



# Standard Test Method for Determination of Elemental Sulfur in Natural Gas<sup>1</sup>

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 ( $\epsilon$ ) 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 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 may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the 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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D1072 Test Method for Total Sulfur in Fuel Gases by Combustion and Barium Chloride Titration
- D1145 Test Method for Sampling Natural Gas (Withdrawn 1986)<sup>3</sup>
- 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 Documents

- ISO 14532 Natural Gas—Vocabulary

## 3. Terminology

### 3.1 Definitions:

3.1.1 *compressed natural gas (CNG), n*—natural gas that is typically pressurized to 24.8 MPa [3,600 psi]. CNG is primarily used as a vehicular fuel. **D4150-08 with modifications**

3.1.2 *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. It exists in several free and combined allotropic forms.

3.1.3 *episulfide, n*—a class of compound that contains a saturated heterocyclic ring consisting of two carbon atoms and one sulfur atom. It is the sulfur analogue of an epoxide. They are also known as thiiranes, olefin sulfides, thioalkylene oxides, and thiacyclopanes.

3.1.4 *liquefied natural gas (LNG), n*—natural gas that has been liquefied, after processing, for storage or transportation purposes. **ISO 14532**

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

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<sup>2</sup> 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.

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

3.1.5 *natural gas, n*—a naturally occurring mixture of hydrocarbon and nonhydrocarbon gases found in porous geological formations (reservoirs) beneath the earth’s surface, often in association with petroleum. The principal constituent of natural gas is methane. **D4150-08**

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

3.1.7 *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.

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

### 3.2 Acronyms:

3.2.1 *DMF*—dimethylformamide

3.2.2 *FPD*—flame photometric detector

3.2.3 *GC*—gas chromatograph

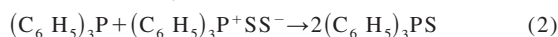
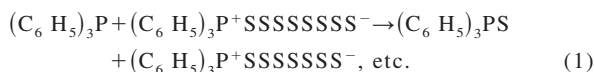
3.2.4 *PFPD*—pulsed flame photometric detector

3.2.5 *SCD*—sulfur chemiluminescence detector

3.2.6 *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).<sup>5</sup>



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.

4.1.1 Natural gas, at a gauge pressure up to 6.8 MPa [1,000 psig], is introduced into a transportable elemental sulfur reactor through a 6 mm [¼ 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

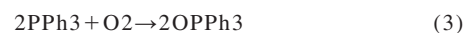
5.1 Elemental sulfur impacts the quality of pipeline natural gas and deposits on pipeline flanges, fittings and valves, thereby impacting their performance. Natural gas suppliers and distributors require a standardized test method for measuring elemental sulfur. Some government regulators are also interested in measuring elemental sulfur since it would provide a means for assessing the contribution of elemental sulfur in pipelines to the SO<sub>x</sub> 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<sub>3</sub>PSe) is an interferent that may be encountered in some biogases.

6.3 Triphenylphosphine oxide (Ph<sub>3</sub>PO) is an interferent resulting from slow oxidation of triphenylphosphine. (Eq 3).



6.4 During the sample collection, Hydrogen Sulfide (H<sub>2</sub>S) in the gas stream at elevated temperatures may react with TPP. Also, residual H<sub>2</sub>S in the medium may react with the TPP at the GC injector temperatures required to volatilize the sample.

6.5 There may also be inadvertent oxidation of the residual H<sub>2</sub>S 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:

<sup>5</sup> “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.

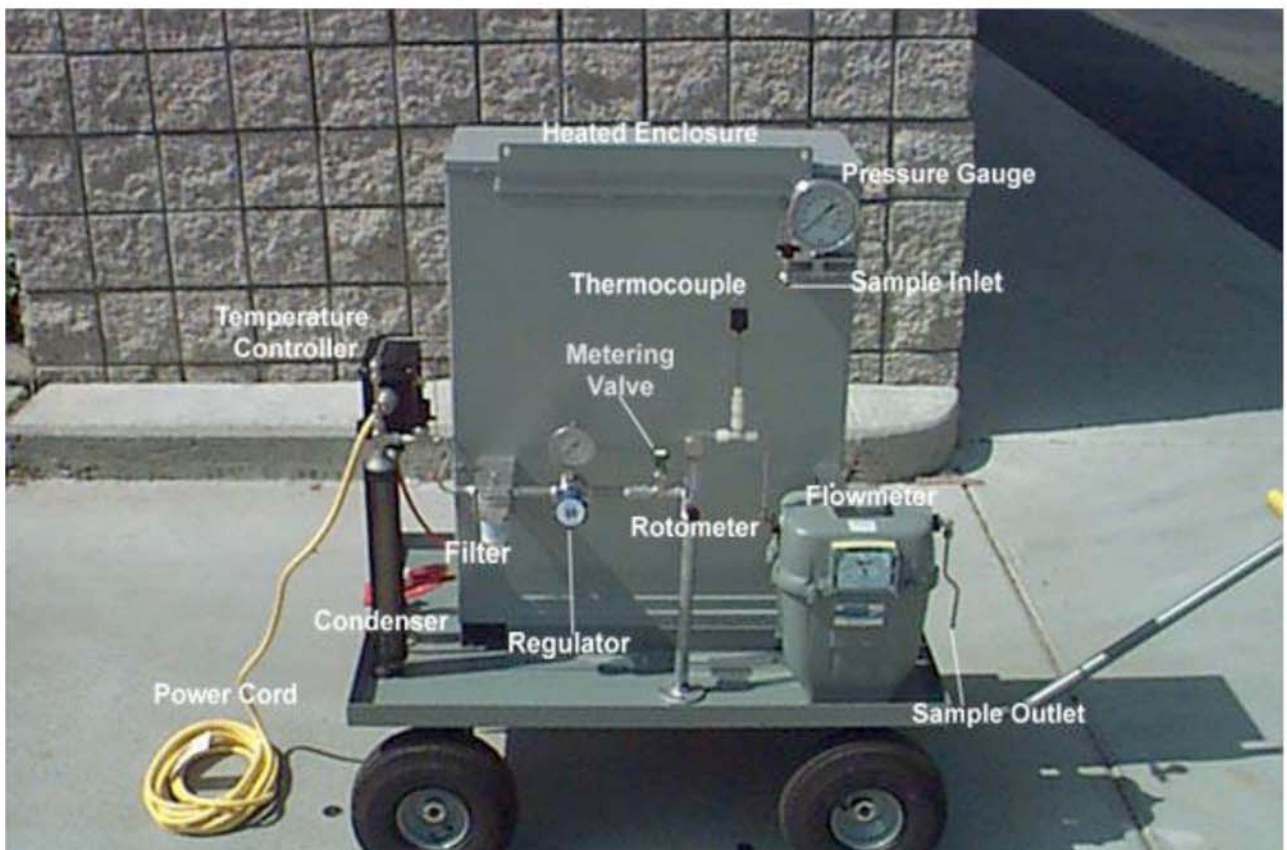
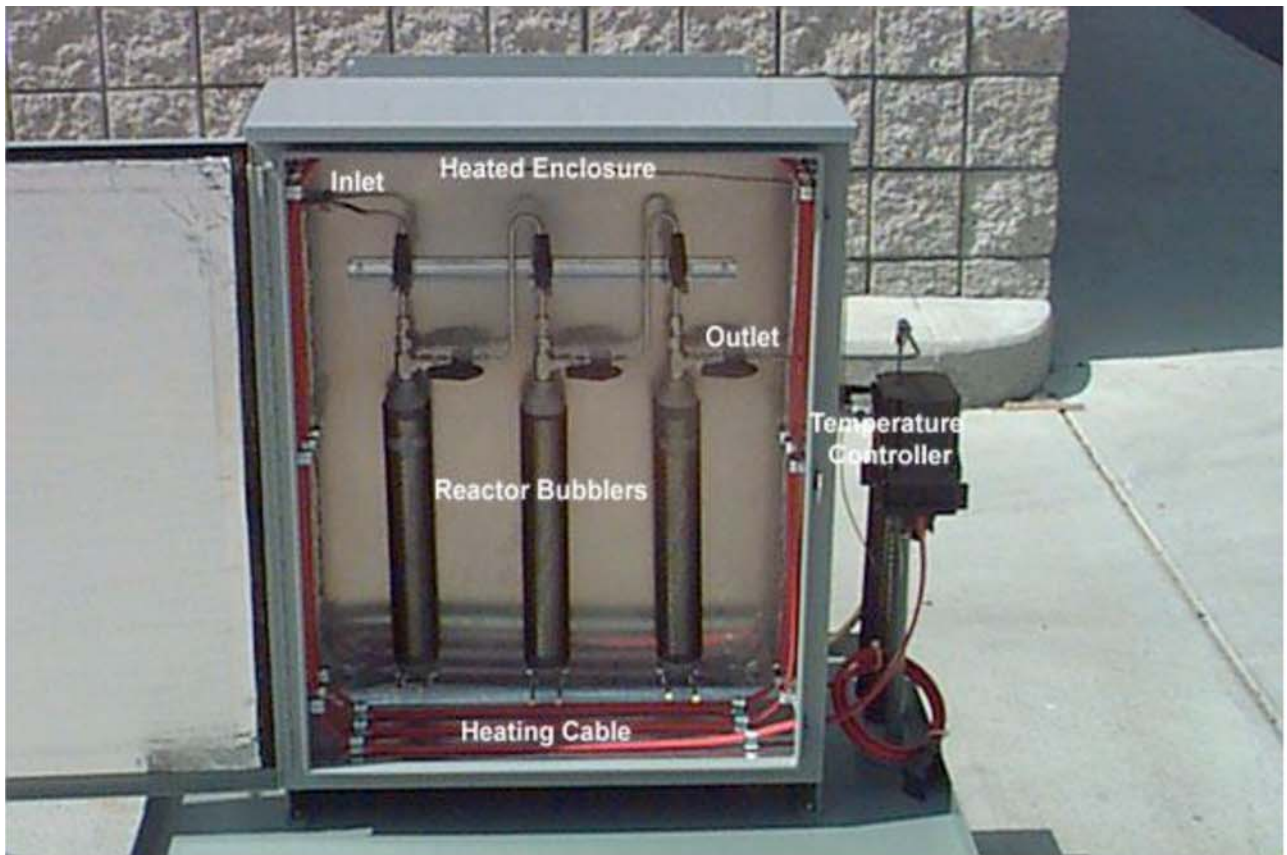


FIG. 1 Reactor



7.1.1 Reactor cart with bubblers filled with TPP 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 to 90 °C [160 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 [¼ 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 [¼ 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 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 may be analyzed by dilution or application of other mitigation efforts provided a spiked sample performed using the mitigation procedure results in recoveries within 10% of theoretical results. Operational features specific to the interface configu-

**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**

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

ration employed are described in the following. For further information on SCD operation and limitations, the user is referred to Test Method **D5504**.

**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)

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 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 (TPPO<sub>4</sub>),
- 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.

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.

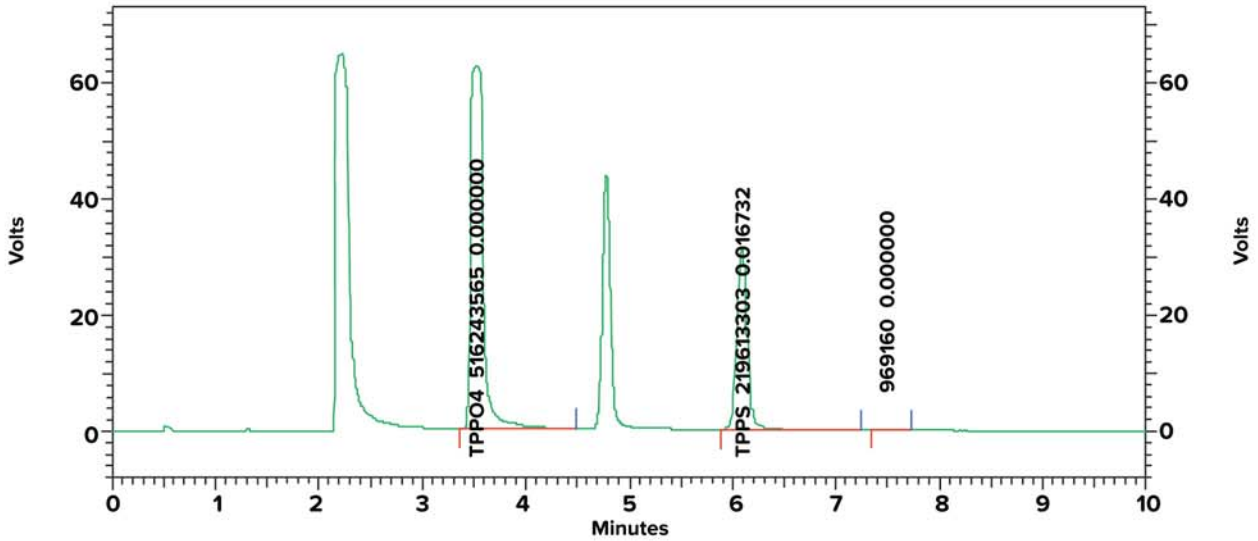
9.3 While working with solutions and performing recrystallizations, users are advised to work under a fume hood. Verify that hood vents are operating properly and that hood glass shields are at the proper elevation to ensure that the

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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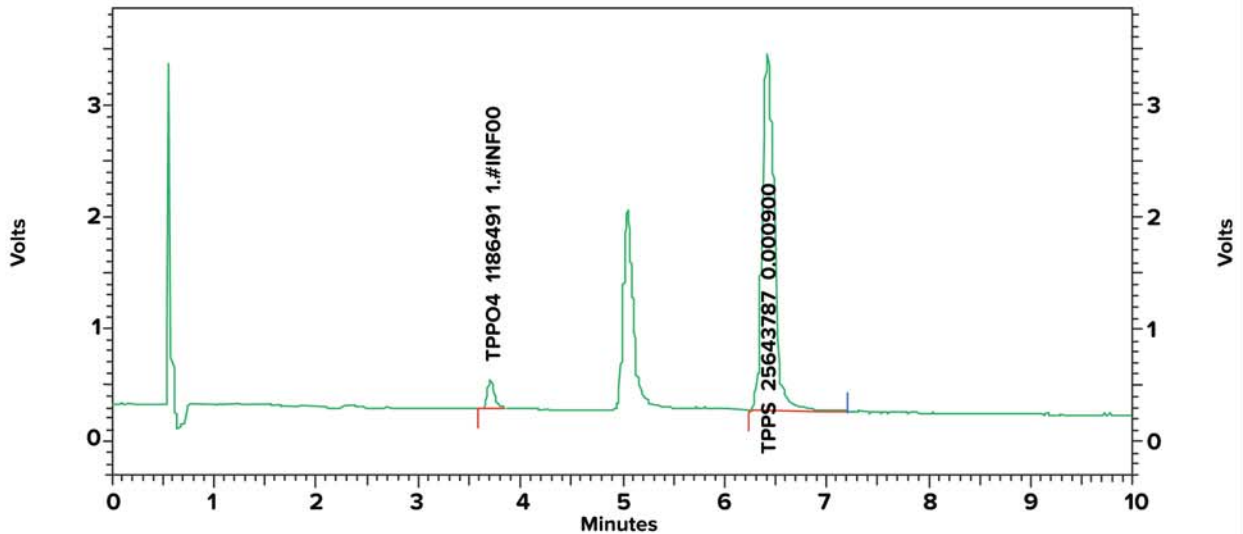


FIG. 2 Elemental Sulfur SCD and FPD Chromatograms

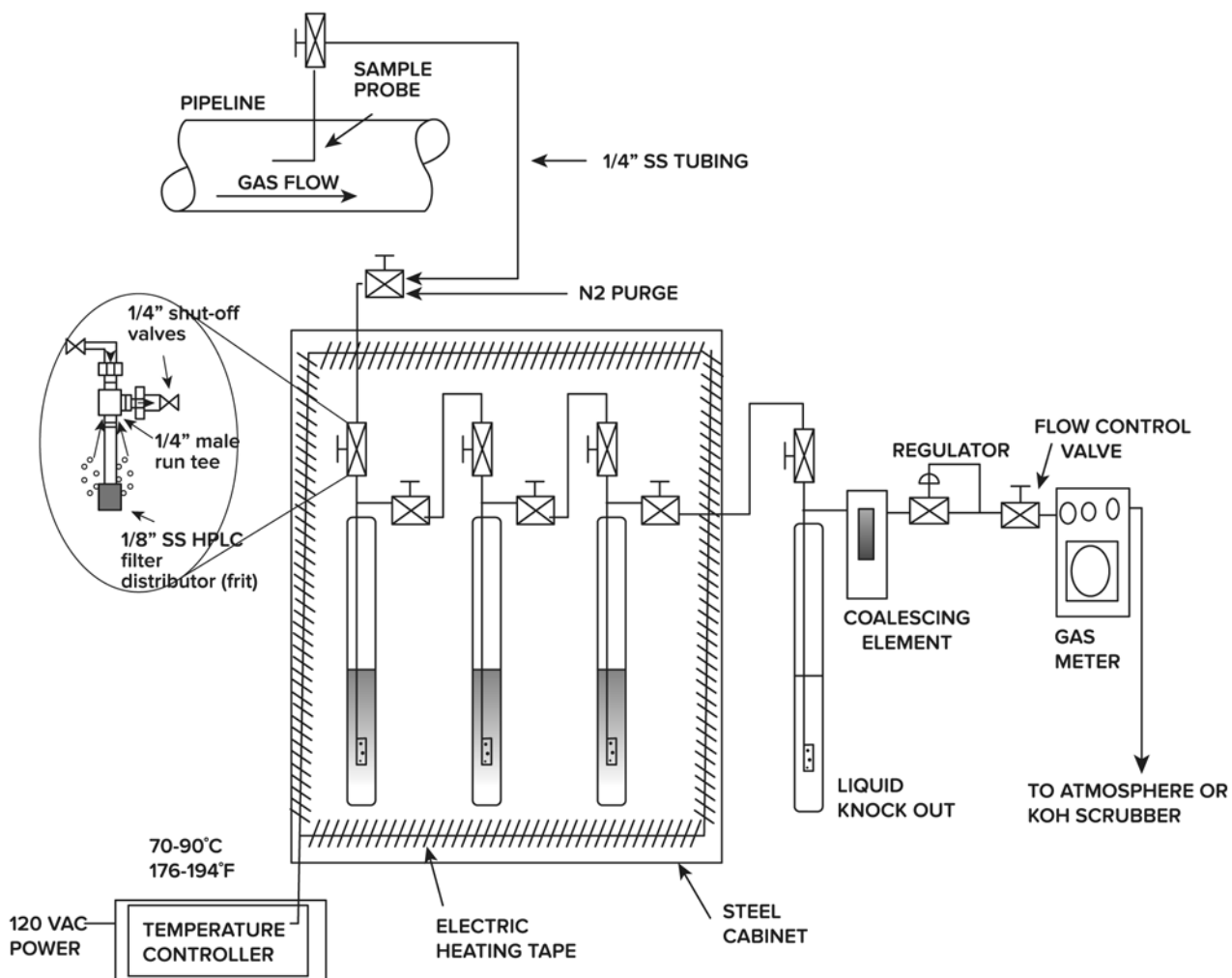


FIG. 5

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

10.2 Add  $1.000 \pm 0.001$  g of triphenylphosphate (TPPO<sub>4</sub>) 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.

10.8 Reinstall the bubblers in the reactor and leak test the system as shown in Fig. 5.

10.9 Connect a UHP nitrogen source with a gauge pressure of less than 138 kPa [20 psig] to the inlet valve of the reactor.

10.9.1 **Warning**—Excessive sudden pressure will damage the bubbler frits!



Test No.  Batch#  Reactor  Bubbler No.

Site

Date Weighed:  Weight (g)

Triphenylphosphine (TPP)

Triphenylphosphate (TPPO4)

Target Sampling Rate  scfm

Target Volume  scf

Initial Meter Read  scf

Final Meter Read  scf

Corrected Volume  scf

Date	Time	Meter			Bubbler		Comments
		Vol. Read	scfm	Temperature	Temperature	Pressure	

Inlet to	Date	Time	Teledyne O2 (ppm)	O2 (ppm)
	Reactor			

Date Logger:	Chem/Share/Spare
Port	Test Point
A	Cabinet
B	MidCyl
C	Meter
D	Outlet

FIG. 6 Elemental Sulfur Reactor Form—Worksheet

10.10 Slowly open the inlet valve and purge the reactor with UHP nitrogen to remove all air (oxygen reacts with TPP and sulfur) for 30 to 60 minutes at 100 to 200 mL/min. Purge the

entire test loop from the gas inlet port to the gas meter. If



possible, monitor the oxygen concentration in the nitrogen as it leaves the apparatus for a better determination of the required purge time.

10.11 Leave a blanket of nitrogen in the system at a nominal gauge pressure of 138 kPa [20 psig].

10.12 Based on the expected elemental sulfur concentration, calculate the desired sampling time. (Based on 300 mL of chemical, a 500 mL/min flow rate, test pressure, and the minimum detection level of the analysis method). See **Table 1** for more details.

10.13 *Transporting Apparatus*

10.13.1 Close all reactor valves.

10.13.2 If the vehicle is equipped with a generator, start the generator and plug in the reactor to heat the enclosure (up to 3 hours before the estimated site arrival time).

10.14 *Site Requirements and Preparation*

10.14.1 A ground fault circuit interrupter adapter,

10.14.2 A 120VAC power (15A circuit or higher) source,

10.14.3 A 18 mm [ $\frac{3}{4}$  in.] or larger full open ball valve on the pipeline,

10.14.4 Pipeline gauge pressure that is less than, or equal to 6.9 MPa [1,000 psig],

10.14.5 Placement of the reactor 15 m [nominally 50 ft.] or further away from the pipeline, and

10.14.6 Plug the reactor into a ground fault circuit interrupter outlet at the sampling site.

**11. Calibration and Standardization**

11.1 Prepare a minimum of five concentrations of TPPS in DMF for calibration of the GC. The concentration range of the standards should span the expected concentration ranges of the samples. A typical calibration range should span from approximately 0.002 mg/mL of TPPS to 0.200 mg/mL of TPPS.

11.2 If TPPO<sub>4</sub> is being used as a surrogate (10.2), a calibration spanning the 1.0 mg/mL concentration of TPPO<sub>4</sub> in the DMF solution used in the reactor will also be required.

**12. Procedure**

12.1 Plug in reactor and set thermostat on the heater. The insulated cabinet temperature is brought up to 71 to 91 °C [160 to 195 °F].

12.2 Plug an electronic thermometer or data logger to the thermocouples on the cabinet, bubbler (mid cylinder), outlet line of the cabinet, and meter.

12.3 When possible, install the sampling probe into the top of the pipe, and insert such that the probe tip is between the middle and a position one-third from the top of the pipe. Connect the stainless steel tubing to the probe valve.

**TABLE 1 Recommended Flow Rates**

<b>Estimated Recovered Sulfur For Various Concentrations in Transmission/Distribution System</b>									
Assume actual flow rate is .500 L/min. (*0.0353147 ft <sup>3</sup> /L= 0.0176573 ft <sup>3</sup> /min.)									
Gas Pressure		GasZFactor	StdGasFlow	*Total Flow Time = 24 hrs.					
(psig)	(psia)	@ 60F, P <sub>ACT</sub> (psia)	(ft <sup>3</sup> /min.)	TotalGasVol. (ft <sup>3</sup> )	Wt.Recovered S <sub>g</sub>				
					@ 0.0001 #MMCF (g)	@ 0.001 #MMCF (g)	@ 0.001 #MMCF (g)	@ 0.1 #MMCF (g)	@ 0.34 #MMCF (g)
1000	1015	0.8765	1.3910	2003	0.0000909	0.0009086	0.0090855	0.0908551	0.3089074
500	515	0.9326	0.6633	955	0.0000433	0.0004333	0.0043326	0.0433258	0.1473079
300	315	0.9575	0.3952	569	0.0000258	0.0002581	0.0025811	0.0258111	0.0877578
200	215	0.9706	0.2661	383	0.0000174	0.0001738	0.0017379	0.0173793	0.0590898
100	115	0.9841	0.1404	202	0.0000092	0.0000917	0.0009168	0.0091684	0.0311726
50	65	0.9911	0.0788	113	0.0000051	0.0000515	0.0005146	0.0051455	0.0174948
40	55	0.9923	0.0666	95.9	0.0000043	0.0000435	0.0004349	0.0043487	0.0147854
30	45	0.9939	0.0544	78.3	0.0000036	0.0000355	0.0003552	0.0035523	0.0120777
20	35	0.9951	0.0422	60.8	0.0000028	0.0000276	0.0002760	0.0027595	0.0093824
10	25	0.9970	0.0301	43.4	0.0000020	0.0000197	0.0001967	0.0019673	0.0066890

Shaded area potentially below detection limit of sulfur in solutions using 3 X 300mL for a 24 hr. flow period, depending on distribution of sulfur in bubblers.

\* Actual flow time may vary depending on pressure and temperature conditions at the point of sampling

12.4 With a small gas flow (100 mL/min) going through the sample tubing, connect the tubing to the reactor.

12.5 Open the isolation valves across each bubbler. Close the metering valve.

12.6 Very slowly, open the reactor inlet needle valve to pressurize the system.

12.6.1 **Warning**—The pressure rise should be less than 1,380 kPa [200 psi per minute], or bubbler frit damage will result!

12.7 Leak test all connections outside of the enclosure.

12.8 Set the regulator to a gauge pressure of roughly 350 kPa [50 psig].

12.9 Do not proceed until the temperature of the bubblers inside the enclosure has reached 71 °C [160 °F]. This typically takes about 2 hours from when initially plugged in.

12.10 If the temperature is still under 71 °C [160 °F] after 2 ½ hours, remove the temperature controller box lid and increase the setting.

12.11 Record the initial meter volume, and the sampling starting time.

12.12 Adjust the metering valve until a 500 mL/min flow rate is achieved.

12.13 Record the gas temperatures from the bubbler and the thermocouple probe in the plastic tee upstream of the meter.

12.14 Take duplicate polyvinyl fluoride bag samples of the natural gas upstream of the bubblers and downstream of the meter. Take duplicate samples of the inlet gas stream using the stainless steel sample containers.

12.15 Analyze the inlet gas stream for oxygen content using an oxygen analyzer.

12.16 Monitor the enclosure temperature for at least ½ hour to ensure proper thermostat operation and record temperatures on form (Fig. 6).

12.17 Lock the reactor enclosure doors and lock the area gate before leaving the reactor unattended.

12.18 Towards the end of the sampling period, take another set of gas samples (repeat 12.14 and 12.15).

12.19 At the end of the sampling period, record the gas temperature, pressure, time, and meter volume reading.

12.20 Detach the reactor from the gas inlet. Reduce the gauge pressure of the system to 483 kPa [70 psig]. Close all the valves in reverse order (metering valve to first cylinder inlet valve).

12.21 Unplug the reactor. Stop and disconnect the data logger from the thermocouples.

12.22 Upon return to the lab, open all valves. Purge the system with nitrogen for one hour at 100 to 200 mL/min.

### 12.23 Removing the Cylinders

12.23.1 Close the inlet and outlet cylinder valves inside the enclosure.

12.23.2 If the cylinders are not numbered, tag each cylinder as either the first, second, or third in the series.

12.23.3 Remove each cylinder from inside the enclosure, leaving the valves on the cylinder.

12.23.4 Using the cylinder outlet valve, depressurize each cylinder down to 350 kPa [50 psig] or less.

12.23.4.1 **Warning**—Hazardous fluid will spray out if the inlet valve is opened!

### 12.24 Transferring the Solution

12.24.1 Label three 250 mL bottles with the cylinder position, sample location, and sample date. Roll each cylinder to wet the entire inner surface of the cylinder and to evenly disperse the solid reactant throughout the solution.

12.24.2 Place the cylinders (one at a time) and the bottles (one at a time) under the hood.

12.24.3 Tip the cylinder toward the bottle to drain the solution from the outlet valve.

12.24.4 Carefully open the valve to slowly drain all the liquid into the bottle, filling it completely to the top in order to minimize the head space.

12.24.5 To drain the remaining liquids, use a low pressure nitrogen purge on the inlet to the cylinder.

12.24.5.1 **Warning**—Do not expose the filled bottles to an increase in temperature or they may burst.

12.24.6 Measure the volume of liquid collected from each cylinder in a graduated cylinder.

12.24.7 For each cylinder, place liquid into vial. Drain the rest of the liquids into the appropriately labeled 250 mL bottle and seal.

12.24.8 Rinse the tubing between the bubblers with acetone.

12.24.9 The apparatus cylinders must then be thoroughly rinsed out with acetone and air dried before being reloaded with a fresh solution aliquot. The apparatus flow lines should likewise be rinsed out.

### 12.25 Condensing Bubbler

12.25.1 Drain the liquid from the condensing bubbler and coalescing filter.

12.25.2 Measure and record the final liquid volume in the condensing bubbler by pouring it in a graduated cylinder.

12.25.3 The solution should be saved into 2 mL Target vial and the rest in a 250 mL bottle, labeled with the bubbler sample location and date.

12.25.4 The filter should be saved in a 20 mL bottle, labeled with the filter position, sample location and date.

12.25.5 For the first few tests, the carryover solution should be analyzed, to assure the solution carry over is prevented.

12.26 *Analyses*—The chromatograms and chromatographic conditions are listed in Fig. 2 and Fig. 3.

12.27 Introduce a representative aliquot of the sample into the gas chromatograph

12.27.1 Obtain chromatographic data using the chromatographic conditions described in Fig. 3 and record the data using an integrator or computer-based chromatographic data system.

12.27.2 Measure the area of the TPPS and TPPO<sub>4</sub> peaks. The measurement of the sample peaks should be consistent with the method used for measuring peak areas in the calibration standards. Typical chromatograms for SCD and FPD detectors are shown in Fig. 2.

12.27.3 Calculate the concentration of elemental sulfur in the natural gas sample using the information in Section 1.

12.28 Analyze the blank and subtract from the results.

12.29 Determine the hydrocarbon and inert composition of the reactor inlet gas samples in the stainless steel cylinder using a gas chromatograph with TCD (Test Method D1945).

12.30 Determine the sulfur composition of the reactor inlet and outlet gas samples in the polyvinyl fluoride bags using a gas chromatograph interfaced to an SCD.

### 13. Calculation or Interpretation of Results

13.1 Calculate the mg/m<sup>3</sup> of elemental sulfur at Standard Temperature and Pressure (15.6°C [60°F]), (1 atm, 101.325 kPa [14.696 psia]) in the gas sample from the GC results of mg/mL TPPS in DMF using Eq 4.

$$S_{gas} = \frac{TPPS_{DMF} \times \frac{32.06mgS}{294.35mgTPPS} \times V_{DMF}}{\left( V_{gas} \times \frac{519.69^{\circ}R}{459.69^{\circ}R + T_{meter}} \times \frac{P_{meter}}{14.696psia} \right)} \quad (4)$$

where

- $S_{gas}$  = Concentration of elemental sulfur in the gas sample, mg/m<sup>3</sup> at 60°F
- $TPPS_{DMF}$  = Total concentration of TPPS in recovered DMF solution, mg/mL
- $V_{DMF}$  = Total volume of DMF solution recovered from reactor, mL
- $V_{gas}$  = Total volume of gas recorded at gas meter (Section 12.19), m<sup>3</sup>
- $T_{meter}$  = Atmospheric temperature recorded at gas meter, °F
- $P_{meter}$  = Atmospheric pressure recorded at gas meter, psia

13.2 The concentration of elemental sulfur can be converted to ppm (mol) using Eq 5.

$$S_{ppm(mol)} = S_{gas} \times \frac{0.02369m^3}{1 mol gas @ 60^{\circ}F} \times \frac{1 \mu mol S}{0.03206 mg S} \quad (5)$$

13.3 Fig. 7 is a Samples Results/Calculation Sheet.

### 14. Precision and Bias

14.1 The method's repeatability and reproducibility will be determined by the statistical examination of the interlaboratory test results in five years from the date of approval.

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

14.2.1 *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 values by only one case in twenty. (Experimental results to be determined).

14.2.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in

TEST SITE	Meter Site	Meter Site	Meter Site
TEST NO.	S02-6	S02-7	S02-8
SAMPLING LOCATION	Stream 1	Stream 2	Stream 3
TEST START DATE/TIME	3/12/02	3/12/02	3/12/02
	12:20 PM	12:23 PM	12:20 PM
TEST STOP DATE/TIME	3/13/02 9:48 AM	3/13/02 9:58 AM	3/13/02 9:45 AM
TOTAL FLOW TIME (hr)	21.47	21.58	21.42
NOMINAL GAS FLOW RATE (acfm)	0.63	0.44	0.73
TOTAL GAS VOLUME (scf)	815	575	936
TOTAL DELIVERY VOLUME (MMscf)	86	38	48
TEMPERATURES (°F)			
Cabinet	185	174	178
Mid Cylinder	158	168	170
Outlet	152	134	146
Meter	52	50	55
PRESSURE (psig)	520	770	550
GAS COMPOSITION by GC (%)			
Methane	90.52	84.64	97.10
Ethane	5.92	10.28	0.95
Propane	1.32	2.27	0.17
iso-Butane	0.08	0.11	0.03
n-Butane	0.12	0.19	0.03
iso-Pentane	0.02	0.03	0.01
n-Pentane	0.01	0.02	0.01
C6+	0.02	0.01	0.02
Carbon Dioxide	1.63	1.98	1.22
Oxygen	0.01	0.04	0.01
Nitrogen	0.37	0.42	0.45
Oxygen by Analyzer (ppm)	32.2	54.3	5.8
Sulfur Compounds by GC (ppm)			
Hydrogen Sulfide/SO2	0.03	0.02	0.04
Carbonyl Sulfide	0.03	0.02	0.04
Methyl Mercaptan	0.02	0.00	0.03
Ethyl Mercaptan	0.06	0.00	0.12
Dimethyl Sulfide	0.01	0.00	0.02
Carbon Disulfide	0.00	0.00	0.00
i-propyl Mercaptan	0.17	0.00	0.37
t-butyl Mercaptan	0.37	0.00	0.05
n-propyl Mercaptan	0.03	0.00	0.09
s-butyl Mercaptan	0.06	0.00	0.13
l-butyl Mercaptan	0.00	0.00	0.00
Tetrahydrothiophene	0.30	0.02	0.10
Unidentified Sulfur	0.03	0.02	0.02
Total Mercaptans	0.70	0.00	0.80
Total Sulfur	1.10	0.08	1.02
RECOVERED SOLUTION (mL)			
Vessel A	198	269	88
Vessel B	222	260	254
Vessel C	169	274	274
Knock Out	268	42	230
Total (ml)	861	846	851
% of initial loaded (%)	96%	94%	95%
MEASURED ELEMENTAL (mg) SULFUR			
Solution A (as TPPS)	1.84	0.63	2.27
Solution B (as TPPS)	0.32	0.22	0.21
Solution C (as TPPS)	0.29	0.19	0.08
Solution KO (as TPPS)	0.03	0.03	0.00
Total	2.48	1.07	2.57
S8 CONTENT OF GAS (ppmv) (combined)	0.10	0.05	0.12
Using SCD-external standards (ppmv)	0.08	0.05	0.07
Using FPD-external standards (ppmv)	0.06	0.02	0.09
Using FPD-internal standards (ppmv)	0.15	0.08	0.19

**FIG. 7 Samples Results/Calculation Sheet**

the long run, exceed the following values only one case in twenty. (Experimental results to be determined).

14.3 *Bias*—No specific accepted gas mixture reference material has been determined yet for determining the bias. (Experimental results to be determined).

## 15. Keywords

15.1 pipelines; gaseous fuels

## APPENDIXES

### (Nonmandatory Information)

#### X1. PREPARATION OF THE SOLUTIONS

X1.1 Since the measurement of low levels of elemental sulfur in natural gas streams involves the sequestering and detection of very small quantities of sulfur, the handling of the test solutions requires meticulous attention to potential contaminants during their preparation, storage and usage. This applies in particular to the careful rinsing of all associated glassware used in the procedures and the cleanliness of the work area. Also, the presence of small amounts of sulfur in the stock TPP reagent itself requires that said compound be purified before the solutions are prepared.

X1.2 *Purification of Stock TPP*—In order to achieve a background sulfur level, arising from residual sulfur in the TPP solutions, which is low enough such that the minimum sulfur concentrations in the test solutions will generate a GC response that is at least twice the background, the triphenylphosphine solid must be recrystallized twice.

X1.2.1 In a 4 L Erlenmeyer flask atop a heating plate, bring 3 L of alcohol to a boil (100°C [approximately 160 °F]). To date in the ASRL laboratory, we have been employing a 50:50 mixture of ACS reagent grade methanol and industrial grade ethanol. In field applications, the use of 100% industrial, denatured ethanol is recommended since it is less toxic and likely cheaper in cost.

X1.2.2 To the boiling solvent, add approximately 300 g of stock TPP. Stir while heating until the TPP completely dissolves.

X1.2.3 Turn off the heat and leave overnight in an ice bath.

X1.2.4 Filter the precipitated TPP and wash with a little cold methanol and dry.

X1.2.5 Repeat the process a second time to recrystallize the final reagent.

X1.2.6 The alcohol solvent will have to be disposed of in a suitable manner.

X1.3 It has been observed that the yield for each recrystallization is approximately 80%. Thus, a 300 g quantity of raw TPP will regenerate about 190 g of purified product through two recrystallizations. It has been our experience that this procedure will reduce the sulfur content of a TPP solution by 50% for each recrystallization step. Thus, starting with a raw TPP stock chemical that yields a background sulfur content of 0.04 mg/300 mL of solution, a solution employing doubly recrystallized TPP will contain only 0.01 mg/300 mL of solution. The background sulfur content of these solutions, measured by GC/PFPD, will also include any sulfur in the TPPO<sub>4</sub> and the solution solvent (DMF). However, the main source of background sulfur is primarily the TPP itself. Each time a batch of TPP is purified it should be tested by adding 0.5 g TPP to 100 mg TPPO<sub>4</sub> in 100 mL of solvent to be used in the actual test, and analyzed by GC.

#### X2. ADDITIONAL REFERENCE MATERIAL

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