



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D1145 Test Method for Sampling Natural Gas (Withdrawn 1986)³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 D03.06.02 on Analysis of Minor 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

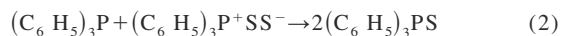
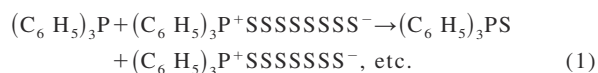
3.4.4 *PFPD*—pulsed flame photometric detector

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.

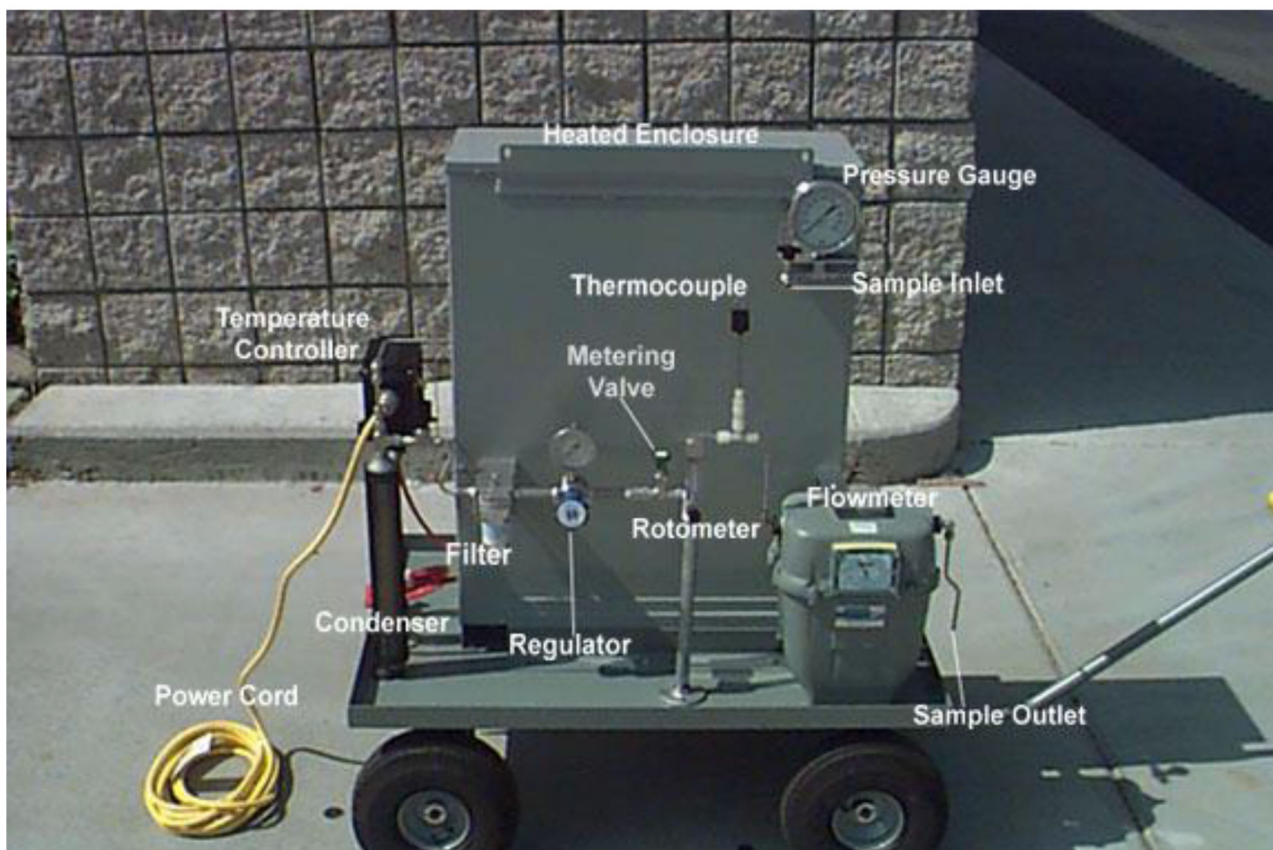
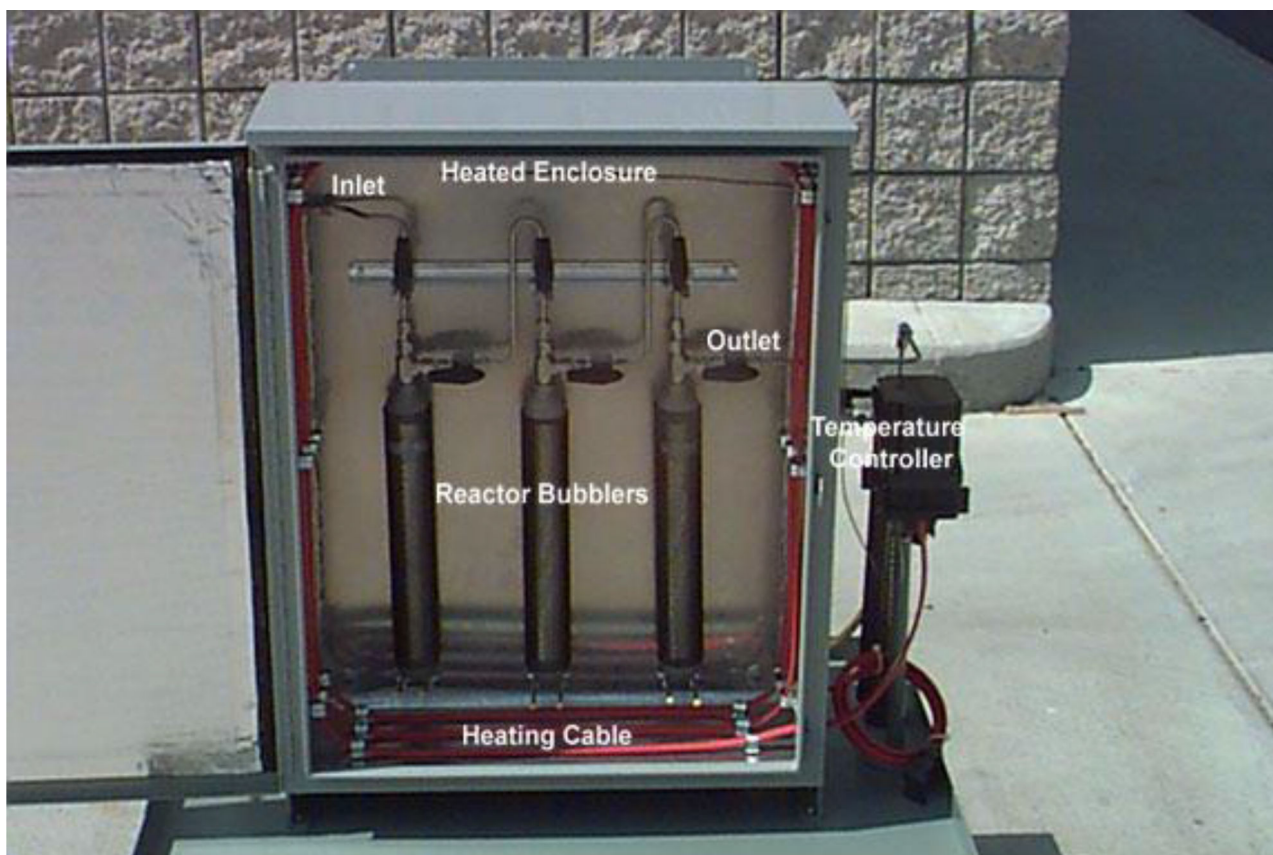


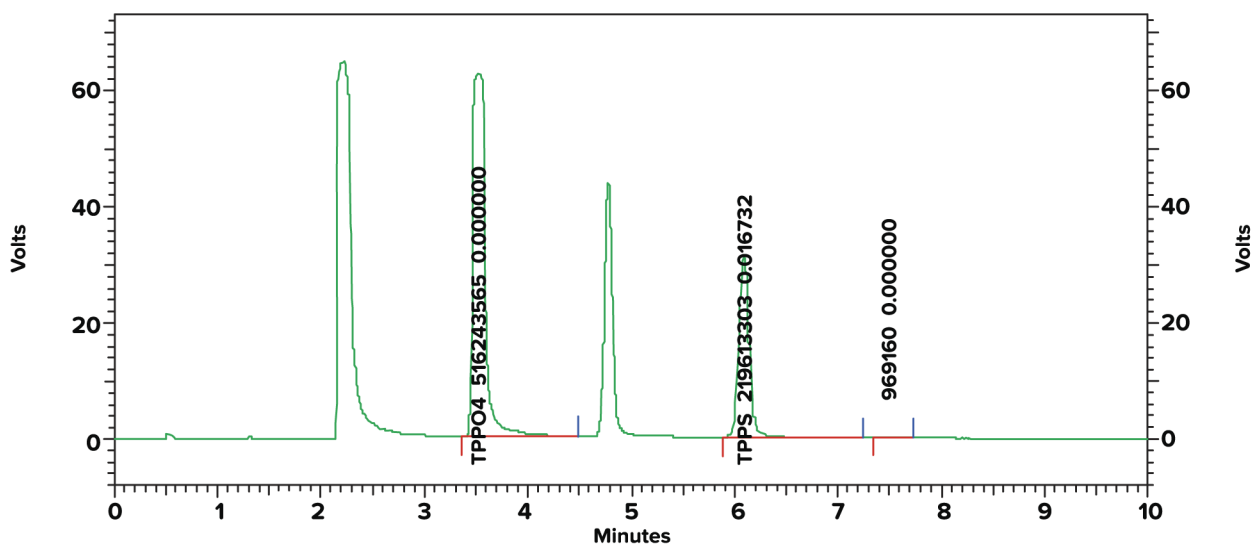
FIG. 1 Reactor

SCD Results

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

Totals

735856868 0.016732



FPD Results

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

Totals

26830278 1.#INF00

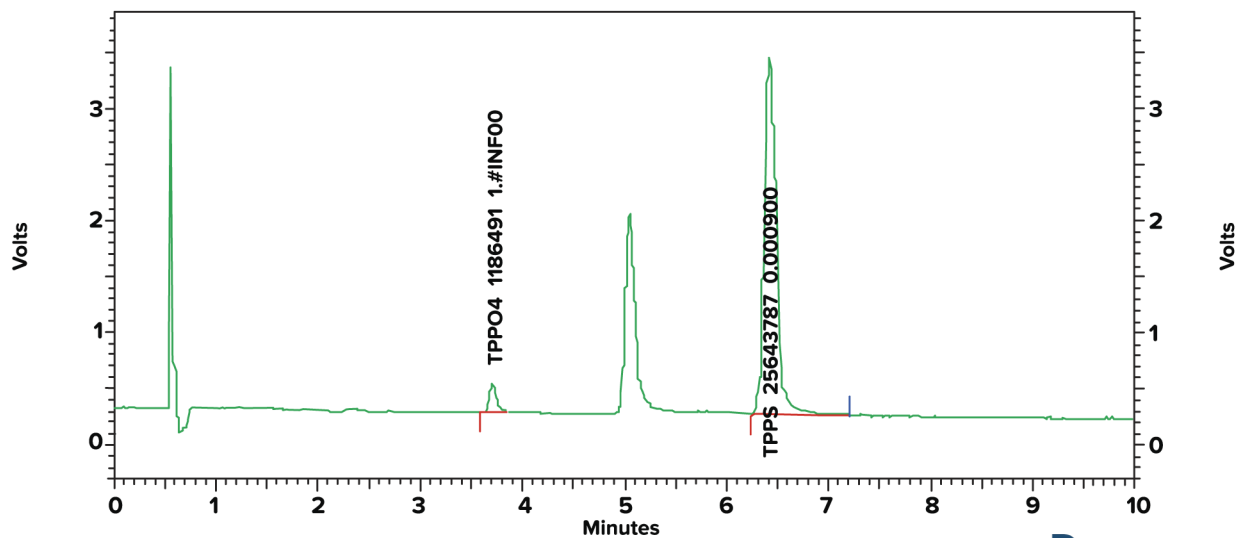


FIG. 2 Elemental Sulfur SCD and FPD Chromatograms



Documents

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