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

1. Scope*

1.1 This test method covers procedures (A and B) for the determination of the hydrogen sulfide (H_2S) content of fuel oils such as marine residual fuels and blend stocks, with viscosity up to $3000 \text{ mm}^2\text{s}^{-1}$ at 50°C , and marine distillate fuels, as measured in the liquid phase.

NOTE 1—Specification fuels falling within the scope of this test method are: ASTM Specification D396, MIL-DTL-16884, and ISO 8217.

1.2 Procedure A has been shown to eliminate interferences such as thiols (mercaptans) and alkyl sulfides. Procedure B can give elevated results if such interferences are present (see Annex A2).

1.3 Valid ranges for the precision are given in Table 2 and Table 3. Measurements can be made outside these ranges however precision has not been determined.

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

ISO 8217 Fuels (Class F) Specification of Marine Fuels

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

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products—Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.14 on Stability and Cleanliness of Liquid Fuels.

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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.

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.

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

2.5 U.S. Department of Defense Specifications:⁷
MIL-DTL-16884 Fuel, Naval Distillate

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 H₂S gas trapped in a liquid by continuous analysis of gases extracted by bubbling air through the test specimen.

3.2.2 *vapor phase processor, n*—apparatus enabling low temperature removal of interfering vapors.

⁷ Available online at <https://assist.dla.mil/quicksearch/> or <http://assistdocs.com/> or from the Standardization Document Order Desk, 700 Robbins Avenue, Building 4D, Philadelphia, PA 19111-5094.

3.2.2.1 Discussion—

The vapor phase processor holds a specific filter cartridge at –20°C during the Procedure A test.

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 H₂S gas. The air with the extracted H₂S is passed, via a vapor phase processor (Procedure A only), to an H₂S specific electro-chemical detector enabling the H₂S content of the air to be measured and the amount in the liquid phase to be calculated in mg/kg. The filter cartridge (see 7.4) is not required for Procedure B.

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 and gas flow detectors.

6.1.1 Procedure A requires the use of a vapor phase processor capable of cooling a specific filter cartridge (see 7.4) to –20 ± 2°C.

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

6.3 *Syringe or Burette*, able to dispense 20 mL for introduction of the diluent oil (see 7.1), accuracy ± 1 %.

6.4 *Refrigerator* (optional), for storing the test sample (see 8.3). 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 8.4.1.1). The oven shall be of a type suitable for use with volatile materials.

6.6 *Pipette*, 1 mL positive displacement pipette, for the introduction of the test specimen. The accuracy as stated by the manufacturer should be typically ± 0.25 %.

6.7 *Disposable Syringe*, 5 mL or 10 mL, for the introduction of the test specimen. Typical accuracy ± 1 %. This may be fitted with a needle or extra tube to allow sample to be taken from 3 cm below the surface, if appropriate.

7. Reagents and Materials

7.1 *Diluent Oil*,⁸ proprietary water white API Group 2 base oil with a typical viscosity of $100 \text{ mm}^2\text{s}^{-1}$ at 40°C.

7.2 *Reference Material; Materials*: pressurized nitrogen, of at least 99.999 % (v/v) purity, containing a certified level of H_2S (23 to 27 ppm (v/v)) traceable to a national standard.

7.2.1 *Reference material*, pressurized nitrogen, of at least 99.999 % (v/v) purity, containing a certified level of H_2S (23 to 27 ppm (v/v)) traceable to a national standard.

7.2.2 Verification solution containing a known concentration of liquid phase hydrogen sulphide.

7.3 *Cleaning Materials*, technical grade.

7.3.1 *Toluene*.

7.3.2 *Petroleum Ether (60/80)*.

7.3.3 *Acetone*.

7.4 *Filter Cartridge*, see Fig. A1.5, individually packed in a sealed envelope, required for use in the vapor phase processor required for use in Procedure A only.

8. Sampling and Test Specimen Preparation

8.1 Unless otherwise agreed, samples shall be taken in accordance with Practice D4057.

8.1.1 During sampling operations, care shall be taken to ensure that the integrity of the material is maintained and the possible loss of H_2S is kept to a minimum. The precision of this method is critically dependent on the sampling, thermal history, and handling of the test sample.

8.1.2 Collect the sample directly in a suitable clean H_2S 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 6.7 and 6.6).

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

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

8.1.4 Where samples are drawn in a manner which does not minimize vapor loss (for example, continuous drip sampling) collect a dedicated sample for H_2S determination.

8.1.5 When samples cannot be collected directly into the sample container, transfer the sample from the sampling device into the sample container and ensure that H_2S loss is kept to a minimum.

NOTE 2—The precision has not been determined for smaller volume containers.

8.2 If a dedicated H_2S sample cannot be taken, then the H_2S measurement shall be the first test carried out on the sample as any additional handling can lead to loss of H_2S and low results.

8.3 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.

8.4 *Test Specimen Preparation*—To minimize the loss of H_2S gas, do not homogenize or transfer the sample to another container, and avoid shaking the sample before taking a test specimen.

8.4.1 The sample needs to be flowing freely enough to allow the test specimen to be drawn into the syringe or pipette (see 6.7 and 6.6).

8.4.1.1 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.

8.4.2 Samples with viscosities greater than $3000 \text{ mm}^2\text{s}^{-1}$ at 50°C may be tested, but the precision has not been determined.

⁸ 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.

NOTE 3—It has been found that samples with a viscosity over ~~500 mm~~ $500 \text{ mm}^2\text{s}^{-1}$, at 50°C , usually require warming.

8.4.3 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 has not been determined.

9. Preparation of Apparatus

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

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 H_2S gas during test specimen introduction and during the measurement.

9.3 Filters and Tubing:

9.3.1 At the beginning of each test inspect the moisture filter and the liquid trap.

9.3.1.1 Replace the moisture filter if any discoloration is visible.

9.3.2 Replace the tubing that connects to the test vessel if any discoloration is visible.

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

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

9.4 *Test Vessel*—Before each test ensure that the test vessel and screw cap are clean and dry. Fit the screw cap tightly.

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

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).

9.6 *H_2S Detector*—Follow the manufacturer’s instructions for installing a new calibrated detector and verify the performance immediately afterwards as described in 10.2.3.

9.7 Switch on the apparatus in accordance with the manufacturer’s instructions.

9.7.1 *Procedure A*—After switch on, initiate the vapor phase processor cooling.

9.7.1.1 Confirm that the temperature of the heater jacket is $60.0 \pm 1.0^\circ\text{C}$ and the vapor phase processor is $-20.0 \pm 2.0^\circ\text{C}$. Air purging of the H_2S detector commences.

9.7.2 *Procedure B*:

9.7.2.1 Confirm that the temperature of the heater jacket is $60.0 \pm 1.0^\circ\text{C}$. Air purging of the H_2S detector commences.

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 $375 \pm 55 \text{ mL/min}$, at least once a month using a suitable calibrated 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 $60.0 \pm 1.0^\circ\text{C}$, 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 *H_2S 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 ppm (v/v) vapor concentration level using pressurized nitrogen (see 7.2) containing a certified level of H_2S . This verification shall be carried out at ambient temperature. If the measurement is not within 10 % of the certified value of the vapor concentration, replace the moisture filter and check the cleanliness of the liquid trap, test vessel and associated tubing. Purge the system with air for ~~30 min~~ **30 min** and attempt the verification again. If the measurement is still outside the allowed tolerance follow the manufacturer’s instructions in recalibrating or replacing the detector.

10.2.4 *Vapor Phase Processor*—Verify that the temperature of the filter cartridge housing is $-20.0 \pm 2.0^\circ\text{C}$ at least every 6 months. If the temperature is outside the allowed tolerance carry out a calibration of the vapor phase processor cooler temperature.

10.2.5 It is recommended that the overall correct operation of the apparatus should be checked at least every three months, or following maintenance, when a new detector is fitted, or according to local quality control requirements, by measurement of a solution of hydrogen sulfide (7.2.2).

10.2.5.1 Stabilized verification solutions⁹ are available by means of participation in a proficiency testing scheme.¹⁰

10.2.5.2 Non-stabilized verification solutions, derived within the testing lab using local procedures, may be used.

⁹ Supporting data have been filed at the Energy Institute, UK www.energyinst.org.uk and may be obtained by requesting the Research Report: Development of Stabilised Liquid Phase Hydrogen Sulfide Verification Materials.

¹⁰ The sole source of supply of stabilized verification solutions known to the committee at this time is Stanhope-Seta, Chertsey, Surrey, KT16 8AP, UK. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

NOTE 5—Non-stabilized verification solutions should be standardized by titration before use and have a very short life of only a few hours.

10.2.5.3 If the result is not within $R/\sqrt{2}$ plus the uncertainty of the verification solution's determined value or the consensus value from a proficiency testing scheme,¹⁰ then for commercially supplied stabilized verification solutions check the validity date. For non-stabilized solutions, make a new batch and repeat the test.

10.2.5.4 If it is not possible to meet the criteria in 10.2.5.3, check the air flow rate (10.2.1) and validate the H₂S sensor (10.2.3). If it is still not possible to meet the criteria in 10.2.5, then follow the manufacturer's instructions regarding fault finding and calibration.

10.3 Calibration:

10.3.1 *Air Flow Rate*—The air flow adjustment is implemented electronically (see 10.1).

10.3.2 *Test Vessel Heater Jacket*—The temperature adjustment is implemented electronically (see 10.1).

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).

10.3.4 *Vapor Phase Processor Temperature*—Follow the manufacturer's instructions to calibrate the temperature of the filter cartridge housing.

11. Procedure

11.1 Initial Conditions:

11.1.1 Procedure A:

11.1.1.1 Confirm that the temperature of the heater jacket is 60.0 ± 1.0 °C and the vapor phase processor is -20.0 ± 2.0 °C.

11.1.1.2 Insert a new filter cartridge (7.4) into the vapor phase processor, and screw on the cap.

11.1.2 Procedure B:

11.1.2.1 Confirm that the temperature of the heater jacket is 60.0 ± 1.0 °C.

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, avoiding the bottom of the container, into the disposable syringe or positive displacement pipette (6.7 and 6.6) and weigh to the nearest 0.001 g (see 6.2). Avoid applying a strong vacuum to the sample when using the syringe or pipette and ensure that the integrity of the material is maintained so that the possible loss of H₂S is kept to a minimum. Do not expel air from the syringe or pipette into the sample. 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.

NOTE 6—A single mass can be entered rather than entering the mass before and after sample introduction if the balance is tared.

11.6 Introduce the test specimen into the test vessel, ensuring that the syringe or pipette is held vertically to avoid sample adhering to the test vessel walls. Ensure that the syringe or pipette does not touch the surface of the diluent liquid. Any pickup of diluent oil onto or into the syringe or pipette will result in the mass of the oil being included in the mass of the empty syringe or pipette leading to an erroneously high result. If this is suspected, abandon the test and repeat it.

11.7 Immediately, after removing the syringe or pipette, screw the cap tightly onto the top of the test vessel.

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

11.8 Weigh the emptied syringe or pipette to the nearest 0.001 g (see 6.2) and using the keypad enter the mass into the apparatus.

11.9 Immediately start the test, which proceeds automatically.

11.10 The detector reading is normalized to zero.

11.11 *Air Path:*

11.11.1 *Procedure A:*

11.11.1.1 Air is pumped directly through the filter cartridge for 3 min. After these 3 min the air is diverted through the diluted test specimen in the test vessel and to the detector.

11.11.2 *Procedure B:*

11.11.2.1 Air is pumped through the test specimen and diluent in the test vessel and to the detector.

11.12 The millivolt readings (mV) from the detector are recorded at least every 4 s throughout the test until 15 min have elapsed. The result is automatically calculated and displayed in mg/kg.

11.13 Air is pumped to purge the detector.

11.14 Remove the test vessel and check that the test specimen and diluent oil have properly mixed. If two distinct phases exist, check the air connections and repeat the test.

11.15 Clean the test vessel.

11.16 For Procedure A, remove and dispose of the cartridge from the vapor phase processor.

12. Calculation

12.1 Report the H₂S content to the nearest 0.01 mg/kg for <10 mg/kg, and 0.1 mg/kg for ≥10 mg/kg.

$$H_2S = (A \times C) / m \text{ mg/kg} \quad (1)$$

where:

A = integrated area of cell output over the test time (mV.s),

C = calibration constant of the detector (μg)/(mV.s), and

m = mass of the test specimen to be tested (g).

13. Report

13.1 The test report shall contain at least the following information:

13.1.1 A reference to this standard and the procedure (A or B) followed,

13.1.2 All details necessary for complete identification of the product tested,

13.1.3 The result of the test (see Section 12),

13.1.4 Any deviations, by agreement or otherwise, from the procedures specified, and

13.1.5 The time and date of the test.

14. Precision and Bias¹¹

14.1 *General:*

14.1.1 *Procedure A (Distillate and Residual Fuels)*—The precision values given in 14.2 and 14.3 were derived from a 2012 Energy Institute ILS which used eight instruments and eight operators, at a single location, to test 12 samples in duplicate and in random order. The precision of the sample types covered the H₂S levels of 0.60 to 12.5 mg/kg.

14.1.2 *Procedure B (Distillate Fuels)*—The precision values for distillate fuels given in 14.2 and 14.3 were derived from a 2011 Energy Institute ILS which used 10 instruments and 10 operators, at a single location, to test 8 samples in duplicate and in random order. The precision of the sample types covered the H₂S levels of 0.40 to 9.70 mg/kg.

¹¹ Supporting data have been filed at the Energy Institute, UK www.energyinst.org.uk and may be obtained by requesting the Research Report: IP 570 Residual fuels and blend stocks (Procedure B), IP 570 Marine distillate fuels (Procedure B) and IP 570 Marine distillate and residual fuels (Procedure A).

TABLE 2 Repeatability

Procedure	Repeatability (mg/kg)	Range (mg/kg)
Procedure A (Distillate and residual fuels)	0.3329 $x^{0.55}$	0.60 – 12.5
Procedure B (Distillate fuels)	0.2099 $x^{0.7}$	0.40 – 9.70
Procedure B (Residual fuels)	0.2970 $x^{0.6}$	0.40 – 15.3

where:

x = the average of the results being compared.