

# Determination of Total and Speciated Sulfur Content in Petrochemical Samples Using a Pulsed Flame Photometric Detector

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## Abstract

The pulsed flame photometric detector (PFPD) has the advantage of being able to measure the concentration of individual sulfur compounds and total sulfur content in a petrochemical sample in a single gas chromatography run. Because it is an equimolar response detector, the PFPD's sulfur response is independent of a compound's molecular structure, and this feature allows quantitation of the total or speciated sulfur content in complex samples using a single calibrant. This paper is a survey describing a variety of applications using the PFPD for sulfur quantitation in petrochemical matrices. Several different approaches to quantitation are described, and simple techniques for circumventing the quenching of the sulfur signal by coeluting hydrocarbon peaks are discussed. Examples from a range of real-world samples are presented.

## Introduction

Analytical measurements of sulfur in petrochemical matrices are performed for a variety of reasons. Two of the most pressing concerns are the need to meet total sulfur content requirements imposed by regulatory agencies and to monitor the concentration of individual sulfur compounds at various stages within the refinery process for quality control purposes. In the first case, the goal of the analysis is usually to determine the total sulfur content in gasoline or diesel fuels to comply with increasingly stringent regulatory limits that are designed to reduce sulfur emissions to the atmosphere. This type of analysis has historically been performed by X-ray fluorescence (XRF). A rapid and relatively inexpensive technique, XRF is limited by the fact that it reports only a bulk measurement of the total sulfur content and does not have the flexibility to measure the concentration

of individual sulfur components.

By contrast, quality control measurements usually focus on determining the identity and concentration of individual sulfur species at different stages throughout the refinery process. The distribution of sulfur compounds present in feedstock, as well as in all types of finished petrochemical products, is essential to establishing the type of desulfurization techniques that will be required and often determines whether a finished product is acceptable to the end user. This type of analysis is typically done by gas chromatography (GC). The individual species are separated chromatographically on a GC column and then detected and measured using a sulfur selective detector. Since its introduction by Brody and Chaney (1) in 1966, the measurement device of choice has been the flame photometric detector (FPD). The FPD has been an important tool for determining individual sulfur components because of its sensitivity and specificity, but its performance has been limited as a consequence of its nonlinearity and compound-dependent response.

In 1991, Atar et al. (2) introduced a new generation of the FPD, the pulsed flame photometric detector (PFPD). The PFPD improves on the original detector's sensitivity and specificity, and the pulsing of the flame creates two significant advantages that

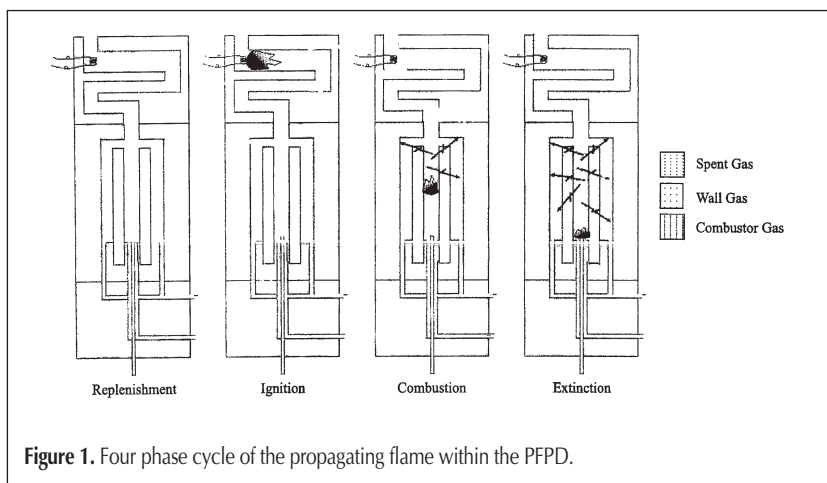


Figure 1. Four phase cycle of the propagating flame within the PFPD.

were not previously achievable: linearity and an equimolar response for sulfur. These factors make the PFPD an indispensable detector for the simplified characterization of individual sulfur species in petrochemical matrices and provide an alternative analytical approach for simultaneous determination of the total sulfur content.

The operational principle of the PFPD has been described extensively elsewhere (3–5). In summary, the PFPD is based on a propagating flame that terminates within a quartz combustor. The gas-phase reactions produced by the propagating flame result in light emissions with element-specific wavelengths and lifetimes. The differences in specific emission lifetimes, combined with the kinetics of the propagating flame, allow both time and wavelength information to be used to improve the selectivity of the PFPD and to decrease the observed noise. The combustor is filled with the combustible gas mixture, the flame is ignited, propagates through the combustor, and burns out when all the fuel is consumed (see Figure 1). The cycle is repeated continuously at a rate of 3–4 Hz. As a result of the pulsing of the flame, the PFPD adds a time dimension to the emission analysis, in addition to the wavelength selectivity of a conventional FPD. By analyzing a specific time slice of the emitted light, the selectivity of the detector is significantly enhanced. Furthermore, because the time separation of the emissions adds selectivity, wide band-pass optical filters can be used, permitting more light to be detected and resulting in increased sensitivity for the PFPD, compared with the FPD.

Figure 2 illustrates the real-time display of a sulfur emission obtained with the PFPD. The *y*-axis represents intensity of the signal response at the photomultiplier tube (PMT). The *x*-axis is a time scale measured in milliseconds, with the intercept representing the initiation of the flame propagation. The sulfur emission has a delayed lifetime, beginning approximately 4 ms after the initial combustion, reaching a maximum intensity between 9 and 13 ms and decaying to baseline at approximately 25 ms. Hydrocarbon emission lifetimes, on the other hand, are not delayed, and their time dependence is governed by the flame velocity and passage of time along the observation window. By analyzing a specific time slice of the emitted radiation, the selectivity of the PFPD is significantly enhanced. For example, if the time slice from 6 to 25 ms is collected, the entire recorded emission is from sulfur species only, with no contribution from the

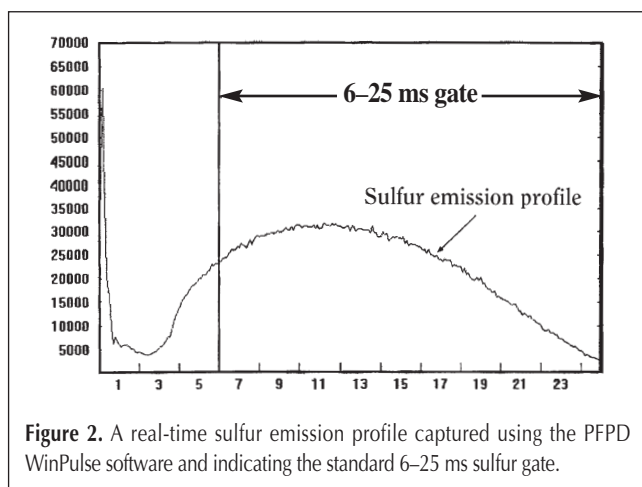


Figure 2. A real-time sulfur emission profile captured using the PFPD WinPulse software and indicating the standard 6–25 ms sulfur gate.

hydrocarbons present. By adjusting the start time for this filter, or gate, the PFPD can be configured to be infinitely selective for sulfur against hydrocarbon.

## Experimental

Analyses of gas-phase samples in this project were performed on an OI Analytical Model 3200 S-PRO system (College Station, TX). The S-PRO is based on an Agilent 6890N (Palo Alto, CA) GC platform with an integrated permeation oven for calibration. Sample introduction was through an OI Analytical volatiles interface with a split/splitless injector, an air-actuated dual valve system in a heated valve box, and a gas-sampling loop. An Agilent GS-GasPro column was used to chromatographically separate the individual volatile sulfur compounds. The OI Analytical Model 5380 PFPD was configured for sulfur-selective detection and quantitation of the sulfur compounds.

A separate instrument, also based on an Agilent 6890N platform, was used for analysis of the benzene, gasoline, and diesel samples. A standard split/splitless injector and a liquid autosampler were used for sample introduction. For the benzene samples, the GC was configured with a DB-WAX (Agilent, Folsom, CA) column (30-m  $\times$  0.25-mm i.d.  $\times$  0.5- $\mu$ m film thickness). Analysis of sulfur in diesel fuels required switching to the less polar DB-5MS boiling-point column (30-m  $\times$  0.25-mm i.d.  $\times$  1- $\mu$ m film thickness). For analysis of the gasoline samples, a slightly more polar column was necessary to give adequate separation of the critical hydrocarbon-sulfur analogue pairs. Several columns have been used for analysis of sulfur in gasoline with good results, including DB-17, DB-5, and Rtx-35 (Restek, Bellefonte, PA). For both analytical systems, the PFPD was configured for sulfur analysis with a 2-mm quartz combustor, BG-12 broadband optical filter, and base temperature of 250°C. The H<sub>2</sub>-to-air flow ratio was adjusted to be slightly H<sub>2</sub> rich and was optimized to support maximum formation of the emitting species, the S<sub>2</sub>\* dimer, within the propagating flame. It should be noted that the S<sub>2</sub>\* dimer naturally produces a quadratic response. This is handled by using the linearization function built into the PFPD detector controller. When the linearization option is selected, as it was for this project, the digital signal processor in the controller is used to mathematically convert the quadratic response into a linear response. This has the additional benefit of providing an equimolar response for sulfur as well.

Finally, the PFPD uses a digital signal processor to analyze the waveforms generated by the detector, and, as a result, the detector controller can generate two independent analogue signals. This controller design allows two time slices of the waveform to be analyzed simultaneously and two corresponding analogue signals to be generated for the data system. For this project, a time slice from 6 to 25 ms was selected for the first signal for capture and display of a sulfur-selective chromatogram. The second signal was chosen using a 1–3-ms window to capture a simultaneous hydrocarbon profile. The hydrocarbon mode of the PFPD is not as sensitive as a true flame ionization detector (FID); but by using the dual channel capability of the controller, a sulfur chromatogram and a simulta-

neous hydrocarbon chromatogram can be generated from a single injection. For most of the following examples, the top chromatogram displays the sulfur trace and the bottom window displays the corresponding simultaneous hydrocarbon profile.

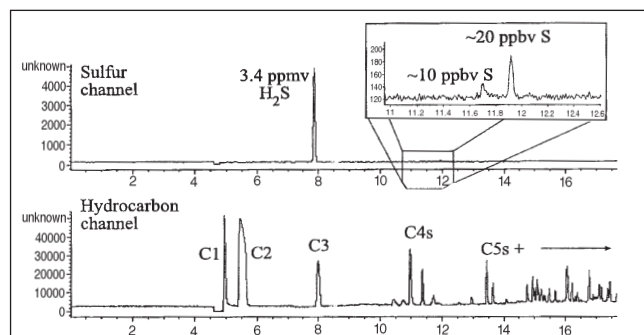
## Results and Discussion

### Sulfur in natural gas

Figure 3 displays the simultaneous sulfur and hydrocarbon chromatograms of a natural gas sample analyzed using the S-PRO system described previously. The natural gas was determined to contain 3.4 ppmv sulfur as  $\text{H}_2\text{S}$ , as well as two unidentified sulfur species at approximately 10 and 20 ppbv sulfur. The  $\text{H}_2\text{S}$  in the natural gas was quantitated using a four-point calibration curve generated by the system's built-in permeation oven and an  $\text{H}_2\text{S}$  permeation device. Dilution gas flow through the permeation oven was varied to change the concentration of the  $\text{H}_2\text{S}$  in the calibration gas, whereas the permeation oven temperature remained constant. Triplicate injections were made at each concentration to verify that the system had reached equilibrium; percent relative standard deviations (%RSD) for replicate analyses of the  $\text{H}_2\text{S}$  gas standard at each concentration were 3% or better. The calibration curve plotted PFPD response as a function of sulfur concentration, and, because the detector has an equimolar response for sulfur, the concentration of sulfur in the two unidentified peaks could be quantitated using the same calibration data. The PFPD was configured with a simultaneous hydrocarbon channel for this project, thus, the hydrocarbon pattern in the natural gas was also obtained. Quantitation of the individual hydrocarbon species present is limited, but qualitative data is beneficial in providing relative proportions of the individual hydrocarbon groups that were present. The data were acquired using a 0.5-mL gas sample loop, 9:1 split ratio, 30-m GS-GasPro column, and isothermal GC oven program.

### COS and $\text{H}_2\text{S}$ in 97% propane

One limitation of the PFPD is that it can be subject to quenching of the sulfur signal in the presence of high concentrations of coeluting hydrocarbons (6). When quenching occurs,

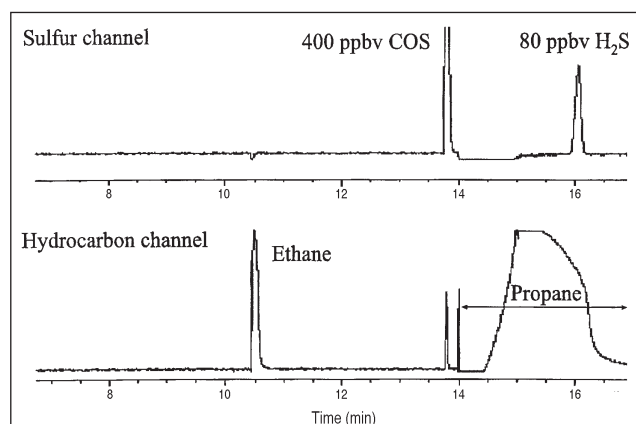


**Figure 3.** Simultaneous sulfur and hydrocarbon chromatograms of a natural gas sample analyzed with the S-PRO system. The sample contained 3.4 ppmv sulfur as  $\text{H}_2\text{S}$  and two unidentified sulfur compounds that were quantitated at 10 and 20 ppbv sulfur using the PFPD equimolar response capability.

the sulfur signal is suppressed by the presence of competing reactions within the PFPD combustor, and the sulfur compounds are either not detected at all or the quantitated results may show a low bias. There are two approaches that can be taken to counter the effects of quenching. The first approach is to minimize the amount of hydrocarbon that is introduced to the PFPD by reducing the injection volume or increasing the split ratio. Because this technique will also limit the amount of sulfur injected, it is usually applied to samples with high total sulfur concentrations, and it is usually used in conjunction with the second technique. In the second approach, an attempt is made to chromatographically resolve the individual sulfur species from the hydrocarbons so that regardless of how much hydrocarbon is present it does not coelute with the sulfur compounds and quenching is not observed.

An extreme example of the potential for quenching is seen in the analysis of low concentrations of COS and  $\text{H}_2\text{S}$  in 97% propane. For this example, it was critical to achieve the lowest possible detection limits, thus, small injection volumes and high split ratios were not an option. The second approach to quenching was adopted, and an attempt was made to find a GC column and oven program that would chromatographically resolve the two sulfur species from the propane. The result is shown in Figure 4. In this chromatogram, which was acquired using a 60-m GS-GasPro column and a 35°C isothermal oven, the large propane peak elutes directly between the two sulfur compounds of interest, COS and  $\text{H}_2\text{S}$ . The flat baseline immediately after the COS peak is indicative of the quenching that has occurred because of the 97% propane matrix. The poorly shaped form labeled "Propane" in the hydrocarbon trace is actually the tail of the propane peak. Even though the  $\text{H}_2\text{S}$  elutes on the tail of the propane, there is insufficient hydrocarbon present at this point to interfere with detection of the sulfur. Close examination of the individual sulfur emissions using the PFPDView post-acquisition software (OI Analytical), confirmed the lack of quenching associated with  $\text{H}_2\text{S}$  through unchanged emission-time dependence (6).

Concentrations of COS and  $\text{H}_2\text{S}$  for this example were measured at 400 and 80 ppbv, respectively, using single-point



**Figure 4.** Simultaneous sulfur and hydrocarbon chromatograms of 97% propane analyzed with the S-PRO system. The concentration of COS (shown off-scale) and  $\text{H}_2\text{S}$  were 400 and 80 ppbv, respectively. The flat baseline immediately after the COS is indicative that quenching has occurred.

response factors generated from individual COS and H<sub>2</sub>S permeation devices in the S-PRO permeation oven. Because H<sub>2</sub>S has been demonstrated to be absorbed to some degree on this GC column and because H<sub>2</sub>S tends to be prone to other types of losses within the system not seen with COS, despite all lines being treated with a sulfur-resistant coating, individual permeation tubes were deemed necessary. This approach produced the most accurate measurement of the concentrations for both species and resulted in minimum detection limits for COS that were approximately half of those for H<sub>2</sub>S. For this example, the sample was introduced using a 0.5-mL gas sample loop and a 9:1 split ratio. Detection of lower concentrations may be possible by using a 1-mL gas sample loop and a 3:1 split ratio.

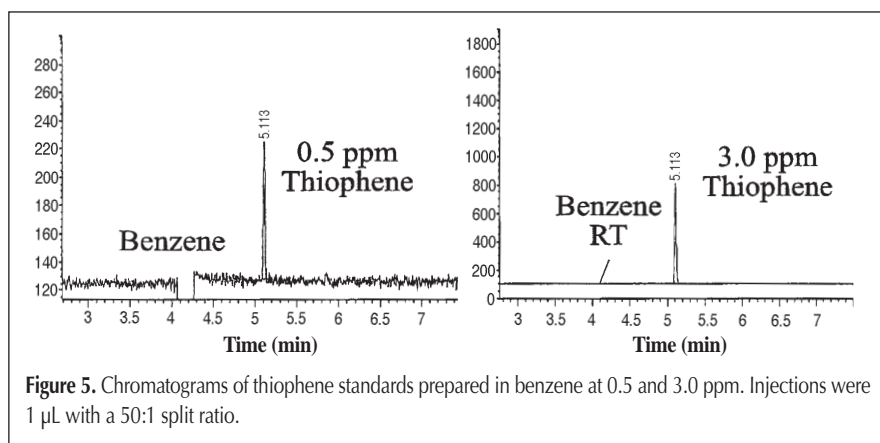
### Thiophene in benzene

American Society for Testing and Materials (ASTM) Standard D4735-96, first approved in 1996 and reapproved in 2000 and 2003, is a standard test method for the determination of trace levels of thiophene in benzene by GC with an FPD. The detector specified in the original ASTM standard was "any flame photometric detector" that would meet the performance criteria outlined in the method. Because the PFPD is approximately tenfold more sensitive and selective than the FPD and has the advantage of providing an equimolar response to sulfur, the PFPD seemed an ideal and logical choice of detectors for this method. The objective of this portion of the project was to establish instrument operating conditions using the PFPD that would meet or exceed performance criteria outlined in Standard D4735-96.

Six calibration standards spanning a range specified from 0.5 to 5.0 ppm thiophene were prepared and analyzed in triplicate.

**Table I. Thiophene in Benzene Calibration: Repeatability of Triplicate Injections at Each Concentration Level**

Calibration level (ppm)	%RSD ( <i>n</i> = 3)
0.5	3.7
1.0	6.1
2.0	1.9
3.0	0.6
4.0	0.2
5.0	0.6



**Figure 5.** Chromatograms of thiophene standards prepared in benzene at 0.5 and 3.0 ppm. Injections were 1  $\mu$ L with a 50:1 split ratio.

The calibration curve was created using the average integrated peak areas at each concentration. Chromatograms of the 0.5- and 3.0-ppm standards are shown in Figure 5. RSDs over the three replicate injections for each concentration are shown in Table I. For the purpose of this experiment, one of the PFPD signals was configured in the quadratic mode, and the second signal was configured to produce a linear sulfur response. This way, linear calibration data from the PFPD could be directly compared with the quadratic and log/log plots specified in the original versions of the ASTM standard. These three different treatments of the same data are illustrated in Figure 6. All three charting techniques resulted in excellent and equivalent calibration curves. However, the use of linearized data simplified the calibration process and allowed quantitation of unknown sulfur peaks that may be detected using the equimolar response feature of the PFPD.

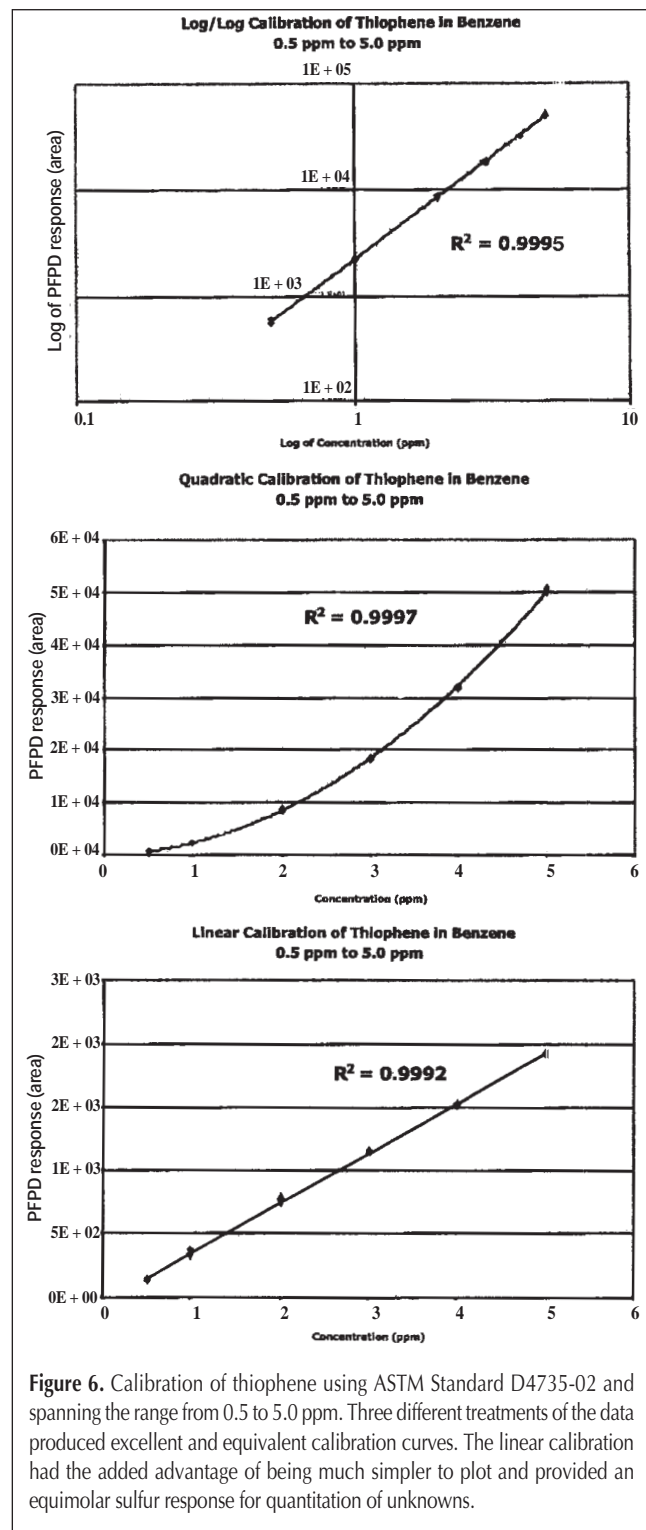
The ASTM method specifies method criteria for precision in terms of "Intermediate Precision" for a single laboratory. The criteria are represented as average measured concentrations with standard deviations reported on an mg/kg (ppm) basis. Table II compares the single laboratory "Intermediate Precision" data from the PFPD in D4735-02 with the data originally reported for D4735-96. The single laboratory data demonstrate that the PFPD is capable of analytical precision 3–4 times better than the FPD used in the original study. The range of the method was also easily extended to include thiophene concentrations as low as 50 ppb or less simply by reducing the split ratio. All of the original performance criteria were met, and the standard was reapproved in mid 2002, with modifications to include the use of the PFPD.

### Sulfur in gasoline

All of the preceding examples describe detection of sulfur in relatively simple matrices with a limited number of hydrocarbons present that can be chromatographically resolved from the sulfur. Gasoline samples, on the other hand, are complex mixtures of hundreds of individual hydrocarbon compounds that elute from the GC column in a characteristic pattern, or fingerprint, and are often only partially resolved from one another. Furthermore, the individual hydrocarbons can cover a wide range of concentrations, making quenching of selected sulfur compounds a possibility if they coelute with a large hydrocarbon peak. The potential for quenching of the sulfur signal in gasoline is mitigated by careful selection of the proper GC column and programming conditions and by using small injection volumes and higher split ratios. Some minor adjustments to the PFPD operating conditions have also proven successful at mitigating the effects of quenching.

Figure 7 illustrates an extreme case which the potential for quenching was initially expected to interfere with the sulfur detection, but in fact did not pose significant difficulty. This gasoline had been analyzed previously and was reported to contain very low sulfur content at approximately 5-ppm total sulfur.

Several modifications were made to the standard PFPD sulfur configuration to mitigate the potential for quenching and to allow a much lower split ratio of 9:1 to be used. The larger 3-mm PFPD combustor was substituted for the standard 2-mm size, and the airflow was increased by approximately 1 mL/min. Using the larger combustor and slightly more air in the combustion gas mixture produced a hotter flame. With a hotter flame, there is a more complete combustion of the hydrocarbon and reduced opportunity for competing side reactions that limit the sulfur



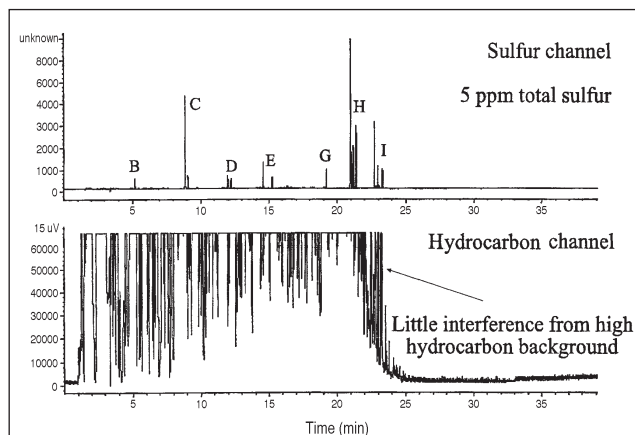
emissions. The detectivity of sulfur is slightly lower under these conditions (approximately 10–20%), but any loss in sensitivity is offset by the ability to use a lower split ratio and introduce more sulfur to the detector. The chromatograms in Figure 7 clearly show that the sulfur gate did not suffer significantly from quenching, in spite of the extensive coeluting hydrocarbon background.

Two additional gasoline applications are shown in Figures 8 and 9, the simultaneous sulfur and hydrocarbon chromatograms of a gasoline before and after desulfurization treatment. Individual peak identifications and compound groups are listed in Table III. A 1- $\mu$ L aliquot of the gasoline was injected using a 100:1 split ratio to minimize the potential for sulfur quenching caused by hydrocarbon coelution. Several dozen hydrocarbons peaks are evident in the bottom trace, with all compounds eluting before 25 min. There was only a very small amount of potential quenching at two points between 1 and 3 min (identified by the slight negative peaks in the sulfur channel), and these did not interfere with any of the sulfur compounds detected.

The calculated concentrations for these two gasoline samples

**Table II. Single Laboratory "Intermediate Precision" Data for D4735-02 Using the OI Analytical PFPD Compared with the Original FPD Data**

Intermediate precision data from D4735-96 (FPD)	
Thiophene concentration (mg/kg)	Intermediate precision (mg/kg)
0.80	0.040
1.80	0.078
Intermediate precision data from D4735-02 (PFPD)	
Thiophene concentration (mg/kg)	Intermediate precision (mg/kg)
0.50	0.010
1.00	0.010
3.00	0.023
5.00	0.031

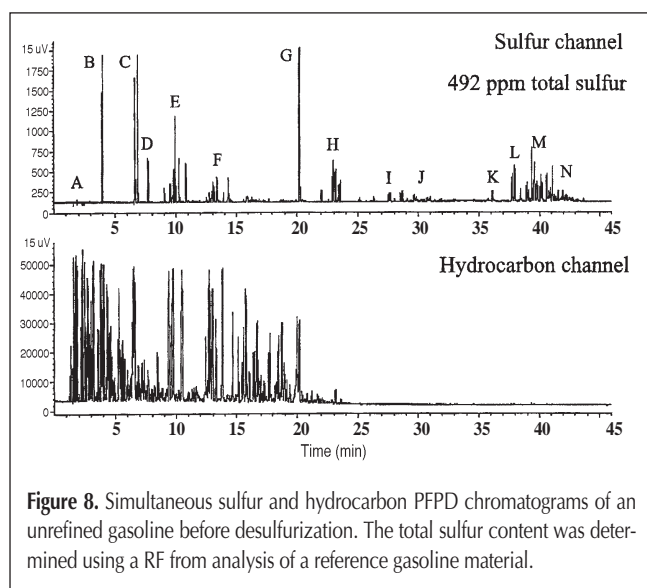


**Figure 7.** Simultaneous sulfur and hydrocarbon PFPD chromatograms of a gasoline reported to contain 5 ppm total sulfur. Note the lack of any significant quenching in spite of the presence of a very high hydrocarbon background.

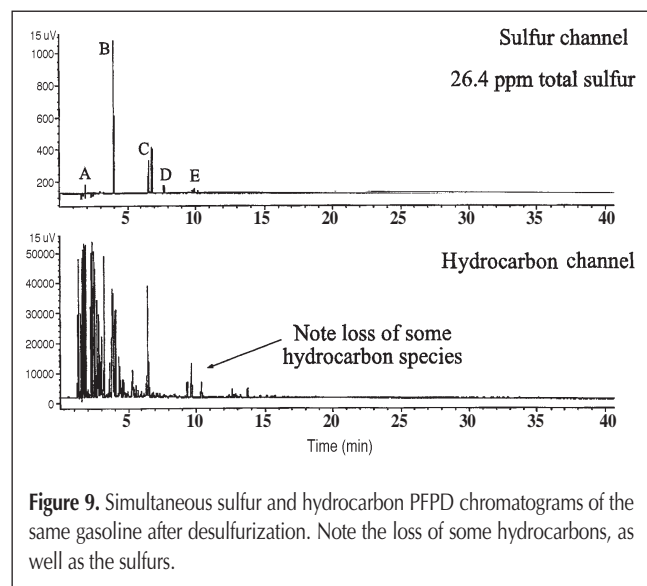
were 492 and 26.4 ppm total sulfur, respectively. The sulfur content was determined by analyzing a gasoline reference material with a known consensus concentration of 55.76 ppm total sulfur. A response factor (RF) was generated by finding the total integrated peak area for the sulfur peaks in the reference matrix chromatogram and dividing by the consensus concentration. The RF was then used to calculate the total sulfur content in the two unknown gasoline samples. The minimum detectability for this technique was limited by the injection volume and split ratio. For the analytical conditions described previously, the minimum detectability for each individual sulfur peak was approximately 200 ppb.

### Sulfur in diesel

Diesel fuels are similar to gasoline in that they contain numerous hydrocarbon compounds. However, they generally have higher boiling points and will elute later in the chromatogram. Figures 10 and 11 are chromatograms of the same diesel fuel quantitated using two different techniques. In Figure



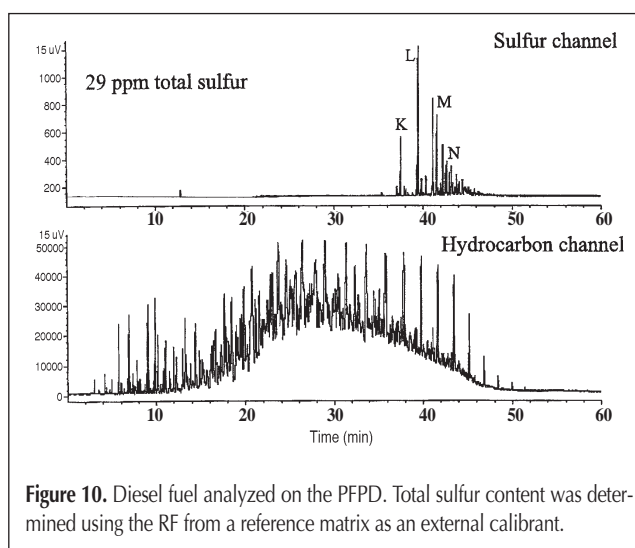
**Figure 8.** Simultaneous sulfur and hydrocarbon PFPD chromatograms of an unrefined gasoline before desulfurization. The total sulfur content was determined using a RF from analysis of a reference gasoline material.



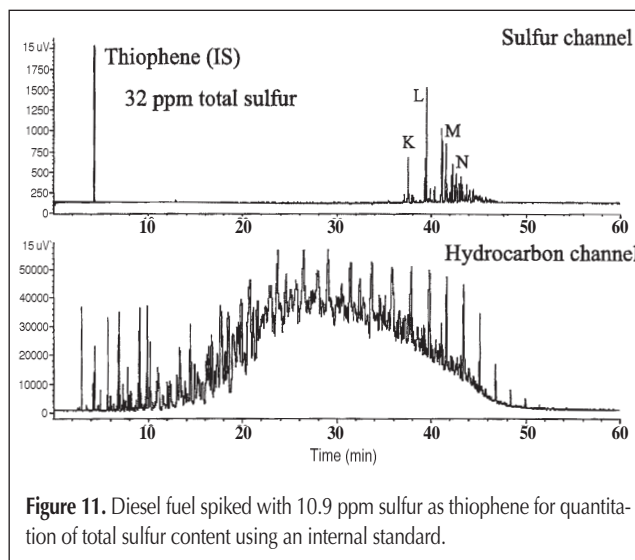
**Figure 9.** Simultaneous sulfur and hydrocarbon PFPD chromatograms of the same gasoline after desulfurization. Note the loss of some hydrocarbons, as well as the sulfurs.

**Table III. Identifications for Individual Compounds and Compound Groups in Figures 7–11**

Designation	Compound or group identification
A	Methyl mercaptan
B	Thiophene
C	C1-thiophenes
D	Tetrahydrothiophene
E	C2-thiophenes
F	C3-thiophenes
G	Benzothiophene
H	C1-benzothiophenes
I	C2-benzothiophenes
J	C3-benzothiophenes
K	Dibenzothiophene
L	C1-dibenzothiophenes
M	C2-dibenzothiophenes
N	C3-dibenzothiophenes



**Figure 10.** Diesel fuel analyzed on the PFPD. Total sulfur content was determined using the RF from a reference matrix as an external calibrant.



**Figure 11.** Diesel fuel spiked with 10.9 ppm sulfur as thiophene for quantitation of total sulfur content using an internal standard.

10, the sulfur content in the fuel was determined using a reference matrix, as described previously. The diesel was then spiked with 10.9 ppm sulfur as thiophene and reanalyzed. Thiophene was chosen as the internal standard because it was not detected in the sample during the first analysis and because it did not elute near the other sulfur compounds detected. An RF for the thiophene was calculated by dividing the thiophene peak area by the concentration of sulfur. The total sulfur content can then be determined in one of two ways. The first way is to simply find the integrated area of all the sulfur peaks together and use the RF to calculate the concentration of total sulfur. An alternative approach is to use the same RF to calculate the concentration of each individual sulfur peak and then sum them for the total sulfur content. The second approach has the added advantage of providing information about the individual species present, as well as the total sulfur content. The calculated concentrations of the total sulfur in this sample using the external and internal calibration technique were 29 and 32 ppm, respectively, demonstrating that the two approaches are approximately equivalent.

When comparing total sulfur content derived using a GC detector with XRF or other values for gasolines and diesel fuels, it is important to remember that GC techniques only measure those organic sulfur compounds that lend themselves to chromatographic separation and may not include very high molecular weight ( $M_r$ ) sulfur compounds or elemental sulfur. If there are sulfur compounds present at concentrations below the minimum detectable limit, they may not be measured and included in the total sulfur concentration. Matrices that contain multiple low-concentration sulfur compounds, elemental sulfur, or high  $M_r$  compounds that do not lend themselves well to GC, may produce total sulfur results that indicate a low bias when compared with XRF or UV fluorescence. However, when these conditions are not present, the GC, XRF, and UV results may be in agreement. Further work is in progress to determine the bias between the PFPD results and those obtained by total sulfur methods used in the petroleum industry.

## Conclusion

The PFPD can be used to determine the total sulfur content in a wide variety of petrochemical products over a wide range of concentrations. Sub-ppm measurements are easily performed for specific compound identification. The PFPD's inherent equimolar response for sulfur allows simple and straightforward quantitation of total sulfur concentration using several different techniques. Identification and quantitation of individual sulfur species can also be easily incorporated into the analytical scheme. Although quenching of the sulfur signal may be experienced in the presence of some hydrocarbon matrices, the effects can be minimized or completely eliminated by optimization of the PFPD and GC operating conditions

## References

1. S. Brody and J. Chaney. Flame photometric detector: the application of a specific detector to phosphorus and sulfur compounds sensitive to subnanogram quantities. *J. Gas Chromatogr.* **4**: 42–46 (1966).
2. E. Atar, S. Cheskis, and A. Amirav. Pulsed flame—a novel concept for molecular detection. *Anal. Chem.* **63**: 2061–64 (1991).
3. S. Cheskis, E. Atar, and A. Amirav. Pulsed flame photometer—a novel gas chromatography detector. *Anal. Chem.* **65**: 539–55 (1993).
4. A. Amirav and H. Jing. Pulsed flame photometric detector for gas chromatography. *Anal. Chem.* **67**: 3305–18 (1995).
5. H. Jing and A. Amirav. Pulsed flame photometric detector—a step forward towards universal heteroatom selective detection. *J. Chromatogr. A* **805**: 177–215 (1998).
6. L. Kalontarov, H. Jing, A. Amirav, and S. Cheskis. Mechanism of sulfur emission quenching in flame photometric detectors. *J. Chromatogr. A* **696**: 245–56 (1995).
7. Standard test method for determination of trace thiophene in refined benzene by gas chromatography. ASTM Standard D4735-02. *Annual Book of ASTM Standards 2002*. **06.04**, ASTM International, West Conshohocken, PA, 2002, pp. 436–39.

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