



ASTM Methods for Sulfur Analysis in Petrochemicals using a Pulsed Flame Photometric Detector (PFPD)

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Introduction

The American Society for Testing and Materials (ASTM) is a not-for-profit organization that provides a forum for the development and publication of voluntary consensus standards. The ASTM is divided into 129 technical committees devoted to specific areas of interest. Several ASTM committees (e.g. D02, D03, and D16) develop standards related to measuring the physical and chemical properties of petrochemical products, including measurement of their sulfur content using gas chromatography (GC) with a sulfur selective detector. Since the analysis of trace levels of sulfur in petrochemical matrices requires both sensitivity and selectivity, the Pulsed Flame Photometric Detector (PFPD) is well suited for some of these analytical standards.

This poster presents a survey of selected ASTM methods for detection and quantitation of sulfur in a variety of petrochemical matrices, and the suitability of the PFPD for those methods. Representative chromatograms for several of the applications are shown using the PFPD.

Principle of Operation

Flame photometric detection has been used for many years to detect and quantify sulfur in petrochemical matrices, and although detector designs may vary, all flame photometric detectors have a common principle of operation. Sulfur compounds are combusted in a hydrogen-rich flame as they elute from the GC column. During combustion the sulfur forms an excited-state sulfur dimer (S_2^*) which emits a characteristic light energy as it returns to the ground state. The emissions from the S_2^* range from very weak to very strong and encompass spectral wavelengths from approximately 300 to 500 nm. The emissions are detected by a photomultiplier tube (PMT), and the response of the PMT is quadratic and proportional to the amount of sulfur present. An optical filter is generally used to minimize interference from other emitting species and to increase optical transmission ⁽¹⁾.

In a conventional flame photometric detector (FPD) the flame remains static, and sulfur selectivity is achieved by using a narrow-band transmission filter that transmits a single band of light from the S_2^* at 394 nm; all other sulfur emissions are blocked. An optical shield is sometimes used with the FPD to prevent hydrocarbon emissions from interfering and causing false positives or high background.

By contrast, the PFPD uses a propagating flame that terminates within a fused silica combustor. The kinetics of the gas phase reactions produced by the propagating flame result in light emissions with specific lifetimes; the S_2^* emissions are chronologically separated from the hydrocarbon emissions. This time difference is responsible for the extreme sulfur-hydrocarbon selectivity of the PFPD, and eliminates the need for a narrow-band filter. Consequently a broad-band transmission filter can be used with the PFPD, transmitting nearly all of the sulfur emissions between 300 and 500 nm and dramatically increasing sensitivity.

The operating principle of the PFPD is depicted in Figure 1. A combustible mixture of H_2 and air is introduced and fills the detector body and cap from the bottom up (1). The combustion mixture is ignited in the cap (2). The resulting flame propagates along the pathway consuming the H_2 /air mixture (3). Compounds eluting from the GC column are combusted within a quartz combustor and emit light at element-specific wavelengths (4). The flame is extinguished when it reaches the bottom of the detector and excited species continue to fluoresce for up to 25 milliseconds. Emissions from the excited species pass along a light pipe and selected emissions are transmitted through an optical filter to a photomultiplier tube for detection (5). The entire pulsed flame cycle is repeated approximately 3 to 4 times per second.

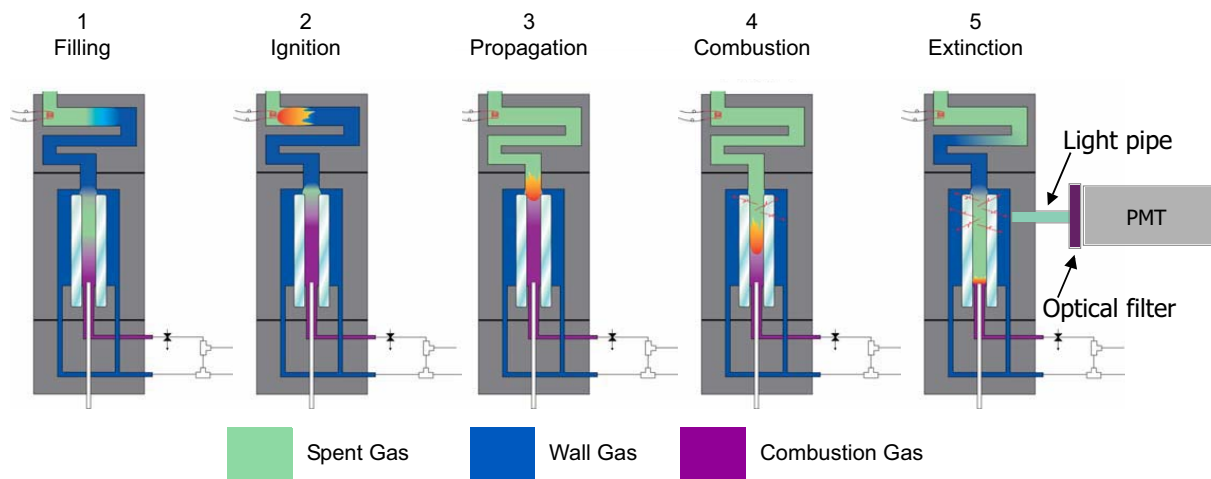


Figure 1. PFPD Principle of Operation

As a result of these design differences, the PFPD has several significant advantages over the conventional FPD including a 10-fold increase in sulfur-hydrocarbon selectivity, 10-fold increase in sensitivity, and long-term flame stability with no flame-outs. The gated electronics of the PFPD also enable a linear and equimolar sulfur signal for easier calibrations, and the acquisition of two simultaneous, mutually selective chromatograms.

Table 1 gives a brief description of seven ASTM methods for determination of sulfur in a variety of petrochemical matrices, and explains how method performance can be enhanced when using the PFPD. Figures 2 – 6 are representative chromatograms from the PFPD when used for these types of applications.

Table 1: Selected ASTM Standards for Detection and Quantitation of Sulfur in Petrochemical Matrices, and Suitability of the Pulsed Flame Photometric Detector (PFPD) for those Methods

Standard Designation (Committee)	D3328 (D19)	D4735 (D16)	D5303 (D02)	D5504 (D03)	D5623 (D02)	D6228 (D03)	D7011 (D16)
Title	Comparison of Waterborne Petroleum Oils by Gas Chromatography	Determination of Trace Thiophene in Refined Benzene by Gas Chromatography	Trace Carbonyl Sulfide in Propylene by Gas Chromatography	Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence	Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection	Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection	Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection
Matrix	Petroleum oils recovered from water or beaches compared to oils from suspect sources.	Refined benzene	Propylene	High methane-content gaseous fuels such as natural gas	Light petroleum liquids such as distillates, gasoline motor fuels, and other petroleum liquids with final boiling point of 230 °C or lower.	Gaseous fuels	Refined benzene
Analytes	Hydrocarbons (FID) and associated sulfur compounds (FPD)	Thiophene	Carbonyl sulfide (COS)	Speciated volatile sulfur-containing compounds such as H ₂ S, COS, SO ₂ , thiols, sulfides, thiophenes, etc.	Volatile sulfur-containing compounds; both unidentified and known individual compounds are determined.	Volatile sulfur-containing compounds; both unidentified and known individual compounds are determined.	Thiophene
Range	Qualitative only; no quantitative range is cited	0.5 to 5.0 mg/kg	0.5 to 4.0 mg/kg	0.01 to 1,000 mg/m ³	0.1 to 100 mg/kg (ppm)	0.02 to 20 mg/m ³ (0.014 to 14 ppmv)	0.02 to 2.0 mg/kg
Detector Cited	FID alone, or FID with flame photometric detection	Any flame photometric detector (FPD or PFPD)	A flame photometric detector	FID and SCD in series, or other sulfur specific detector	A sulfur selective detector that produces a linear and equimolar response to sulfur compounds	Any flame photometric detector (FPD or PFPD)	Pulsed flame photometric detector, sulfur chemiluminescence detector, atomic emission detector, or any other sulfur selective detector.
Detector Specification	<ul style="list-style-type: none"> A flame photometric detector is cited when independent, selective detection of HC and S is desired to improve identification of oil Linearization of the sulfur signal is recommended 	Signal-to-noise of at least 2-to-1 for 0.5 mg/kg (ppm) thiophene in benzene (4-µL injection with FPD or 1-µL injection with PFPD)	Signal-to-noise of at least 2-to-1 for 0.1 mg/kg COS in propylene	Sulfur specific detectors other than the SCD can be used provided that they have sufficient sensitivity, respond to all eluted sulfur compounds, do not suffer from interferences, and satisfy quality assurance criteria.	<ul style="list-style-type: none"> Linearity of 10⁴ 5-pg sulfur/second minimum detectability Approximate equimolar response to sulfur No interference from co-eluting hydrocarbons 	<ul style="list-style-type: none"> Linearity of 10² Minimum detectable level of less than 0.02 mg/kg thiophene in benzene Selectivity of sulfur to carbon greater than 10³ Absence of quenching that affect results 	<ul style="list-style-type: none"> Linearity of 10² Minimum detectable level of less than 0.02 mg/kg thiophene in benzene Selectivity of sulfur to carbon greater than 10³ Absence of quenching that affect results
PFPD Suitability	A PFPD with increased sensitivity, equimolar sulfur response, and linear signal provides maximum information about the number, distribution, and relative concentrations of the sulfur species present for positive identification of the suspect oil.	The PFPD provides additional sensitivity, down to 0.02 mg/kg (ppm), when lower concentrations of thiophene in benzene must be measured.	Linear, equimolar response of the PFPD eliminates log/log plots, simplifies calibrations, and enables quantitation of any unknown sulfur peaks that may be present along with the COS.	The PFPD exceeds requirements for "other sulfur specific detectors", including all QA criteria. The two-signal output of the PFPD provides a simultaneous fingerprint of the hydrocarbon matrix along with the sulfur chromatogram.	Linear, equimolar response of the PFPD allows accurate quantitation of individual known and unknown sulfur compounds down to 25-ppb sulfur or lower.	Increased sensitivity of the PFPD allows quantitation of sulfur at concentrations 5 to 10 times lower than an FPD. Linear, equimolar response of the PFPD allows accurate quantitation of the sulfur content in unknowns.	Long-term stability and ease of use make the PFPD well suited for use in production facilities with limited staff, and where low detection limits are required.

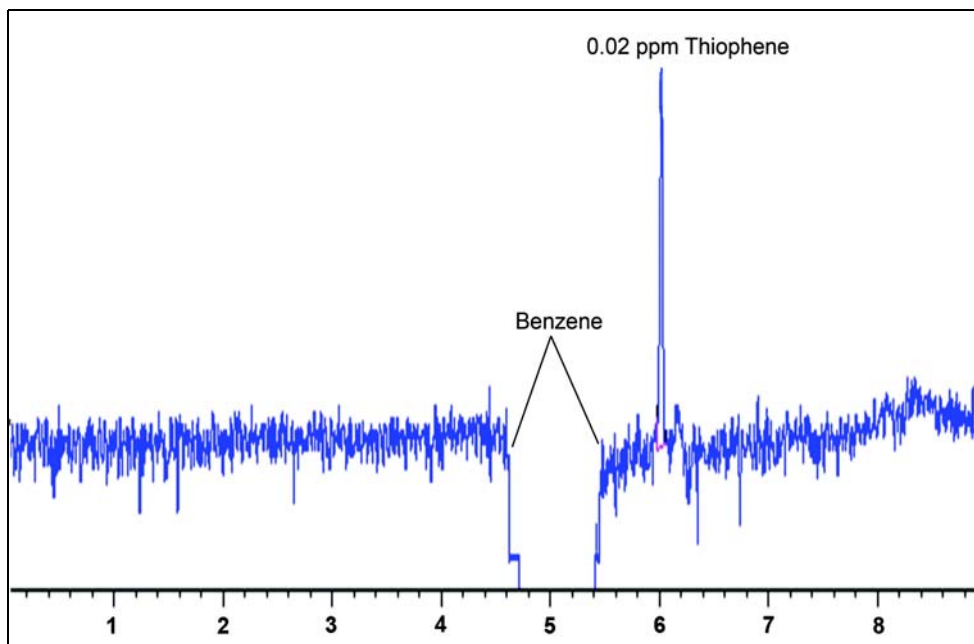


Figure 2. Chromatogram of 0.02-ppm thiophene in refined benzene run on the PFPD.
(Conditions: 1- μ L injection, 3-to-1 split ratio, DB-WAX Column.)

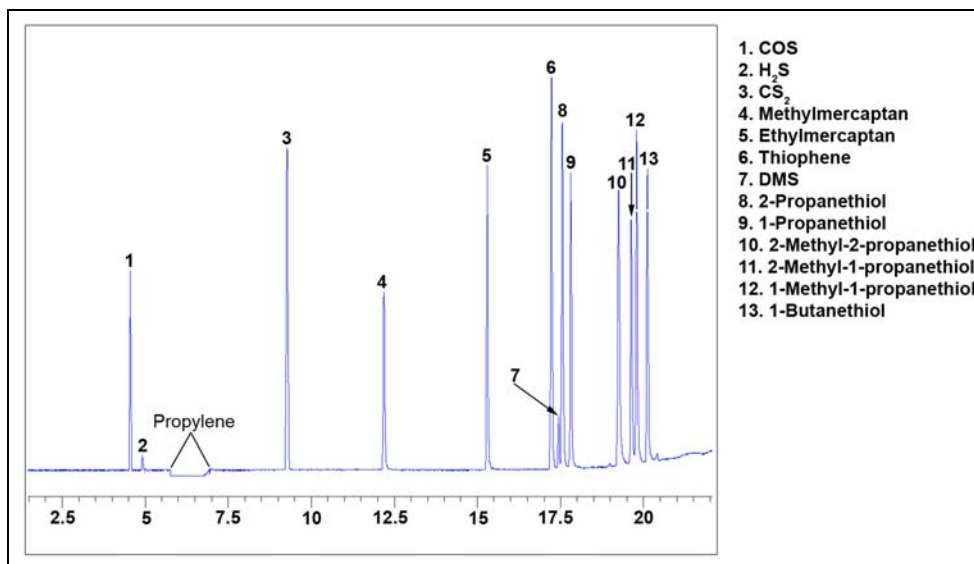


Figure 3. Chromatogram of 13 sulfur compounds in a propylene standard run on the PFPD.
All compounds except H_2S are present at approximately 1 ppmv.
(Conditions: 0.2-mL GSL, 5-to-1 split ratio, GS-GasPro column.)

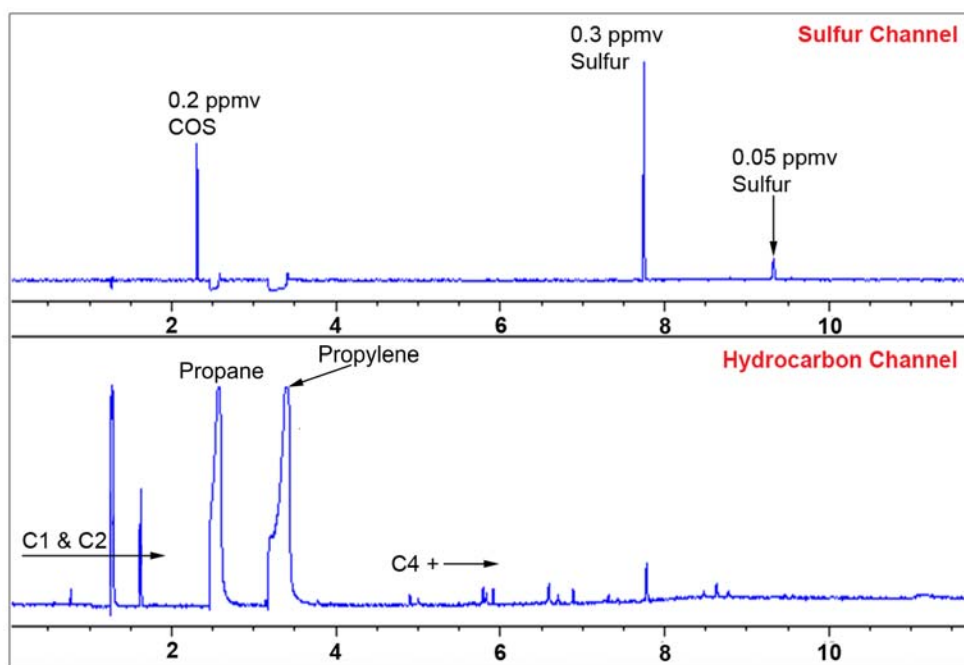


Figure 4. Simultaneous sulfur and hydrocarbon chromatograms from a propane/propylene mix run on a PFPD and showing COS and two unknown sulfur compounds. (Conditions: 0.2-mL GSL, 5-to-1 split ratio, GS-GasPro column.)

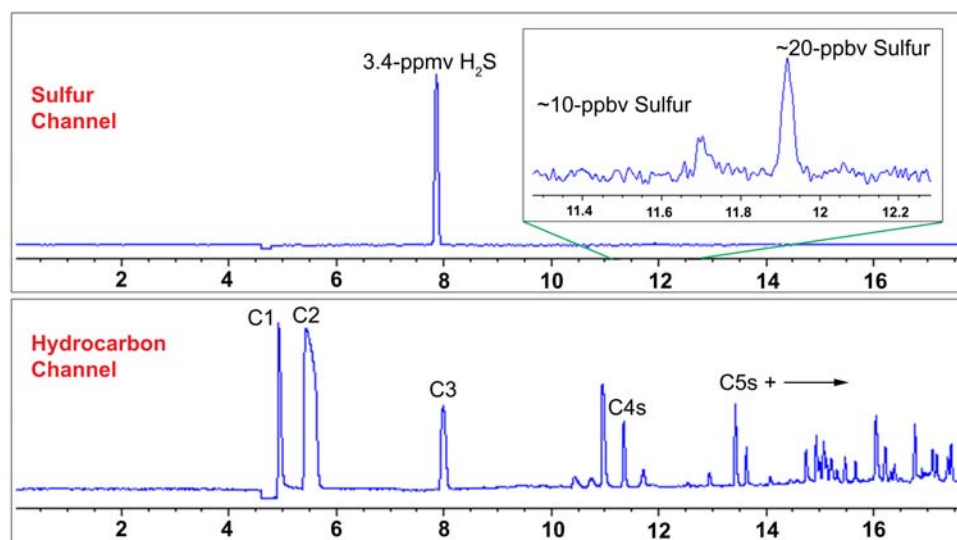


Figure 5. Simultaneous sulfur and hydrocarbon chromatograms from a pipeline natural gas run on a PFPD and showing H₂S and two unknown sulfur compounds in the ppbv range. (Conditions: 0.5-mL GSL, 8-to-1 split ratio, GS-GasPro column.)

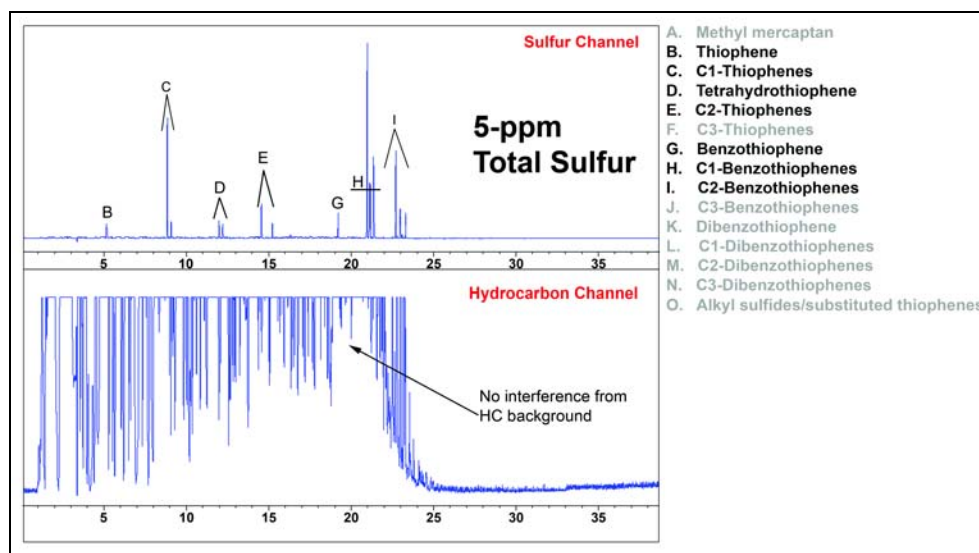


Figure 6. Simultaneous sulfur and hydrocarbon chromatograms from a gasoline containing 5-ppm total sulfur run on a PFPD.
(Conditions: 1- μ L injection; 10-to-1 split ratio, DB-5MS column.)

Summary and Conclusions

Several ASTM methods are available for the identification and quantitation of Sulfur in petrochemical matrices. Because of its selectivity for sulfur versus hydrocarbon and excellent sensitivity, the PFPD has proven to be a suitable and reliable detector for these methods.

References

1. ASTM Standard E 840-95, 2005, "Standard Practice for Using Flame Photometric Detectors in Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org
2. ASTM Standard D 3328-06, "Standard Test Method for Comparison of Waterborne Petroleum Oils by Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org
3. ASTM Standard D 4735-02, "Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org
4. ASTM Standard D 5303-92, "Standard Test Method for Trace Carbonyl sulfide in Propylene by Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org
5. ASTM Standard D 5504-01, "Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence," ASTM International, West Conshohocken, PA, www.astm.org

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6. ASTM Standard D 5623-94, "Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection," ASTM International, West Conshohocken, PA, www.astm.org
 7. ASTM Standard D 6228-98 "Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection," ASTM International, West Conshohocken, PA, www.astm.org
 8. ASTM Standard D 7011-04, "Standard Test Method for Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection," ASTM International, West Conshohocken, PA, www.astm.org



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