



Designation: D7621 – 10



IP 570

Standard Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction^{1, 2}

This standard is issued under the fixed designation D7621; 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 a procedure for the determination of the hydrogen sulfide (H_2S) content of fuel oils such as marine residual fuels and blend stocks, in the range 0.40 to 15.0 mg/kg as measured in the liquid phase.

1.2 This test method is applicable for materials with a viscosity up to $3000 \text{ mm}^2\text{s}^{-1}$ at 50°C .

NOTE 1—ASTM specification fuels falling within the scope of this test method are: Specification D396 Grade Nos 5 (light), 5 (heavy) and 6.

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

1.4 *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:*³
- D396 Specification for Fuel Oils
 - D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
 - D5705 Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils
 - D6021 Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection
 - D6300 Practice for Determination of Precision and Bias

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.

Current edition approved May 1, 2010. Published August 2010.

² This test method has been developed through the cooperative effort between ASTM and the Energy Institute, London. The IP and ASTM logos imply that the ASTM and IP standards are technically equivalent, but their use does not imply that both standards are editorially identical.

³ 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.

Data for Use in Test Methods for Petroleum Products and Lubricants

2.2 *ASTM Adjuncts:*⁴

ADJ6300 D2PP Determination of Precision and Bias data for Use in Test Methods for Petroleum Products

2.3 *ISO Standards:*⁵

ISO TR 13739 Petroleum Products—Procedures for the Transfer of Bunker Fuel(s) to Ships

ISO 4259 Petroleum Products—Determination and Application of Precision Data in Relation to Methods of Test

2.4 *Energy Institute Standards:*⁶

IP 399 Test Method for Determination of Hydrogen Sulfide in Fuel Oils

IP 570 Test Method for Determination of Hydrogen Sulfide in Fuel Oils—Rapid Liquid Phase Extraction Method

3. Terminology

3.1 *Definitions:*

3.1.1 *residual fuel oil, n*—fuel oil comprising a blend of viscous long, short or cracked residue from a petroleum refining process and lighter distillates (blend stocks) blended to a fuel oil viscosity specification, burned for the generation of heat in a furnace or firebox or for the generation of power in an engine.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *liquid phase extraction, n*—technique to determine the concentration of H_2S gas trapped in a liquid by continuous analysis of gases extracted by bubbling air through the test specimen.

4. Summary of Test Method

4.1 A weighed test specimen is introduced into a heated test vessel containing a diluent base oil. Air is bubbled through the oil to extract the H_2S gas. The H_2S is passed, with the air, over

⁴ For referenced ASTM adjuncts contact ASTM Customer Service at service@astm.org.

⁵ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

⁶ Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., http://www.energyinst.org.uk.

an H₂S specific electro-chemical detector to enable the H₂S content of the air to be measured and the amount in the liquid phase to be calculated in mg/kg.

5. Significance and Use

5.1 Excessive levels of hydrogen sulfide in the vapor phase above residual fuel oils in storage tanks can result in health hazards, violation of local occupational health and safety regulations, and public complaint. An additional concern is corrosion that can be caused by the presence of H₂S during refining or other activities. Control measures to maintain safe levels of H₂S require a precise method for the measurement of potentially hazardous levels of H₂S in fuel oils. (**Warning—Safety.** Hydrogen sulfide (H₂S) is a very dangerous, toxic, explosive and flammable, colorless and transparent gas which can be found in crude oil and can be formed during the manufacture of the fuel at the refinery and can be released during handling, storage, and distribution. At very low concentrations, the gas has the characteristic smell of rotten eggs. However, at higher concentrations, it causes a loss of smell, headaches, and dizziness, and at very high concentrations, it causes instantaneous death. It is strongly recommended that personnel involved in the testing for hydrogen sulfide are aware of the hazards of vapor-phase H₂S and have in place appropriate processes and procedures to manage the risk of exposure.)

5.2 This test method was developed so refiners, fuel terminal operators, and independent testing laboratory personnel can rapidly and precisely measure the amount of H₂S in residual fuel oils and distillate blend stocks, with a minimum of training, in a wide range of locations.

5.3 Test Method **D5705** provides a simple and consistent field test method for the rapid determination of H₂S in the residual fuel oils vapor phase. However it does not necessarily simulate the vapor phase H₂S concentration of a fuel storage tank nor does it provide any indication of the liquid phase H₂S concentration.

5.4 Test Method **D6021** does measure the H₂S concentration of H₂S in the liquid phase, however it requires a laboratory and a skilled operator to perform the complex procedure and calculations, and does not offer any reproducibility data. This test method (D7621) offers a 15 min automated test, simplicity, full precision, and a degree of portability.

5.5 H₂S 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. The equilibrium of the vapor phase is disrupted the moment a vent or access point is opened to collect a sample.

6. Apparatus

6.1 *General*—The apparatus, as detailed in **Annex A1**, comprises an air pump, test vessel, heating jacket, filters, H₂S specific detector, integral computer, automatic solenoid valves, gas flow detectors, a disposable syringe, and a 1 mL positive displacement pipette.

6.2 *Analytical Balance*, single pan or double pan balance capable of weighing to the nearest 0.001 g.

6.3 *Syringe*, 20 mL polypropylene disposable type, for introduction of the diluent oil (see **7.1**), accuracy $\pm 1\%$.

6.4 *Refrigerator* (optional), for storing the test sample (see **8.5**). The refrigerator shall be of a type suitable for storing flammable, volatile materials.

6.5 *Oven/Water Bath* (optional), for warming the sample to 40°C with an accuracy of $\pm 2^\circ\text{C}$ (see **9.4.2.1**). The oven shall be of a type suitable for use with volatile materials.

7. Reagents and Materials

7.1 *Diluent Oil*,⁷ proprietary water white API Group 2 base oil with a typical viscosity of 100 mm²s⁻¹ at 40 °C.

7.2 *Reference Material*,⁷ pressurized nitrogen, of at least 99.999 % (v/v) purity, containing a certified level of H₂S (nominally 25 mg/kg).

7.3 *Cleaning Materials*, technical grade.

7.3.1 *Toluene*.

7.3.2 *Petroleum Ether (60/80)*.

7.3.3 *Acetone*.

8. Sampling

8.1 Unless otherwise agreed, samples shall be taken in accordance with Practice **D4057** or **ISO TR 13739**.

8.2 During sampling operations, care shall be taken to ensure that the integrity of the material is maintained and the possible loss of H₂S is kept to a minimum. The precision of this method is critically dependent on the sampling, thermal history, and handling of the test sample.

8.3 Draw the sample directly into a suitable clean H₂S inert container, of a minimum volume of 500 mL, with an impervious gas-tight closure. Suitable containers include amber glass bottles and epoxy lined containers. The closure aperture shall allow the drawing of a test specimen with the syringe or pipette (see **A1.1.13** and **A1.1.12**).

8.3.1 Epoxy lined containers shall be visually inspected to ensure that the lining has not been damaged and that the containers are not dented.

8.3.2 To ensure sample integrity fill the sample container to approximately 95 % full and cap immediately.

NOTE 2—Lower volume containers may be used, however the precision could be affected.

8.4 If a dedicated H₂S sample cannot be taken, then the H₂S measurement shall be the first test carried out on the sample as any additional handling can lead to loss of H₂S and low results.

8.5 Take the samples to the laboratory as soon as is practicable after sampling. Test immediately if possible. If samples are not tested immediately, store in a cool place such as a refrigerator (**6.4**), and analyze within 3 days after sampling.

9. Preparation of Apparatus

9.1 *General*—Follow the manufacturer's instructions for the correct set up, verification, calibration and operation of the apparatus.

⁷ The following reagents and materials were used to develop the precision statements: Seta Diluent SA4000-004 and Seta Verification Gas SA4001-001. Stanhope-Seta, Chertsey, Surrey, KT16 8AP, UK. This is not an endorsement or certification by ASTM International.

9.2 *Location of Apparatus*—Use the apparatus under a suitable fume hood or equivalent well-ventilated work space, and vent the gas exit tube to a suitable extractor as the test will release small amounts of H₂S gas during test specimen introduction and during the measurement.

9.3 *Filters:*

9.3.1 The inlet air filter shall be replaced every 3 months, or earlier if any discoloration is visible.

9.3.2 Follow the manufacturer’s instructions regarding the replacement intervals of the air pump and moisture filters.

9.3.3 Replace the moisture filter if any discoloration is visible.

9.4 *Sample Preparation:*

9.4.1 To minimize the loss of H₂S gas, do not homogenize or transfer the sample to another container, and avoid shaking the sample before taking a test specimen.

9.4.2 The sample needs to be flowing freely enough to allow the test specimen to be drawn into the syringe or pipette (see A1.1.13 and A1.1.12).

9.4.2.1 A sample that is not free flowing at ambient temperature shall be gently warmed in a water bath or oven (see 6.5) set at a temperature not exceeding 40°C.

9.4.2.2 Samples with viscosities greater than 3000 mm²s⁻¹ at 50°C may be tested, but the precision could be affected.

9.4.3 By using a smaller volume of sample it is possible to extend the range of the instrument to over 200 mg/kg but the precision could be affected.

NOTE 3—It has been found that samples with a viscosity over 500 mm²s⁻¹, at 50°C, usually require warming.

9.5 *Test Vessel*—Clean the test vessel and screw cap before each test. Fit the screw cap tightly.

9.6 *Liquid Trap*—Empty and clean the liquid trap if any liquid or discoloration is visible.

9.7 *H₂S Detector*—Follow the manufacturer’s instructions for installing a new calibrated detector and verify the performance immediately afterwards as described in 10.2.3.

NOTE 4—Toluene, followed by petroleum ether (60/80), and acetone, are effective in cleaning the test vessel, cap, and liquid trap (see 7.3).

10. Calibration and Standardization

10.1 Ensure that all of the manufacturer’s instructions for verification and calibration of the mechanical and electronic systems, and operation of the apparatus are followed. Calibration functions are separated from the usual operator controls and are all implemented electronically using the integral display and keyboard.

10.2 *Verification:*

10.2.1 *Air Flow Rate*—Verify that the air flow rate is 375 ± 55 mL/min, at least once a year using a suitable flow meter connected to the air output connection. If the flow rate is incorrect, recalibrate the flow (see 10.3.1).

10.2.2 *Test Vessel Heater Jacket*—Verify that the temperature of the heater jacket is 60.0 ± 1.0 °C, at least every six months, by inserting a calibrated temperature sensor into the heater jacket. If the temperature is incorrect, recalibrate (see 10.3.2).

10.2.3 *H₂S Detector*—Verify the performance of the detector at least every month, or when a new detector is fitted, at

zero using air, and at a nominal 25 mg/kg vapor concentration level using pressurized nitrogen (see 7.2) containing a certified level of H₂S.

10.3 *Calibration:*

10.3.1 *Air Flow Rate*—The air flow adjustment is implemented electronically.

10.3.2 *Test Vessel Heater Jacket*—The temperature adjustment is implemented electronically.

10.3.3 *H₂S Detector*—The detector is factory calibrated using the reference material (see 7.2) (static calibration) and using factory calibration liquids with known mg/kg liquid concentrations of H₂S (dynamic calibration). This calibration information is held digitally on the detector assembly and is read directly by the computer in the apparatus. The calibration enables results in mg/kg to be calculated from the test results. The dynamic calibration is a function of the detector and apparatus, and has a fixed value.

10.3.3.1 The static calibration is implemented electronically following a verification (see 10.2.3).

11. Procedure

11.1 At switch on, the H₂S apparatus shall control the test vessel heater jacket to 60.0 ± 1.0 °C, and purge by pumping air directly to the detector.

11.2 Remove the screw cap from the cleaned test vessel (see 9.5) and introduce 20.0 ± 0.5 mL of diluent oil (see 7.1) using the syringe (see 6.3) and then replace the screw cap. Place the test vessel in the temperature controlled heating jacket and fit the input/output tubing.

11.3 Air is pumped through the diluent in the test vessel and to the detector for 5 min. This allows the diluent oil to warm up, and the system to be purged.

11.4 Air is then pumped directly to the detector, bypassing the test vessel, to allow the test specimen to be introduced without purge air affecting the concentration of the H₂S. Ensure that the instrument is operating in bypass mode before introducing the test specimen. Introducing the test specimen before this condition is met will likely result in premature loss of H₂S and an erroneously low result. If this is suspected or the instrument indicates that an incorrect procedure has been followed, abandon the test and repeat using a fresh test specimen.

11.5 Depending on the expected H₂S concentration, draw the appropriate volume of the sample from at least 3 cm below the sample surface into the disposable syringe or positive displacement pipette (A1.1.13 and A1.1.12) and weigh to the nearest 0.001 g (see 6.2). Using the keypad, enter the total mass, which includes the syringe/pipette and sample, into the apparatus. The appropriate volume shall be determined by reference to Table 1.

TABLE 1 Appropriate Test Volume for Expected H₂S Concentration

Expected H ₂ S Concentration	Required Test Volume	Sample Introduction
0 to 10 mg/kg	5 mL	Disposable syringe
10 to 20 mg/kg	2 mL	Disposable syringe
>20 mg/kg	1 mL	Pipette