



Designation: D7800/D7800M – 23

Standard Test Method for Determination of Elemental Sulfur in Natural Gas¹

This standard is issued under the fixed designation D7800/D7800M; 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 is primarily for the determination of elemental sulfur in natural gas pipelines, but it may be applied to other gaseous fuel pipelines and applications provided the user has validated its suitability for use. The detection range for elemental sulfur, reported as sulfur, is 0.0018 mg/L to 30 mg/L. The results may also be reported in units of mg/kg or ppm.

1.2 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are not necessarily exact equivalents; therefore, to ensure conformance with the standard, each system shall be used independently of the other, and values from the two systems shall not be combined.

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.*

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

D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration

D1145 Test Method for Sampling Natural Gas (Withdrawn 1986)³

D1945 Test Method for Analysis of Natural Gas by Gas Chromatography

D3609 Practice for Calibration Techniques Using Permeation Tubes

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

D4150 Terminology Relating to Gaseous Fuels

D4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry

D4626 Practice for Calculation of Gas Chromatographic Response Factors

D5287 Practice for Automatic Sampling of Gaseous Fuels

D5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence

D6228 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection

D7165 Practice for Gas Chromatograph Based On-line/At-line Analysis for Sulfur Content of Gaseous Fuels

D7166 Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels

D7551 Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence

D7607 Test Method for Analysis of Oxygen in Gaseous Fuels (Electrochemical Sensor Method)

E840 Practice for Using Flame Photometric Detectors in Gas Chromatography

2.2 ISO Documents⁴

ISO 14532 Natural Gas—Vocabulary

3. Terminology

3.1 Definitions:

3.2 For definitions of general terms used in D03 Gaseous Fuels standards, refer to Terminology D4150.

3.3 Definitions of Terms Specific to This Standard:

¹ This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.06.01 on Analysis of Major Constituents by Gas Chromatography.

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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.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

3.3.1 *elemental sulfur, n*—a pale yellow nonmetallic element occurring in nature and found as a particulate in diesel exhaust, natural gas, and other gaseous fuels.

3.3.1.1 *Discussion*—Elemental sulfur exists in several free and combined allotropic forms.

3.3.2 *episulfide, n*—a class of compound that contains a saturated heterocyclic ring consisting of two carbon atoms and one sulfur atom.

3.3.2.1 *Discussion*—Episulfides are the sulfur analogue of an epoxide. They are also known as thiiranes, olefin sulfides, thioalkylene oxides, and thiacyclopropanes.

3.3.3 *natural gas pipeline, n*—pipeline in which natural gas is transported.

3.3.4 *pipeline, n*—all parts of those physical facilities through which gas moves in transportation, including pipe, valves, and other appurtenance attached to pipe, compressor units, metering stations, regulator stations, delivery stations, holders, and fabricated assemblies.

3.3.5 *polysulfide, n*—a class of chemical compounds containing chains of sulfur atoms.

3.3.5.1 *Discussion*—The two main classes of polysulfides are anions with the general formula Sn^{2-} . These anions are the conjugate bases of the hydrogen polysulfides H_2Sn . Organic polysulfides are also known; the main representatives of which have the formulae $RSnR$, where R = alkyl or aryl.

3.4 Abbreviations and Acronyms:

3.4.1 *DMF*—dimethylformamide

3.4.2 *FPD*—flame photometric detector

3.4.3 *GC*—gas chromatograph

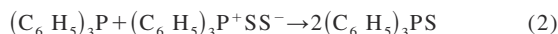
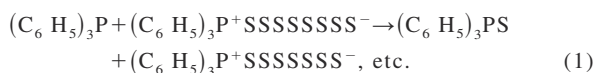
3.4.4 *PFPD*—pulsed flame photometric detector

3.4.5 *SCD*—sulfur chemiluminescence detector

3.4.6 *TPP*—triphenylphosphine

4. Summary of Test Method

4.1 A transportable elemental sulfur reactor is used to convert elemental sulfur in the side stream of a flowing gas stream into an easily detectable species. This is accomplished by sampling a representative portion of the natural gas stream and bubbling it through a chemical reactor containing triphenylphosphine (TPP) in a solution of dimethylformamide (DMF). This solution selectively reacts with crystals of elemental sulfur to produce the elemental sulfur adduct triphenylphosphine sulfide (TPPS) (Eq 1 and Eq 2).⁵



Liquid samples extracted from the transportable elemental sulfur reactor are injected into a gas chromatograph (GC) interfaced to a SCD, FPD, or a PFPD operating in the phosphorus mode. The concentration of TPPS is proportional to the concentration of elemental sulfur found in the gas.

⁵ “Reactions of Elemental Sulfur: I: The Uncatalyzed Reaction of Sulfur with Triarylphosphines,” Bartlett, P. D. and Garbis Meguerian. *Journal of the American Chemical Society*, vol. 78, No. 15, pp 3710, 1956.

4.1.1 Natural gas, at a gauge pressure up to 6.8 MPa [1000 psig], is introduced into a transportable elemental sulfur reactor through a 6 mm [$\frac{1}{4}$ in.] stainless steel probe located in the middle to top third of a pipeline. The reactor consists of an enclosure that is heated to approximately 71 °C [160 °F] and contains a series of three high pressure bubblers, which contain the reaction solution. A fourth bubbler is located outside the heated enclosure to act as a reaction solution vapor condenser. The gas flows through a coalescing filter to remove any liquid droplets present to keep the meter from being contaminated. The gas is regulated to provide a constant pressure to a metering valve that is used to control the flow rate of gas through the system. The meter records the total volume that has passed through the reactor during the test period. The apparatus is depicted in Fig. 1.

4.1.2 Liquid samples extracted from the transportable elemental sulfur reactor are injected into a gas chromatograph interfaced to an SCD, FPD or PFPD configured to detect phosphorus. The TPPS and surrogate, $TPPO_4$, are chromatographically resolved from other compounds in the sample, integrated, and concentration of elemental sulfur in the original natural gas sample is calculated using the equations described in subsection 4.1.

5. Significance and Use

5.1 Elemental sulfur impacts the quality of pipeline natural gas and deposits on pipeline flanges, fittings and valves, thereby impacting their performance. Natural gas suppliers and distributors require a standardized test method for measuring elemental sulfur. Some government regulators are also interested in measuring elemental sulfur since it would provide a means for assessing the contribution of elemental sulfur in pipelines to the SO_x emission inventory from burning of gaseous fuels. Use of this method in concert with sulfur gas laboratory test methods such as Test Methods **D4084**, **D4468**, **D5504**, and **D6228** or on-line methods such as **D7165** or **D7166** can provide users with a comprehensive sulfur compound profile for natural gas or other gaseous fuels. Other applications may include elemental sulfur in particulate deposits such as diesel exhausts.

6. Interferences

6.1 Triphenylphosphine abstracts sulfur from polysulfide and episulfides, as well as elemental sulfur. Hence, polysulfide and episulfides that react with TPPS can interfere with this analysis. Simple organosulfur compounds such as thiols and thioethers are unreactive.

6.2 Triphenylphosphine selenide (Ph_3PSe) is an interferent that may be encountered in some biogases.

6.3 Triphenylphosphine oxide (Ph_3PO) is an interferent resulting from slow oxidation of triphenylphosphine. (Eq 3).



6.4 During the sample collection, Hydrogen Sulfide (H_2S) in the gas stream at elevated temperatures may react with TPP. Also, residual H_2S in the medium may react with the TPP at the GC injector temperatures required to volatilize the sample.



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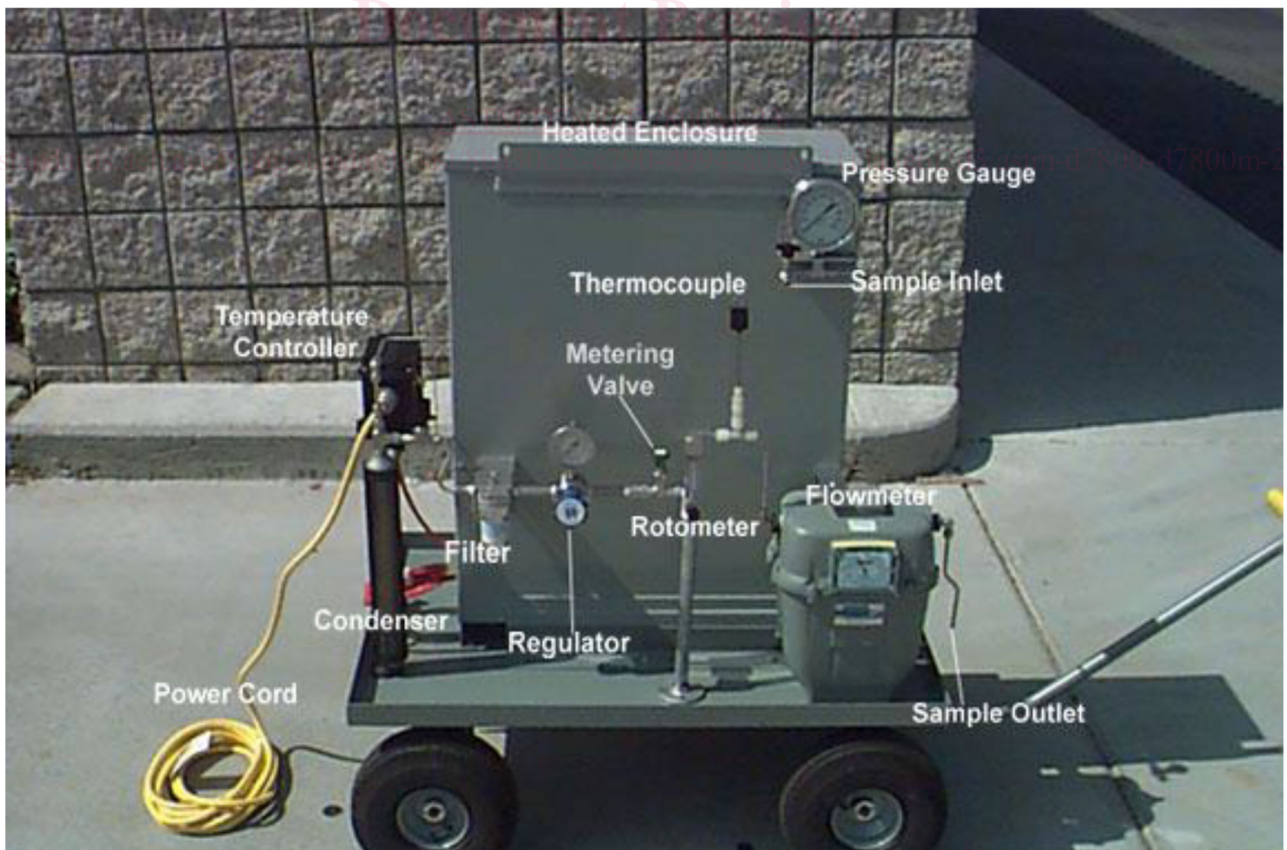
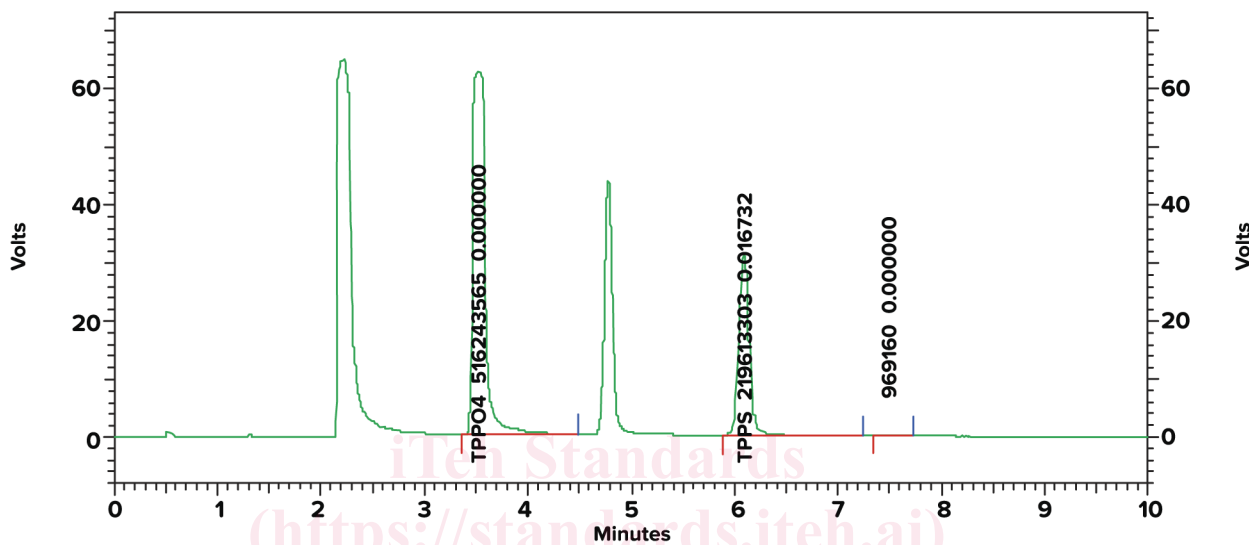


FIG. 1 Reactor

SCD Results

Name	Retention Time	Area	ESTD concentration
TPPO4	3.528	516243565	0.000000
TPPS	6.095	219613303	0.016732

Totals		735856868	0.016732
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FPD Results

Name	Retention Time	Area	ESTD concentration
TPPO4	3.715	1186491	1.#INF00
TPPS	6.427	25643787	0.000900

Totals		26830278	1.#INF00
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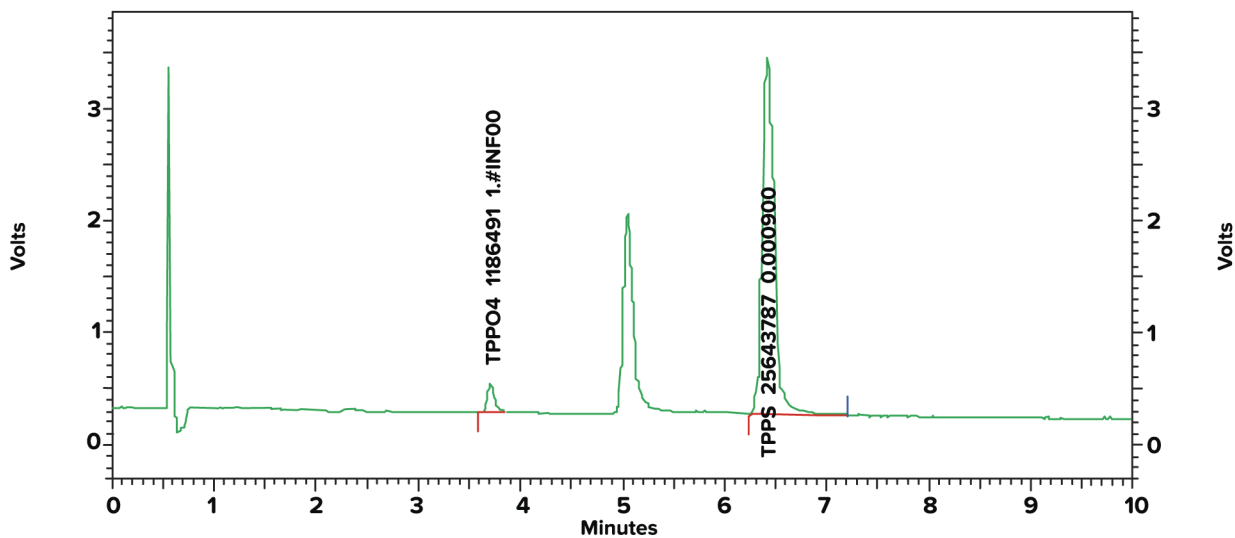


FIG. 2 Elemental Sulfur SCD and FPD Chromatograms

6.5 There may also be inadvertent oxidation of the residual H₂S to elemental sulfur. To avoid extraneous oxidation, precautions are taken with respect to preparation of the test solutions, cleaning of the apparatus and handling of the reacted solutions.

7. Apparatus

7.1 For each test site, the following equipment is needed:

7.1.1 Reactor cart with bubblers filled with TPPS in a solution of DMF and purged with nitrogen. The bubblers are three 500 mL polytetrafluoroethylene-lined steel cylinders. The three cylinders are housed in an insulated cabinet fitted with heat trace tape to generate elevated temperatures, nominally 70 °C to 90 °C [160 °F to 195 °F], required for the test. A fourth 500 mL steel cylinder is connected downstream outside of the insulated cabinet. The interior of the reactor is rated for operation in a Class 1 Division 2 hazardous environment, however, the heating cable termination cap and the thermostat box may be rated NEMA 4 (weather proof), so the reactor is typically located at least 4.6 m [15 ft.] away from the pipeline;

7.1.2 Coalescing filter and filter element,

7.1.3 A 6 mm [$\frac{1}{4}$ in.] sample probe of suitable length so that the probe tip can be positioned between the middle and a position one-third from the top of the pipe,

7.1.4 A 4.6 m [15 ft] length of 6 mm [$\frac{1}{4}$ in.] stainless tubing (or longer depending on site),

7.1.5 Thermocouple probe,

7.1.6 Thin wire thermocouple,

7.1.7 Electronic thermometer or data logger,

7.1.8 Stopwatch,

7.1.9 Oxygen analyzer, and

7.1.10 Electrical connection and 15 m [nominally 50 ft] cord (or longer depending on site).

7.2 The following laboratory equipment is needed:

7.2.1 Chromatograph,

7.2.1.1 Any gas chromatograph of standard manufacture, with hardware necessary for interfacing to an SCD, PFPD, or FPD, and containing all features necessary for the intended application(s) can be used. The detector should be configured for selective detection of phosphorus and placed in service in accordance with the manufacturer's instructions. This analysis can be performed under a wide range of operating conditions. Typical, minimal performance criteria for chromatographic conditions are:

(a) Operating conditions must be set such that TPPS separates from the matrix and other sulfur species that may be present in a sample.

(b) The injection system must transfer the TPPS to the GC column without loss or absorption, without reaction to the TPPS and without excessive carryover between samples.

The operating conditions presented in Fig. 3 and Fig. 4 have been successfully used to fulfill the above criteria. Fig. 2 illustrates a typical analysis of TPPS determined from a natural gas sample.

7.2.1.2 SCD—Place in service in accordance with the manufacturer's instructions, and configure the detector for phosphorus-selective detection or other selective sulfur mode to achieve sulfur speciation. Matrix interference is occasionally

FIG. 3 Example of General SCD Method Parameters

Method Description

Program for Analysis of TPPS
 Injection Temperature = 275 °C
 Column Temperature = 155:1 at 25 > 275:9.2
 Valve On = 0
 Detector Temperature = Off

GC Parameters

Temperature Setup
 Oven Parameters
 Oven: On
 Oven Equilib Time: 0.00 min
 Oven Max Temperature: 320 °C
 Oven Cryo: Off
 Oven Cryo Blast: Off
 Oven Ambient: 20 °C
 Oven Temperature Program

Init Level

Final Temp: 155.00 °C
 Final Time: 1.00 min
 Level 1
 Rate: 25.00 °C/min
 Final Temp: 275.00 °C
 Final Time: 4.70 min
 Zone Temperatures
 Injector A Setpoint: 275 °C

Detector Setup

Detector B: On
 Det. B Negative Polarity: Off
 Signal 1 Parameters
 Source: Det. B
 Attenuation: 0
 Range: 0
 Auto Zero: Off
 Inlet A
 Constant Flow: On
 Constant Flow Pressure: 12.60 kPa
 Constant Flow Temperature: 100.00 °C
 Column Length: 50.00 m
 Column ID: 0.52 mm
 Column Gas: He

Vacuum Compensation: Off

Split Flow: 0.00 mL/min
 Split Ratio: (0.00 : 1)
 Inlet A Pressure Program

Init Level

Pressure: 0.00 kPa
 Final Time: 0.00 min
 Pressure: 0.00 kPa
 Final Time: 0.00 min
 Inlet Temperature Setup

Inlet A

Zone Temperature: On
 Setpoint Temperature: 275 °C
 Oven Track: Off
 Inlet A Temperature Program

Init Level

Final Temp: 0.00 °C
 Final Time: 0.00 min
 Init Level

Final Temp: 0.00 °C
 Final Time: 0.00 min
 Instrument Setup

Minimum Stable Baseline Time: 15.0 min
 Maximum Test Time: 15.0 min

observed when changing sample size. Matrix interference is also indicated by recoveries less than 90 % or greater than 110 % for samples spiked with calibration gas or samples diluted with air. When matrix interference is indicated, samples

FIG. 4 Example of General FPD Method Parameters
Temperature Setup

Oven Parameters
 Oven: On
 Oven Equilib Time: 0.00 min
 Oven Max Temperature: 300 °C
 Oven Cryo: Off
 Oven Cryo Blast: Off
 Oven Ambient: 20 °C
 Timeout Detection: Off
 Timeout Detector: 10.00 min
 Fault Detection: Off
 Oven Temperature Program
 Level Rate Next Temp Hold Time
 Initial 250.00 °C 10.00 min
 Zone Temperatures
 Front Inlet Setpoint: 300 °C
 Back Inlet Setpoint: Off
 Front Detector Setpoint: Off
 Back Detector Setpoint: 250 °C
 Aux 1 Setpoint: Off
 Aux 2 Setpoint: 250 °C
 Inlet Temperature Setup
 Inlet: Front
 Oven Track: Off
 Zone Temperature: Off
 Inlet Temperature Program: Off
 Inlet: Back
 Oven Track: Off
 Zone Temperature: Off
 Inlet Temperature Program: Off
 Inlet: Aux 1
 Oven Track: Off
 Zone Temperature: Off
 Inlet Temperature Program: Off
 Inlet: Aux 2
 Oven Track: Off
 Zone Temperature: 250 °C
 Inlet Temperature Program: Off

Inlet Pressure Setup

General Inlet Settings
 Split Mode: Splitless
 Purge Flow: 10.00 mL/min at 0.00 min
 Gas Saver: Off

Column Setup

Column 1
 Capillary Column
 Length: 30.00 m
 Inside Diameter: 0.53 mm
 Film Thickness: 1.50 µm
 Inlet: Front
 Gas: Helium
 Carrier Flow
 Column Mode: Constant Flow
 Flow: 9.80 mL/min
 Signals Setup
 Signal 1 Parameters
 Detector: Back Det.
 Range: 0
 Attenuation: 0
 Auto Zero: Off
 Quantitation: Area
 Calibration Flag: Replace
 Calibration Weight: 0
 Calibration Unit: mg/mL
 Group Table
 Acquisition: Yes
 Current Frequency: 20 (Hz)
 Run Time: 10 (min)
 Delay: 0 (min)

tion procedure results in recoveries within 10 % of theoretical results. Operational features specific to the interface configuration employed are described in the following. For further information on SCD operation and limitations, the user is referred to Test Method **D5504**.

7.2.1.3 PFPD and FPD—Place into service in accordance with manufacturer’s instructions, and configure the gas flow rates and optical filter for phosphorus-selective detection. For further information on PFPD and FPD operation see Practice **E840**.

7.2.1.4 Column—A variety of columns can be used in performing the determination of elemental sulfur according to this standard. Typically, a 60 m x 0.53 mm ID fused silica open tubular column containing a 5 µm film thickness of bonded methyl silicone liquid phase is used. The selected column must provide retention and resolution characteristics such as those listed in **Fig. 5**. The column must be inert towards TPPS. The column must also demonstrate a sufficiently low liquid phase bleed at high temperature such that loss of detector response is not encountered while operating the column at 200 °C [392 °F].

7.2.2 Recorder. A 0 mV to 1 mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less can be used.

7.2.3 Integrator. An electronic integrating device or computer can be used. The device and software must have the following capabilities:

- 7.2.3.1** Graphic presentation of the chromatogram,
- 7.2.3.2** Digital display of chromatographic peak areas,
- 7.2.3.3** Identification of TPPS chromatographic peak by retention time or relative retention time, or both,
- 7.2.3.4** Calculation and use of the TPPS response factor, and
- 7.2.3.5** External standard calculation and data presentation.

8. Reagents and Materials

8.1 For each test site the following reagents and materials are needed:

- 8.1.1** 1 L ACS reagent grade dimethylformamide (DMF),
- 8.1.2** 5 g of doubly recrystallized TPP supplied,
- 8.1.3** 1 g of triphenylphosphate (TPPO₄),
- 8.1.4** 1 L acetone,
- 8.1.5** Four 250 mL plastic bottles with lids and labels,
- 8.1.6** One 100 mL plastic bottles with lids and labels,
- 8.1.7** One 20 mL plastic bottle with lid and label,
- 8.1.8** Five 8 mL glass vials with lids and labels,
- 8.1.9** Ten 2 mL Target vials,
- 8.1.10** Ultra-high purity (UHP) nitrogen,
- 8.1.11** Eight polyvinyl fluoride bags (optional), and
- 8.1.12** Four stainless steel cylinders.

9. Hazards

9.1 Improper use of an elemental sulfur reactor can result in burns, fires, or explosions; therefore, users are advised to familiarize themselves with the chemical and physical properties of each of the reagents and materials listed in Section **8** and the safe operation of the apparatus listed in Section **7**.

may be analyzed by dilution or application of other mitigation efforts provided a spiked sample performed using the mitiga-

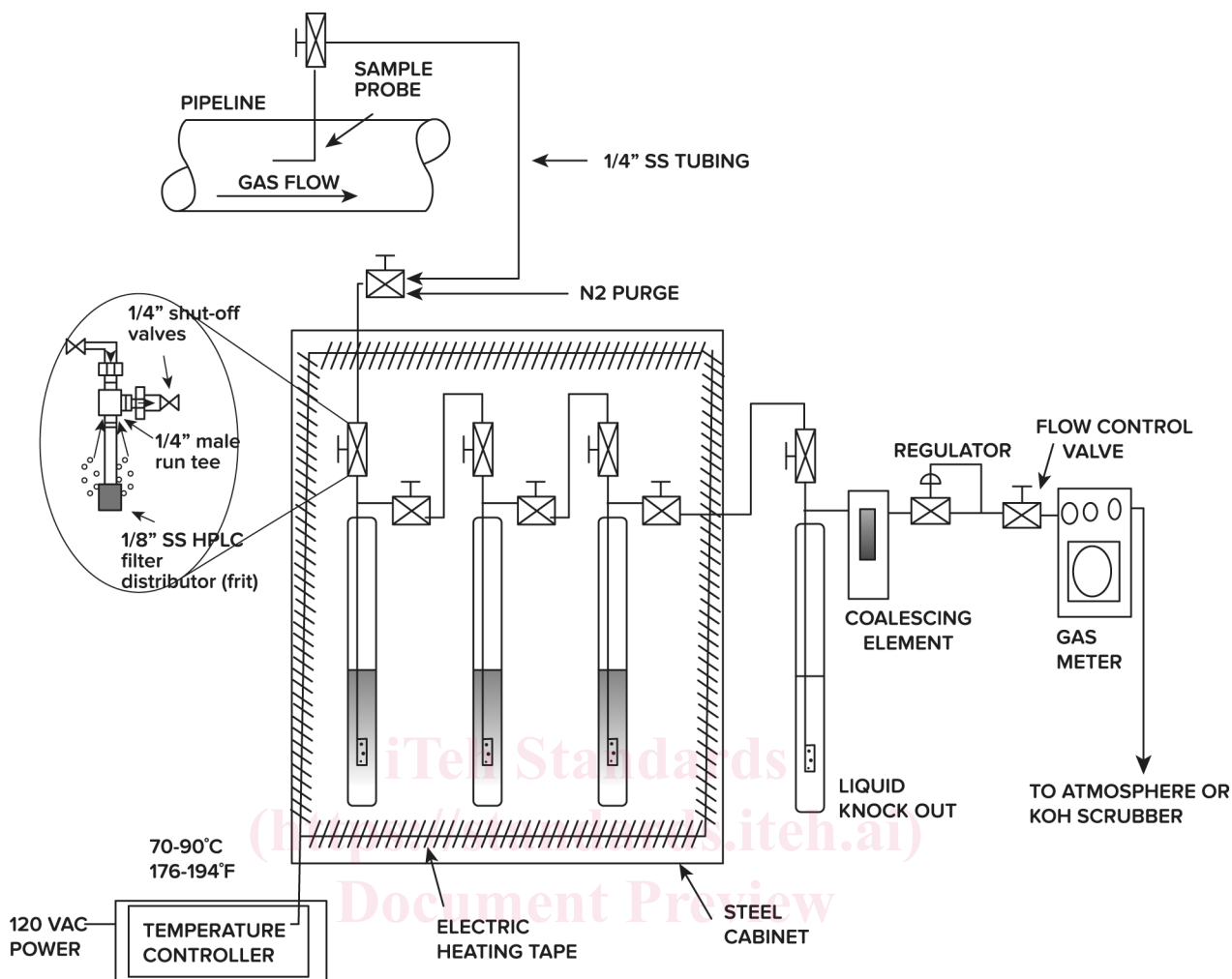


FIG. 5

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9.2 Gloves, safety glasses, and lab coat must be worn during the entire preparation of apparatus and transferring of solution. Avoid any contact of the chemicals on clothing and exposed skin.

9.3 While working with solutions and performing recrystallizations, users are advised to work under a fume hood. Verify that hood vents are operating properly and that hood glass shields are at the proper elevation to ensure that the average ventilation rate is 0.5 m/s [100 linear feet per minute] with a minimum of 0.36 m/s [70 linear feet per minute] at any single point.

9.4 Field safety precautions must be taken when at the test site and working with high pressure pipeline gas. Wear goggles, gloves, and hard hats.

10. Preparation of Apparatus

NOTE 1—Read and understand the hazards of using TPP and DMF as described in the material safety data sheets before preparing solutions used in this standard.

10.1 Weigh $5.00 \text{ g} \pm 0.01 \text{ g}$ of doubly recrystallized triphenylphosphine (TPP) into a 1 L volumetric flask.

10.2 Add $1.000 \text{ g} \pm 0.001 \text{ g}$ of triphenylphosphate (TPPO₄) as a surrogate. Record the exact weight on a form such as that in Fig. 6.

10.3 Add ACS reagent grade dimethylformamide (DMF) to dissolve the compounds and make up exactly 1 L. Mix the solution with a magnetic stirrer until all solids are dissolved.

10.4 Keep the volumetric flask sealed with a glass stopper and wrapped with parafilm. The shelf life of the reagent is several weeks.

10.5 Add 10 mL of acetone or DMF into a bubbler to rinse out any sulfur residue. Repeat this three times. Repeat for all other bubblers. Similarly clean the connective piping and filter housing.

10.6 Pipette precisely 300 mL of the TPP solution into each of three bubblers.

10.7 Any remaining solution (there should be ~ 100 mL left) should be split between a plastic bottle and vial which are sealed and labeled as “blank” with an identifying test number.