



Designation: **D6021–12 (Reapproved 2017) D6021 – 22**

Standard Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection¹

This standard is issued under the fixed designation D6021; 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 Scope*

1.1 This test method covers a method suitable for measuring the total amount of hydrogen sulfide (H_2S) in heavy distillates, heavy distillate/residual fuel blends, or residual fuels as defined in Specification **D396** Grade 4, 5 (Light), 5 (Heavy), and 6, when the H_2S concentration in the fuel is in the 0.01 $\mu\text{g/g}$ (ppmw) to 100 $\mu\text{g/g}$ (ppmw) range.

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

1.3 *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.* For specific warning statements, see **7.5**, **8.2**, **9.2**, **10.1.4**, and **11.1**.

1.4 *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](#)

[D1193 Specification for Reagent Water](#)

[D2420 Test Method for Hydrogen Sulfide in Liquefied Petroleum \(LP\) Gases \(Lead Acetate Method\)](#)

[D3609 Practice for Calibration Techniques Using Permeation Tubes](#)

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

[D4084 Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels \(Lead Acetate Reaction Rate Method\)](#)

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D4323 Test Method for Hydrogen Sulfide in the Atmosphere by Rate of Change of Reflectance](#)

[D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence](#)

[D5705 Test Method for Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils](#)

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

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 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. Terminology

3.1 Definitions:

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

3.1.2 *heavy distillate, n*—a fuel produced from the distillation of crude oil which has a kinematic viscosity at 40 °C between 5.5 mm²/s and 24.0 mm²/s, inclusive.

3.1.3 *heavy distillate/residual fuel blend, n*—a blend of heavy distillate and residual fuel oil having a viscosity at 40 °C between 5.5 mm²/s and 24.0 mm²/s, inclusive.

3.1.4 *multiple headspace extraction, n*—a technique to determine the total concentration of a gas trapped in a liquid by analysis of successive gas extractions from the vapor space of a closed vessel containing a known amount of the sample.

3.1.5 *residual fuel oil, n*—any liquid or liquefiable petroleum product having a kinematic viscosity at 100 °C between 5.0 mm²/s and 50.0 mm²/s, inclusive, burned for the generation of heat in a furnace or firebox or for the generation of power in an engine.

4. Summary of Test Method

4.1 A representative sample of residual fuel oil is obtained in sufficient quantity to completely fill the sample container. The sample is taken to the laboratory preferably within one to 4 h, within 24 h maximum and placed in a refrigerator until the hydrogen sulfide analysis can be run. At that time, the sample is removed from the refrigerator and allowed to sit at ambient temperature until it flows freely.

4.2 A 0.05 g to 5.0 g test specimen (aliquot) is placed in a headspace vial and heated in an oven at 60 °C for more than five but less than 15 min. The headspace gas is sampled and injected into either of two types of apparatus capable of measuring the hydrogen sulfide concentration in the gaseous sample.³ The two types of apparatus are those using the reaction of lead acetate with H₂S (see Test Method [D4084](#) or Test Method [D4323](#)) and those based on chemiluminescence (see Test Method [D5504](#)).

4.3 The remaining contents of the headspace vial are cooled for 5 min, then again heated in the oven. The headspace contents are again transferred to the hydrogen sulfide measuring instrument. The procedure is repeated for a third time. This is known as multiple headspace extraction procedure (MHE). [ASTM D6021-22](#)

<https://standards.iteh.ai/catalog/standards/sist/5155ad2a-0905-4c56-95d5-7fa20d274fc8/astm-d6021-22>

4.4 A linear plot of the natural logarithm of the area or peak height difference of the instrument reading against the number of injections is indicative of the correctness of the extraction procedure. The difference in area or peak height of the first two injections is used to calculate a total area or total peak height difference. The total area or total peak height difference is multiplied by a response factor determined from a direct gas calibration mixture and divided by the weight of the test specimen to determine the concentration of H₂S in the residual fuel in µg/g (ppmw).

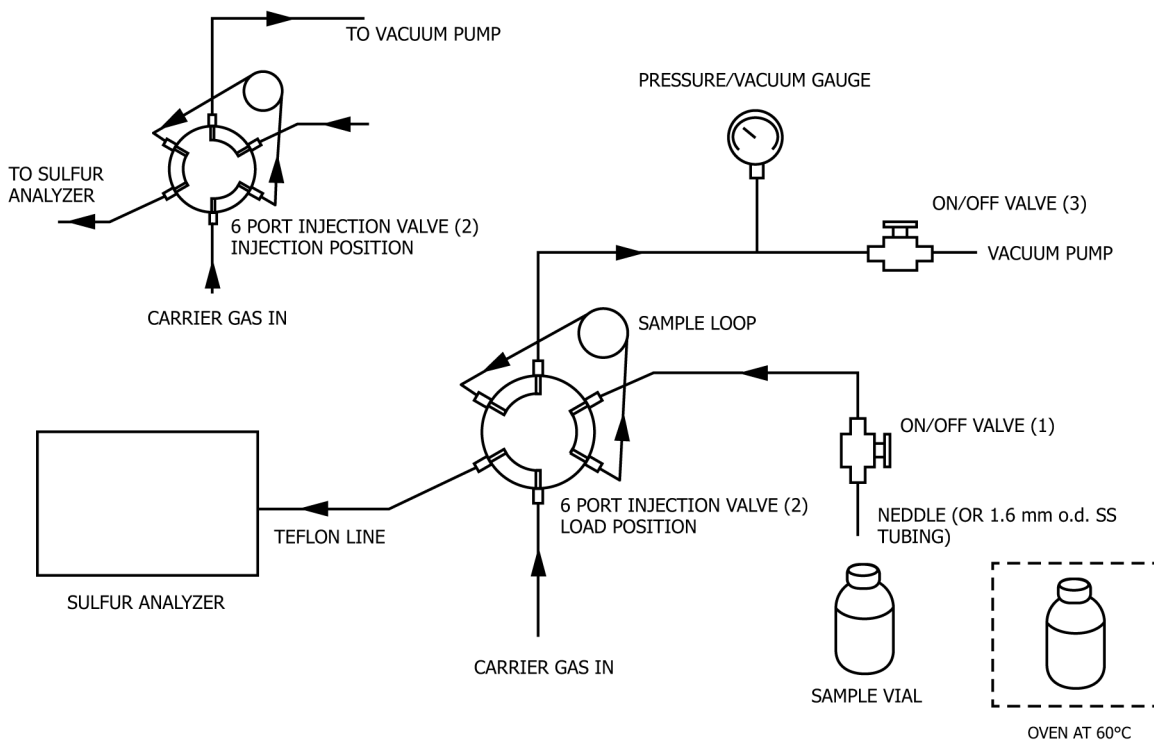
5. Significance and Use

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 so refiners, fuel terminal operators and independent testing laboratory personnel can analytically measure the amount of H₂S in the liquid phase of residual fuel oils.

³ Determination of H₂S in Residual Fuel Oils by Multiple Headspace Extraction: A Critical Evaluation of Available Analytical Methods. Silva, B., Carvajal, N., Gonzalez, A., Eastern Analytical Symposium, sponsored by American Chemical Society and the American Microchemical Society, November 16–20, 1992, Somerset, N.J.



DETAILED VIEW OF INJECTION SYSTEM
FIG. 1 Schematic of Headspace Analysis System

iTeh Standards
<https://standards.iteh.ai>
 Document Preview

NOTE 1—Test Method D6021 is one of three test methods for quantitatively measuring H₂S in residual fuels:

- 1) Test Method **D5705** is a simple field test method for determining H₂S levels in the vapor phase.
- 2) Test Method **D7621** is a rapid test method to determine H₂S levels in the liquid phase.

<https://standards.iteh.ai/catalog/standards/sist/5155ad2a-0905-4c56-95d5-7fa20d274fc8/astm-d6021-22>

5.3 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. A concentration of 1 mg/kg (µg/g) (ppmw) of H₂S in the liquid phase of a residual fuel can typically generate an actual gas concentration of >50 µL/L(ppmv) to 100 µL/L(ppmv) of H₂S in the vapor phase, but the equilibrium of the vapor phase is disrupted the moment a vent or access point is opened to collect a sample.

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.

6. Apparatus

6.1 A schematic of the headspace sampling system required for this analysis is shown in Fig. 1. It consists of:

6.1.1 *Sampling On/Off Valve*, with 3.2 mm o.d. connector (Valve 1).

6.1.2 *Six-Port External Loop Injection Valve*, made with 316 stainless steel, resistant to attack by sulfur compounds and having 3.2 mm o.d. tubing from each port (Valve 2).

6.1.3 *Polytetrafluoroethylene (PTFE) Sample Loops*, of 0.5 mL, 2.5 mL, and 10 mL are used for H₂S content of 1 ppmw to 100 ppmw, 0.1 ppmw to 50 ppmw, and 0.01 ppmw to 10 ppmw, respectively.

6.1.4 *Pressure/Vacuum Gauge*, 6.3 mm diameter dial type with range of –100 kPag to 200 kPag, 5 kPa divisions from –100 kPag to 0 kPag and 10 kPa divisions from 0 kPag to 200 kPag.

6.1.5 *Vacuum On/Off Valve*, 3.2 mm o.d. connector (Valve 3).

6.1.6 *Sulfur Selective Detector*, any H₂S specific detector capable of measuring H₂S in the gas from 1 ppmv to 10 000 ppmv with a repeatability of $\pm 2\%$ of full scale.

NOTE 3—Good performance has been obtained with a lead acetate tape detector and a sulfur chemiluminescence detector.

6.1.7 *Fluorocarbon Tubing*, 0.6 m long by 3.2 mm o.d. to connect components together.

6.2 *Vacuum pump*, 3.2 mm o.d. outlet, capable of achieving a 0.2 kPa vacuum and with a capacity of 100 mL/min.

6.3 *Headspace Oven*, capable of operating at $60\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$ with internal dimensions of 30 cm by 30 cm by 30 cm. An optional vent line is recommended in case a vial leaks.

6.4 *Analytical Balance*, sensitivity of 0.01 mg, maximum weight of 250 g.

6.5 *Data Handling System*, such as electronic integrator or any computer unit that can work with a chromatographic signal.

6.6 If sulfur specific detectors are used instead of an H₂S analyzer then a chromatographic system equipped with a suitable column and oven is required to separate H₂S from other sulfur compounds (see Test Method [D5504](#)).

6.7 *Hand Crimper*, to crimp 20 mm diameter aluminum seals.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Acetic Acid Solution*—Add 50 mL of glacial acetic acid (CH₃COOH) to a 1 L volumetric flask and then add Type II distilled water, as specified in Specification [D1193](#), to the 1 L mark to make a 5 % acetic acid solution.

7.3 *Aluminum Seals*, 20 mm diameter to seal septas to headspace sample vials.

7.4 *Headspace Vials*, 30 mL, 60 mL, or 120 mL borosilicate glass vials with 20 mm mouth diameter.

7.5 *Hydrogen Sulfide Gas Calibration Standard*, 1 $\mu\text{L/L}$, 10 $\mu\text{L/L}$, and 100 $\mu\text{L/L}$ H₂S in helium or nitrogen high pressure cylinders (obtain from gas supply company). (**Warning**—Hydrogen sulfide is an extremely toxic gas.)

7.6 *Gases*, helium or nitrogen (H₂S free), chemically pure grade or purified, as carrier gas to sweep sample into the detector.

7.7 *Lead Acetate Sensing Paper*—Prepare in accordance with Test Method [D2420](#), using appropriate size strips and drying in an H₂S-free environment. Commercially available test paper has been found satisfactory.

NOTE 4—Reagents from [7.2](#) and [7.7](#) are only needed if using an H₂S lead acetate tape detector.

7.8 *Nuts and Ferrules*, Polytetrafluoroethylene (PTFE) and stainless steel (3.2 mm).

⁴ *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.9 *Septas*, 20 mm diameter PTFE silicone/fluorocarbon to seal headspace sample vials.

7.10 *Side Port Needles*, for pressure lock, A-gas series (with reduction union 3.2 mm to 1.6 mm).

7.11 *Syringe Needles*, common dischargeable (dosing needle).

8. Sampling

8.1 Using a suitable H₂S inert container of 250 mL to 500 mL, collect a representative sample by Practice **D4057**. Suitable containers can be made of borosilicate glass or aluminum. If the sample temperature is below 60 °C then a high density polyethylene bottle can be used.

8.2 Fill the container completely to the top so that there is no headspace in the container. Cap immediately. (**Warning**— At no time should the container temperature be allowed to exceed the temperature of the sample at the time.)

8.3 Take the samples to the laboratory preferably within one to four hours, within 24 h maximum. Place the samples in refrigerated storage. Store samples until analysis time but not more than three days.

9. Preparation of Apparatus

9.1 Assemble the headspace sampling system as shown in **Fig. 1**.

9.2 Because of the chemical activity and adsorptive properties of H₂S, it is highly desirable to connect the components of the test apparatus together using minimum lengths of aluminum or fluorocarbon sample lines. (**Warning**—To preclude the formation of mercaptide gels and to reduce problems associated with corrosion do not use brass or copper flow system parts.)

10. Calibration and Standardization

10.1 *Filling Head Space Vial With Gas Calibration Standard:*

10.1.1 Depending on the expected concentration use, a 1 μL/L (≤0.1 μg/g) in a ~~120 mL~~ 120 mL headspace vial, 10 μL/L (~1 μg/g) in a 60 mL headspace vial, or 100 μL/L (~10 μg/g) in a 30 mL headspace vial, H₂S gas standard to calibrate the headspace sampling system.

NOTE 5—Parts per million by volume units (μL/L), equivalent to micro moles per mole, are used because of the convenience in use of volume measurements rather than weight for a gas standard.

10.1.2 Insert a silicone/fluorocarbon septum, with the PTFE side pointing inwards, into the headspace vial, cover it with an aluminum seal, and crimp the aluminum seal with the hand crimper.

10.1.3 Insert the inlet needle attached to the H₂S calibration cylinder (see **Fig. 2**) through the septum with the flow control set to zero. Also insert an open syringe needle into the septum as an outlet vent.

10.1.4 Set the pressure of the H₂S calibration cylinder to 105 kPa, and open the flow control to purge the vial as follows: (**Warning**—Because of the toxicity of H₂S the vial should be in a hood during the purging operation.)

30 mL vial—purge for 3 min at a flow of 100 mL/min.
 60 mL vial—purge for 6 min at a flow of 100 mL/min.
 120 mL vial—purge for 10 min at a flow of 120 mL/min.

10.1.5 Turn the flow control to zero flow and remove the inlet needle, leaving the outlet vent in the vial.

10.1.6 Allow the vial to equilibrate to atmospheric pressure for 1.0 min, then remove the outlet vent.

10.1.7 Record the laboratory ambient temperature in °C and the laboratory barometric pressure in kPa.

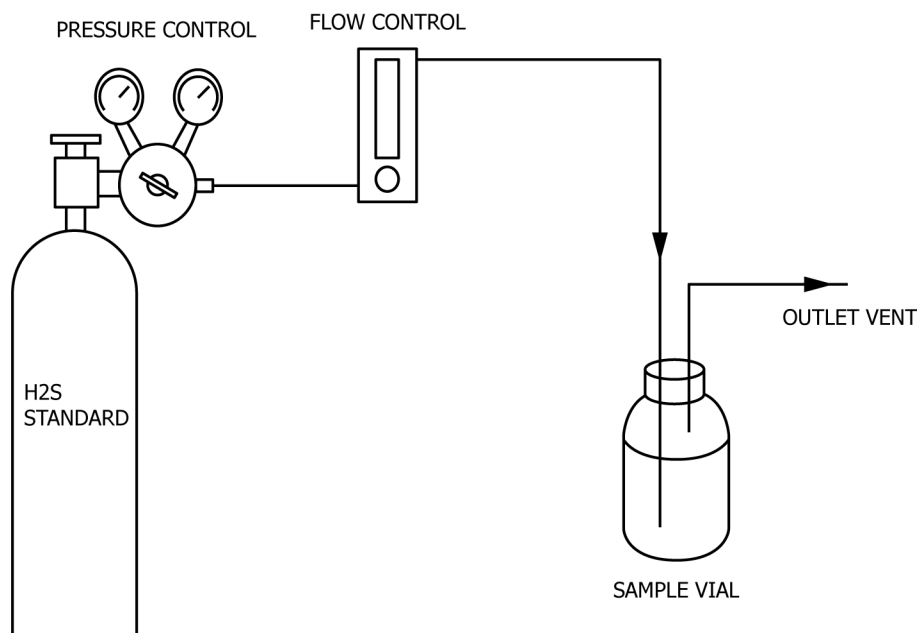


FIG. 2 Gas Calibration Standard Preparation

10.1.8 Immediately after preparing a calibration standard obtain its analyzer response as shown in 10.2.1 – 10.2.7.

NOTE 6—Alternative methods for preparing a calibration standard include: heating a solid to generate H₂S and then using a permeation tube as discussed in Practice D3609 or using pure H₂S and a movable piston as discussed in Test Method D4084.

10.2 Calibration of Analyzer:

10.2.1 Place the headspace vial in a 60 °C oven for at least 5 min but for no more than 15 min. Install an 0.5 mL sample loop if using the 100 µL/L H₂S standard, a 2.5 mL sample loop if using the 10 µL/L H₂S standard, and a 10 mL sample loop if using the 1 µL/L H₂S standard. With Valve 2 in the load position, see Fig. 1 and Valve 1 closed, evacuate the sample loop by opening Valve 3. When a vacuum of at least -70 kPag is achieved, then close Valve 3.

10.2.2 Immediately insert the sampling needle (Fig. 1) through the septum of the headspace vial containing the calibration gas mixture.

10.2.3 Open Valve 1 and let the sample fill the injection loop until a reading of 0 kPag is achieved on the pressure/vacuum gauge. Close Valve 1.

10.2.4 Place Valve 2 in the Inject position (see Fig. 1) for 10 s to allow the carrier gas to sweep the sample to the H₂S analyzer. Return Valve 2 to the load position. Remove sampling needle from the vial. Record reading from the analyzer as reading A₁.

10.2.5 After the injection step, insert needle connected to a line containing nitrogen at atmospheric pressure into the septum to reestablish atmospheric pressure within the vial.

10.2.6 Repeat steps 10.2.1 – 10.2.5 with the same headspace vial but record the reading from the analyzer as reading A₂.

10.2.7 Repeat steps 10.2.1 – 10.2.5 with the same headspace vial but record the reading from the analyzer as reading A₃. Two injections are sufficient for the required calculations, but three are required to verify the correctness of the calibration procedure.

10.2.8 Regress the natural log (ln) of readings A₁, A₂, and A₃ against the number of injections one, two, and three. A linear correlation (correlation coefficient R² > 0.95) must exist to insure the correctness of the calibration procedure. If R² is not greater than 0.95, then repeat the calibration.

10.3 Analyzer Response Factor:

10.3.1 Calculate the total area difference (or total height difference) using Eq 1:⁵

$$A_T = \sum A_n = \frac{A_1^2}{A_1 - A_2} \quad (1)$$

where:

A_T = total area difference (or total height difference),
 A_1 = area (or height) obtained from the first injection, and
 A_2 = area (or height) obtained from the second injection.

10.3.2 Assuming the ideal gas law, calculate the weight of H₂S in the calibration standard by Eq 2:

$$W_{(H_2S)_s} = \frac{PV_v C_{(H_2S)_s} (34.0759) (g/g \times mole) 10^{-6} (\mu L/L) 10^6 (\mu g/g)}{(8313.7162) (mL \times kPa/g \times mole \times ^\circ K) T} \quad (2)$$

where:

$W_{(H_2S)_s}$ = weight of H₂S in calibration standard, μg ,
 P = laboratory barometric pressure, kPa,
 V_v = volume of headspace vial, mL,
 $C_{(H_2S)_s}$ = concentration of H₂S in calibration standard, $\mu L/L$,
 34.0759 = molecular weight of H₂S, g/g \times mole,
 8313.7162 = (mL \times kPa)/(g \times mole \times $^\circ K$) = R = ideal gas constant, and
 T = laboratory ambient temperature, $^\circ K$.

If $P = 101\,325$ kPa, $V_v = 120$ mL, $C_{(H_2S)_s} = 10$ $\mu L/L$ and $T = 298.15$ $^\circ K$ then:

$$\begin{aligned} W_{(H_2S)_s} &= \frac{(101\,325)(kPa)(120)(mL)(10)(\mu L/L)}{(34.0759)(g/g \times mole) 10^{-6} (L/\mu L) 10^6 (\mu g/g)} \\ &= \frac{(8313.7162)(mL \times kPa/g \times mole \times ^\circ K) (298.15)(^\circ K)}{1.67} \mu g \end{aligned} \quad (3)$$

10.3.3 Calculate the response factor from the weight of the H₂S in the calibration standard divided by the total area difference obtained for the standard, Eq 3:

$$R_{F_{H_2S}} = \frac{W_{(H_2S)_s} \mu g}{A_{T_s} \text{ area}} \quad (4)$$

where:

$R_{F_{H_2S}}$ = H₂S response factor, $\mu g/\text{area}$, and
 A_{T_s} = total area or peak height difference from H₂S calibration standard analysis.

11. Procedure

11.1 Remove a sample from refrigerated storage and allow it to stand in the laboratory until it flows freely. A sample can be analyzed as soon as it flows freely. A sample that is still not free flowing after sitting at laboratory ambient for 1 h should be heated gently just until it flows freely. (**Warning**—At no time should the container temperature be allowed to exceed the temperature of the sample at the time.)

11.2 To avoid possible loss of H₂S in the headspace vial by reaction with oxygen, displace the air in the vial with nitrogen prior to transferring a sample into it. Weigh the nitrogen flushed headspace vial and septum seal to the nearest 0.1 mg and then transfer, by any suitable means, as quickly as possible to minimize losses, between 0.05 g and 5.0 g of residual fuel oil sample directly into the nitrogen filled headspace vial, and seal the vial immediately with the septum seal to avoid H₂S losses PTFE side of the septum

⁵ This is one standard formula used in headspace analysis. For the derivation of this formula see Ioffe, B. V., and Vitenberg, A. G., "Head-Space G., "Head-Space Analysis and Related Method in Gas Chromatography," Wiley-Interscience, John Wiley & Sons, New York, 1984, pp. 131–142.