



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

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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 sulphur content using gas chromatography (GC) with a sulphur selective detector. Since the analysis of trace levels of sulphur in petrochemical matrices requires both sensitivity and selectivity, the Pulsed Flame Photometric Detector (PFPD) is well suited for some of these analytical standards. This survey presents an overview of selected ASTM methods for detection and quantitation of sulphur 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 sulphur in petrochemical matrices, and although detector designs may vary, all flame photometric detectors have a common principle of operation. Sulphur compounds are combusted in a hydrogen-rich flame as they elute from the GC column. During combustion, the sulphur forms an excited-state sulphur 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 sulphur present. An optical filter is generally used to minimize interference from other emitting species and to increase optical transmission.

In a conventional flame photometric detector (FPD) the flame remains static, and sulphur 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 sulphur emissions are blocked. An optical shield is sometimes used with the FPD to prevent hydrocarbon

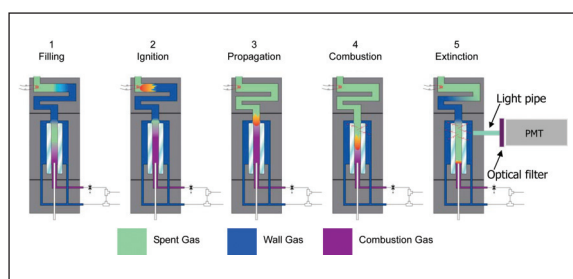


Figure 1: PFPD Principle of Operation

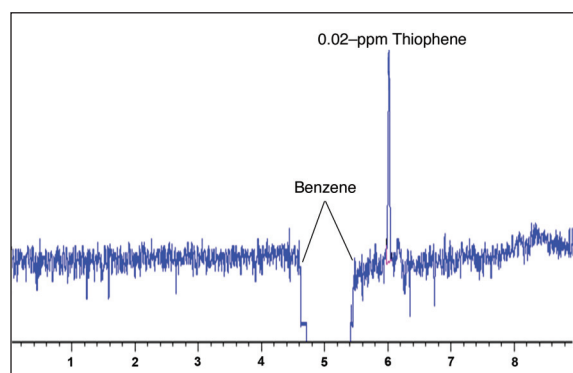


Figure 2: Chromatogram of 0.02-ppm thiophene in refined benzene run on the PFPD. (Conditions: 1- $\mu$ L injection, 3-to-1 split ratio, DB-WAX Column.)

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 $H_2S$ , 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 <sup>3</sup>	0.1 to 100 mg/kg (ppm)	0.02 to 20 mg/m <sup>3</sup> (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"> <li>A flame photometric detector is cited when independent, selective detection of HC and S is desired to improve identification of oil</li> <li>Linearization of the sulfur signal is recommended</li> </ul>	Signal-to-noise of at least 2-to-1 for 0.5 mg/kg (ppm) thiophene in benzene (4- $\mu$ L injection with FPD or 1- $\mu$ L 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"> <li>Linearity of <math>10^4</math></li> <li>5-pg sulfur/second minimum detectability</li> <li>Approximate equimolar response to sulfur</li> <li>No interference from co-eluting hydrocarbons</li> </ul>	Any flame photometric detector calibrated in the sulfur-specific mode is used for this test method	<ul style="list-style-type: none"> <li>Linearity of <math>10^2</math></li> <li>Minimum detectable level of less than 0.02 mg/kg thiophene in benzene</li> <li>Selectivity of sulfur to carbon greater than <math>10^3</math></li> <li>Absence of quenching that affect results</li> </ul>
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.

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

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 sulphur-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 sulphur 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

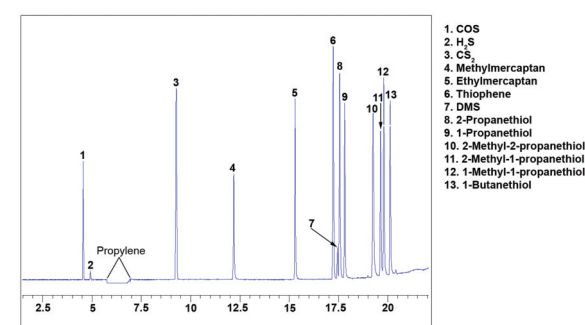


Figure 3: Chromatogram of 13 sulphur compounds in a propylene standard run on the PFPD. All compounds except  $H_2S$  are present at approximately 1 ppmv. (Conditions: 0.2-mL GSL, 5-to-1 split ratio, GS-GasPro column.)

optical filter to a photomultiplier tube for detection (5). The entire pulsed flame cycle is repeated approximately 3 to 4 times per second.

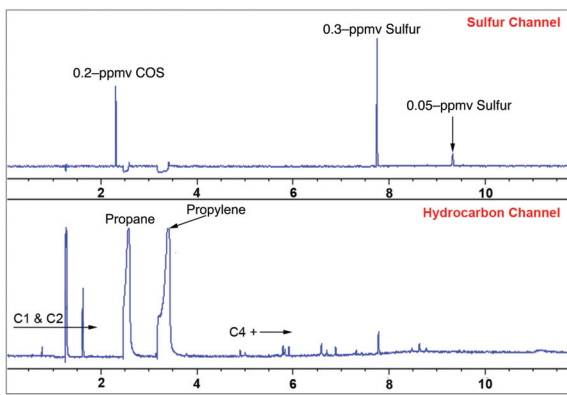


Figure 4: Simultaneous sulphur and hydrocarbon chromatograms from a propane/propylene mix run on a PFPD and showing COS and two unknown sulphur compounds. (Conditions: 0.2-mL GSL, 5-to-1 split ratio, GS-GasPro column.)

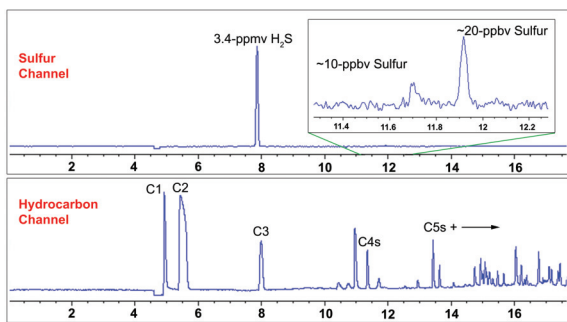


Figure 5: Simultaneous sulphur and hydrocarbon chromatograms from a pipeline natural gas run on a PFPD and showing H<sub>2</sub>S and two unknown sulphur compounds in the ppbv range. (Conditions: 0.5-mL GSL, 8-to-1 split ratio, GS-GasPro column.)

As a result of these design differences, the PFPD has several significant advantages over the conventional FPD including a 10-fold increase in sulphur-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 sulphur signal for easier calibrations, and the acquisition of two simultaneous, mutually selective chromatograms.

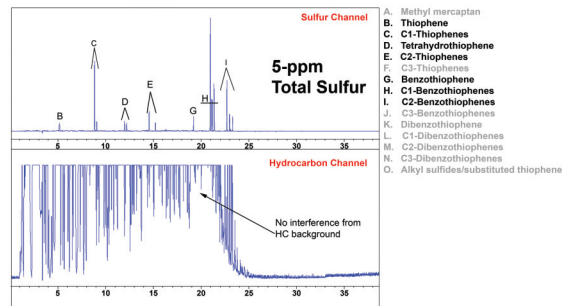


Figure 6: Simultaneous sulphur and hydrocarbon chromatograms from a gasoline containing 5-ppm total sulphur run on a PFPD. (Conditions: 1- $\mu$ L injection; 10-to-1 split ratio, DB-5MS column.)

Table 1 gives a brief description of seven ASTM methods for determination of sulphur 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.

### Summary and Conclusions

Several ASTM methods are available for the identification and quantitation of sulphur in petrochemical matrices. Because of its selectivity for

sulphur 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
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