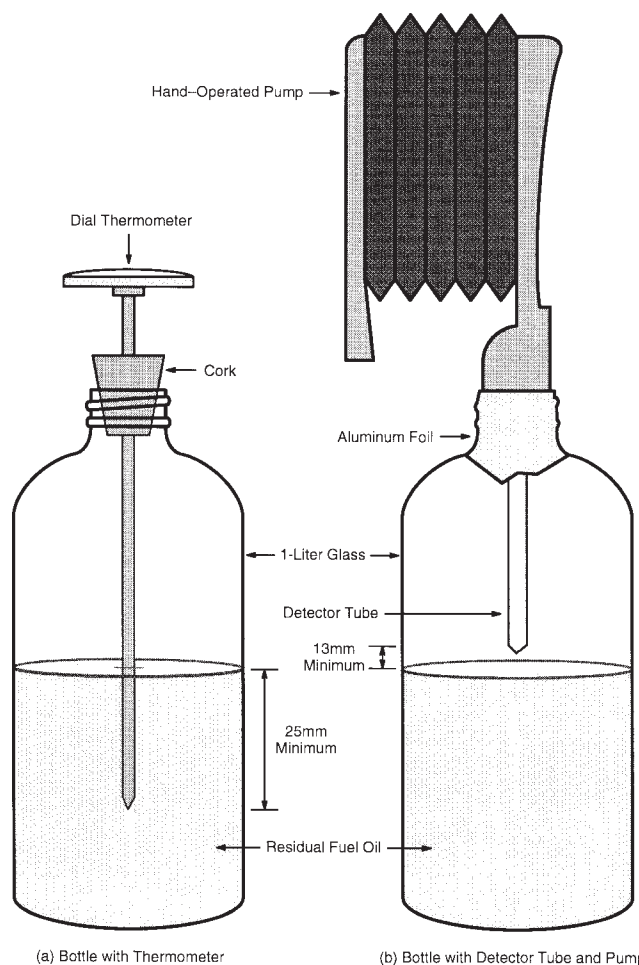


FIG. 1 Measurement of H_2S in the Vapor Phase of Residual Fuel Oil

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_2S 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 D 4057 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.

³ Baxter Scientific Product Models 3518 and 30100, or equivalent, are suitable for this test.

⁴ Direct Reading Colorimetric Indicator Tubes Manual, First Edition, American Industrial Hygiene Association, Akron, OH 44311, 1976.

(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 1—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 1.

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 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 ± 1°C, until the sample temperature reaches 60 ± 1°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°C.

NOTE 2—If the sample temperature does not reach 60°C, low results will be obtained for the H₂S concentration. If the temperature exceeds 60°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.

10.5 Remove the test bottle from the oven and place it in the four-prong clamp of the shaker. Shake at 220 rpm for 3 min ± 1 s to achieve H₂S equilibrium between the liquid and the vapor phase.

10.6 Rest the test bottle on a flat surface, remove the stopper with the dial thermometer, and *immediately* seal the top of the bottle with aluminum foil.

10.7 Select a detector tube with a range that best encompasses the expected H₂S concentration. Reading accuracy is improved when the stain length extends into the upper half of the calibration scale.

10.8 Break off the tube tips and insert the tube into the pump, observing the flow direction indication on the tube. Insert the tube through the aluminum foil on the test bottle. Rest the pump on top of the test bottle with the detector tube only contacting the sample's vapor phase. Do not allow the detector tube to contact the liquid, see Fig. 1(b). Use *one full compression stroke*.

10.9 Remove the detector tube *after* complete decompression of the pump and immediately read the H₂S concentration from the tube's calibration scale or from the charts provided in the box of tubes. Read the tube at the maximum point of the stain. If *channeling* has occurred (non-uniform stain length), read the maximum and minimum stain lengths and average the two readings. **(Warning—**If the calibration scale is not printed directly on the detector tube, be certain that any separate calibration chart is the proper match for the tube in use to avoid incorrect results.)

10.10 If the calibration scale specifies more than one stroke, correct the reading as below:

$$\text{ppm v/v (corrected)} = \text{ppm v/v (reading)} \times \text{specified strokes} \quad (1)$$

NOTE 3—If the test is being conducted at an altitude above 610 m, corrections for barometric pressure are significant. In this case, correct the reading as below:

$$\begin{aligned} \text{ppm v/v (corrected)} = & \text{ppm v/v (reading)} \\ & \times (101.325 \text{ kPa})/(\text{barometric pressure, kPa}) \end{aligned} \quad (2)$$

10.11 If the detector tube reading is over- or under-ranged, take another detector tube of a different range and test a second sample of the fuel oil. Do not repeat testing on a previously tested sample or reuse detector tubes. Continue the testing using different ranged detector tubes and new samples until either the reading is on-scale or less than 5 ppm v/v.

10.12 After obtaining a satisfactory first result, repeat the test with another sample of the same fuel oil and a fresh detector tube.

10.13 Record the raw readings, the readings corrected for number of strokes, the readings corrected for barometric pressure, and the test temperature.

11. Calculation and Report

11.1 Determine the average of the readings from the duplicate test samples and report the average H₂S concentration in parts per million (ppm v/v) for each test along with the test temperature.

12. Precision and Bias ⁵

12.1 *Precision*—The precision of this test method as determined by statistical examination of interlaboratory test results is as follows:

NOTE 4—The precision data were developed in a 1993 two-phase cooperative testing program. Each phase involved four fuels tested by eight participants in four locations. Since samples could not be shipped

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1358.

too far and could not be kept for different time periods before testing, the four locations were in a specific geographic area for each phase. All participants tested each sample on the same day. All participants ran each fuel oil four times using separate samples and fresh detector tubes. The first two results were averaged, and the last two results were averaged. The two average numbers were used to derive the precision statement. Five of the participants in Phase 1 were also in Phase 2. The fuels tested had hydrogen sulfide contents between 9 and 4000 ppm and a viscosity range from 80 mm²/s to 700 mm²/s at 50°C. In the precision program detector tubes and pumps from National Drager Inc. (see Annex A1) were used for all samples having less than 2000 ppm H₂S while Mine Safety Appliances tubes and pumps were used for the one sample exceeding this concentration.

12.1.1 Repeatability—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following value only in one case in twenty, where X = average of two test results:

$$\text{repeatability} = 0.20X + 10 \quad (3)$$

12.1.2 Reproducibility—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following value only in one case in twenty, where X = average of the two results:

$$\text{reproducibility} = 0.30X + 15 \quad (4)$$

12.2 Bias—Since there is no accepted reference material suitable for determining bias for the procedure in Test Method D 5705 for measuring hydrogen sulfide, bias has not been determined. Furthermore, any bias in measurements made by using different length-of-stain detector tubes from different manufacturers is not known.

13. Keywords

13.1 hydrogen sulfide; length-of-stain detector tube; residual fuel oil

ANNEX

(Mandatory Information)

A1. USAGE OF LENGTH-OF-STAIN DETECTOR TUBE

A1.1 Examples of detector tubes with different ranges are presented in Table A1.1.

A1.2 Disposal of tubes with reagent may be done by soaking the opened tubes in water prior to tube disposal. The water should be pH neutralized prior to its disposal.

TABLE A1.1 Detector Tubes with Different Ranges

Detector Tube Identification ^A	Range, ppm v/v (One Stroke)
0.5/a	5–150
1/c	10–200
2/a	20–200
5/b	50–600
100/b	100–2000
Detector Tube Identification ^B	Range, ppm v/v (One Stroke)
460058	2.5–1000
463875	12.5–2000
487339	1–200
487340	10–4000

^A Manufactured by National Drager Inc. and available from local distributors.

^B Manufactured by Mine Safety Appliances and available from local distributors.

SUMMARY OF CHANGES

Subcommittee D02.E0 has identified the location of selected changes to this standard since the last issue (D 5705–95(2000)^{e1}) that may impact the use of this standard.

(1) Updated 7.3 to define the functional requirements that need to be met.

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