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## **Determination of Total Sulfur Content in Petrochemical Samples Using a Pulsed Flame Photometric Detector (PFPD)**

### **Introduction**

Sulfur compounds are present in nearly all petrochemical products at a wide range of concentrations, and analysis of the total sulfur content is an integral part of most petrochemical quality control processes. There are over a dozen different test methods available for total sulfur determination, including atomic absorption, X-ray fluorescence, microcoulemetric, UV fluorescence, and GC methods, each with their own benefits and difficulties. Only the GC methods using a sulfur-selective detector have the advantage of simultaneous quantitation of both individual sulfur species and total sulfur content.

This application note will illustrate several different approaches to quantitation of sulfur in petrochemical products using the equimolar response capability of the Pulsed Flame Photometric Detector (PFPD). Total sulfur quantitation using a single compound or a reference matrix as well as calibration curves for speciated sulfur standards using an internal standard will be demonstrated. Results from the analyses of several consensus value QC standards used in ASTM round robin studies are shown. Examples of total sulfur analyses in “real world” samples are also included.

### **PFPD Equimolar Response**

The PFPD has the advantage of being an inherently equimolar response detector. The sulfur’s chemiluminescence response is independent of a compound’s molecular structure. A fixed concentration of sulfur will give the same PFPD response regardless of the parent compound, and this feature allows quantitation of the sulfur content in complex samples. Calibration with a known concentration of a single sulfur compound or mix will allow quantitation of the sulfur content in individual GC peaks or complex chromatographic patterns.

### **Total Sulfur Quantitation Using a Single Compound**

To use the PFPD equimolar response feature to do total sulfur quantitation using a single compound, begin by selecting a single sulfur-containing compound with a molecular structure similar to those expected to be found in the matrix (e.g., thiophene, sulfide, mercaptan, etc.). Using the single compound, prepare calibration standards at several concentrations spanning the range of interest and analyze them under the same conditions that will be used for the samples. Prepare a calibration curve in the usual manner, plotting

PFPD response (peak area) as a function of the sulfur concentration, being sure to use the concentration of sulfur in the solutions and not the concentration of the compound chosen. Determine the equation for the line and the correlation coefficient ( $R^2$ ). A typical, single-peak calibration standard and linear calibration curve are shown in Figures 1 and 2.

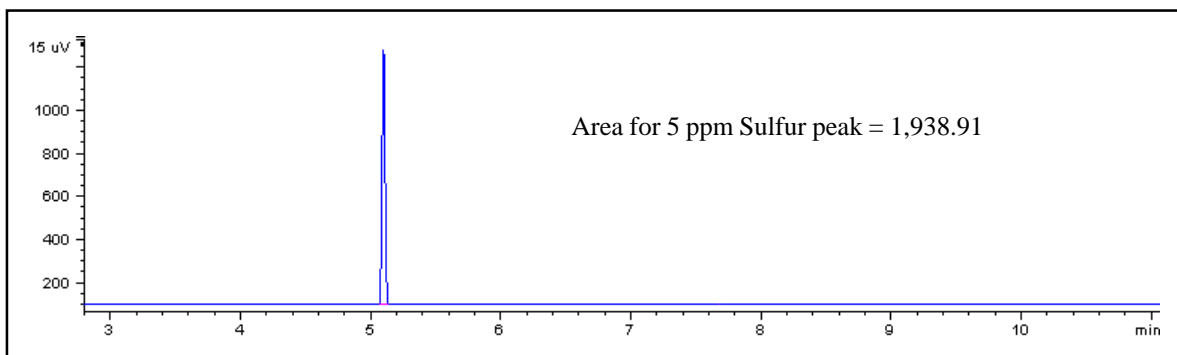


Figure 1. Integrated Area for a Single Sulfur Peak at 5 ppm

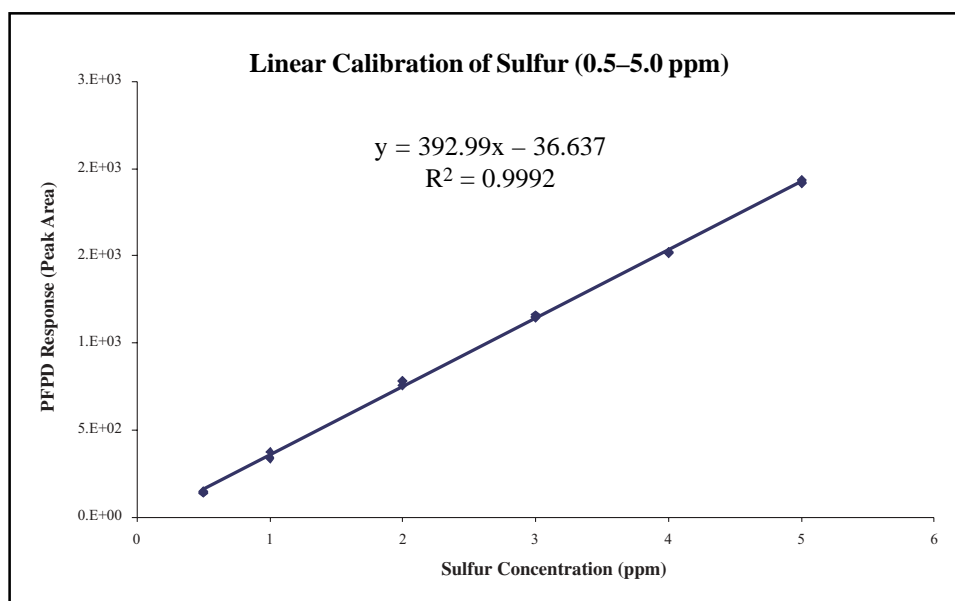


Figure 2. Calibration Curve Plotting Peak Area as a Function of Sulfur Concentration

Acquire data for the unknown sample and determine the total integrated peak area across the chromatogram. Using the linear equation from the calibration curve, calculate the total concentration of sulfur in the unknown sample. The sulfur content in each individual peak can also be calculated separately, then summed for a total sulfur determination. Because of differences in peak shape and width, this technique works best when applied to samples with a limited number of well-resolved chromatographic peaks and when the calibrant is closely matched to the type of compounds expected to be in the sample.

## Speciated Sulfur

To measure the concentration of individual sulfur species, purchase or prepare a single stock standard solution containing all of the sulfur compounds of interest. Use the stock solution to prepare calibration standards at several concentrations spanning the range of interest and analyze them under the same conditions that will be used for the unknown samples. Prepare a calibration curve for each compound, plotting PFPD response (peak area) as a function of the sulfur concentration and determine the linear equation and correlation coefficient ( $R^2$ ) for each line. For speciated sulfur, either the concentration of sulfur in the solution or the concentration of the compound can be used for the calibration curve. Acquire data for the unknown sample and determine the integrated peak area for each peak with a retention time matching those in the standard. Use the linear equations to calculate the concentration for each identified peak. To calculate the sulfur content of an unknown peak, use the equation for the compound of a similar structure and peak width, being sure that the calibration curve has been created using the concentration of sulfur rather than the concentration of the compound. The chromatogram of a typical calibration solution for determination of sulfides is shown in Figure 3 and its corresponding calibration curves in Figure 4.

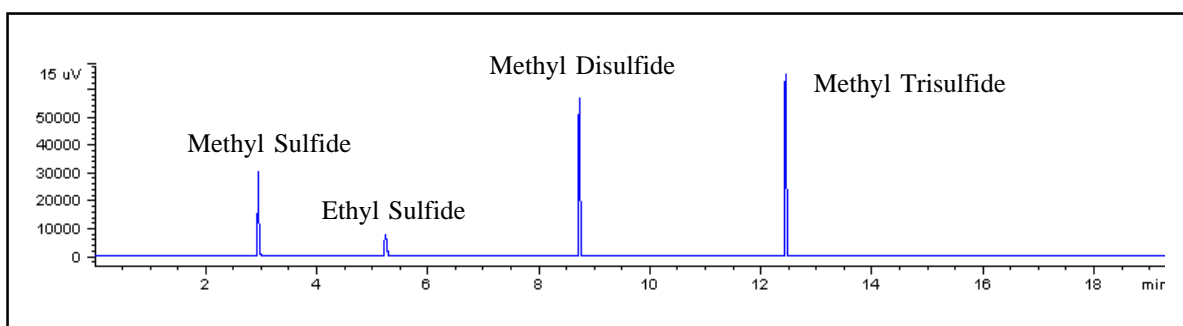


Figure 3. Chromatogram of Sulfur Standard Containing Four Different Sulfur Species

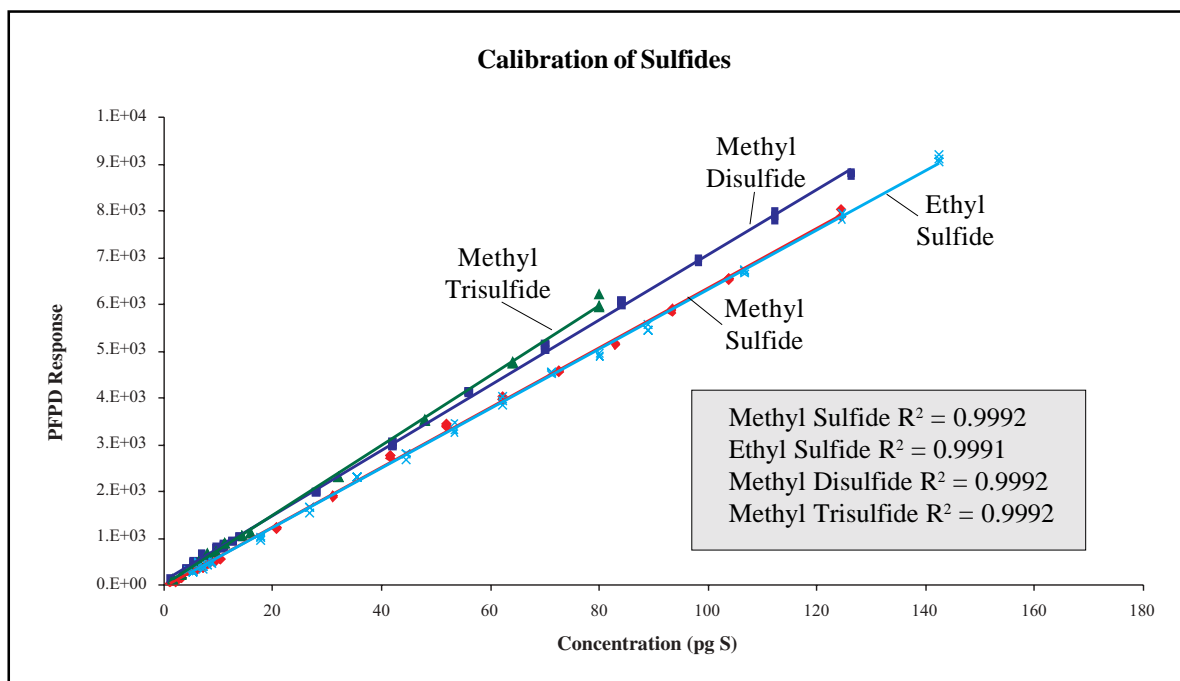


Figure 4. Linear Calibration Curve for Four Sulfide Compounds

### **Total Sulfur Quantitation Using a Reference Matrix**

Many petrochemical products involve complex hydrocarbon backgrounds and multiple sulfur species that may or may not be completely resolved chromatographically. To determine the total concentration of sulfur in a matrix of this type, begin by purchasing a reference material of known sulfur concentration in a matrix similar to the samples that will be analyzed (e.g., gasoline, diesel, fuel oil, etc.). The sulfur concentration in the standard should be in the same approximate range as that expected to be found in the sample. Analyze the reference material under the same conditions that will be used for the sample. Determine the total integrated peak area across the PFPD sulfur chromatogram and use it to calculate a response factor (RF) for sulfur as illustrated in Figure 5.

$$\text{RF} = \text{Total Peak Area}/\text{Sulfur Concentration}$$

Acquire data for the unknown sample and determine the total integrated peak area across the chromatogram. Use the RF to calculate the total sulfur concentration in the sample.

$$\text{Sulfur Concentration} = \text{Total Peak Area}/\text{RF}$$

Illustrations of this type of total sulfur determination are included in the examples below.

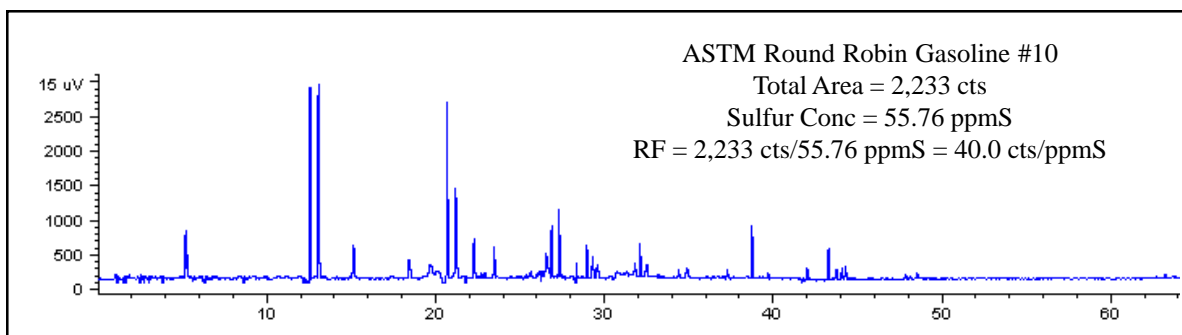


Figure 5. Calculation of Sulfur RF Using the ASTM Round Robin Gasoline Reference Matrix with a Total Sulfur Concentration of 55.76 ppm

### **Hints For Best Results**

- To take advantage of the PFPD's equimolar response capability for sulfur, it is essential that the detector be operated in the linear "Square Root ON" mode, and that all responses be measured as peak areas, rather than peak heights.
- Like other flame photometric detectors, the PFPD sulfur signal can be "quenched" (decreased) when the sulfur peak is co-eluting with a large (e.g., >50 ng) hydrocarbon peak. Therefore, for best results it is important to ensure that maximum chromatographic separation exists between the sulfur compounds and any large matrix hydrocarbon peaks in the sample. Sulfur has a decreased time delay when quenching is present, and this phenomenon is easily identified using the PFPD's WinPulse or PFPDView software.
- The GC/PFPD determination of total sulfur concentration measures only those organic sulfur compounds that can be easily passed through and separated by a gas chromatographic column. Sulfur content determined by other techniques, such as AA, XRF, microcoulemetric, etc., might not necessarily match concentrations determined by GC due to the differences inherent in the instrumentation.
- To maintain maximum peak areas within the dynamic range of the PFPD, careful selection of the GC conditions (e.g., sample size, split ratio) is necessary.

### H<sub>2</sub>S and Unknown Sulfur Compounds in Natural Gas

Figure 6 is a chromatogram of 3.4 ppmv H<sub>2</sub>S and two unknown sulfur compounds in a pipeline natural gas matrix. The H<sub>2</sub>S in the natural gas was quantified using an H<sub>2</sub>S gas standard generated by the system's built-in permeation oven and an H<sub>2</sub>S permeation device. The concentrations of the two unknown sulfur peaks were calculated using the equimolar response feature of the PFPD described earlier. A simultaneous hydrocarbon channel is available with the PFPD, and thus, the hydrocarbon pattern in the natural gas is also obtained. Quantitation on this hydrocarbon channel is limited, but qualitative data is beneficial in many applications. The data were acquired on the OI Analytical S-PRO 3200 Series GC System using a 0.5-mL gas sample loop, a 9:1 split ratio, an Agilent GS-GasPro® column, and an isothermal GC oven program.

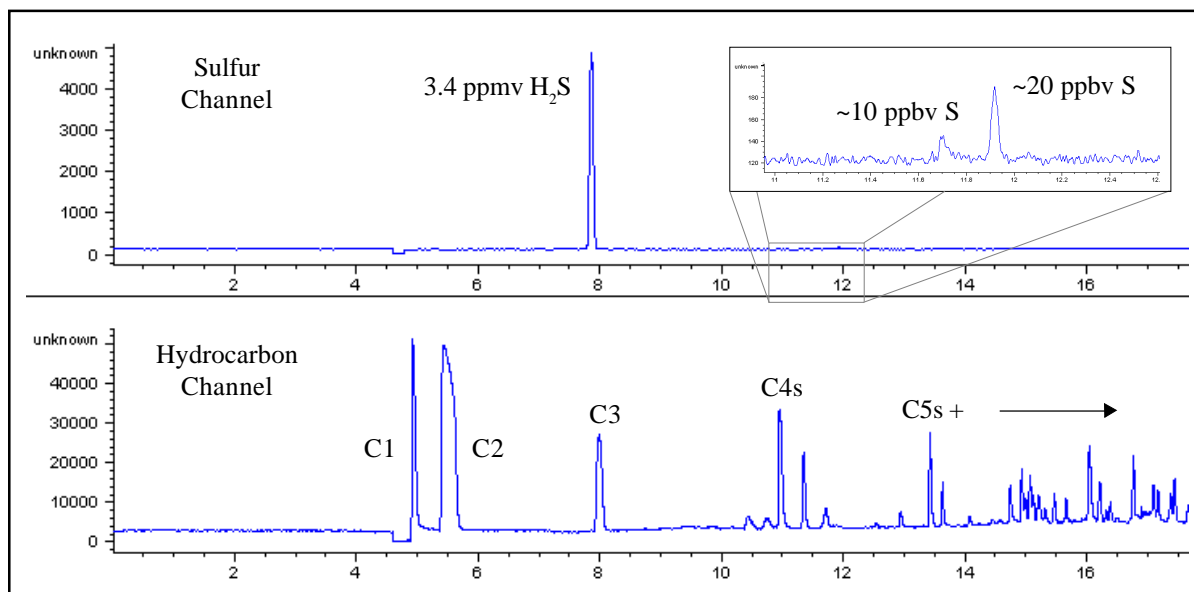


Figure 6. PFPD Chromatogram of 3.4 ppmv H<sub>2</sub>S and Two Unknown Sulfur Compounds in a Natural Gas Matrix

### Total Sulfur in Gasoline Reference Material

Four aliquots of three different gasoline reference materials were analyzed on a PFPD that had been configured and optimized for sulfur analysis. One gasoline reference material (ASTM Round Robin Gasoline #10-02) with a consensus total sulfur concentration of 55.76 ppm was used as a calibration standard to generate an RF. The remaining three gasoline samples were analyzed using the same GC conditions, and their total sulfur concentrations were calculated using the initial RF. Figures 7, 8, and 9 display the results. Note that the complex hydrocarbon matrix did cause some minor quenching of the sulfur signal (identified by the slight negative peaks in the sulfur channels), but it did not significantly affect the determination of total sulfur concentration in the “unknowns.” Using a slower GC oven program or a higher split ratio can further reduce this quenching effect. These data were acquired with the PFPD configured and optimized for sulfur with a 3-mm combustor and a BG-12 filter. All injections were 1 µL, split 9:1 onto a Restek Rtx-35MS column with a ramped oven program.

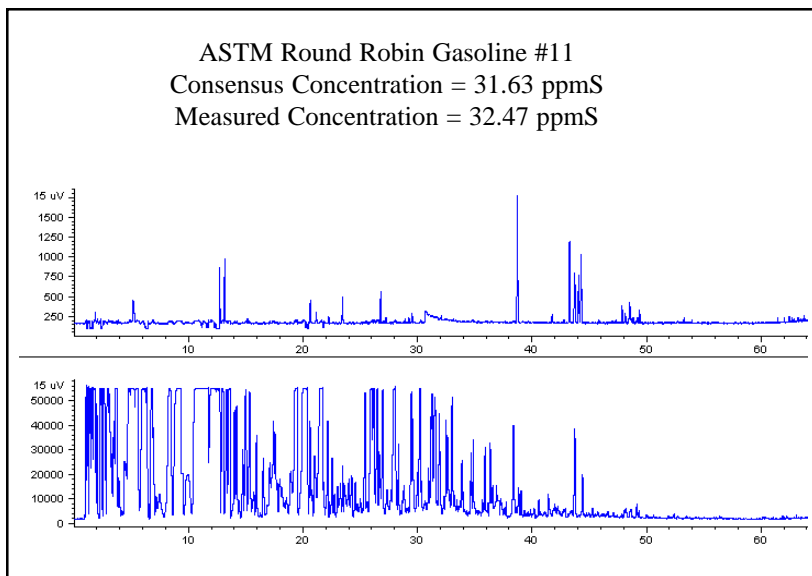


Figure 7. PFPD Chromatogram of ASTM Round Robin Gasoline #11 with a Consensus Concentration of 31.63 ppm Total Sulfur. Calculated Concentration was 32.47 ppm Total Sulfur (~103% of the Consensus Value).

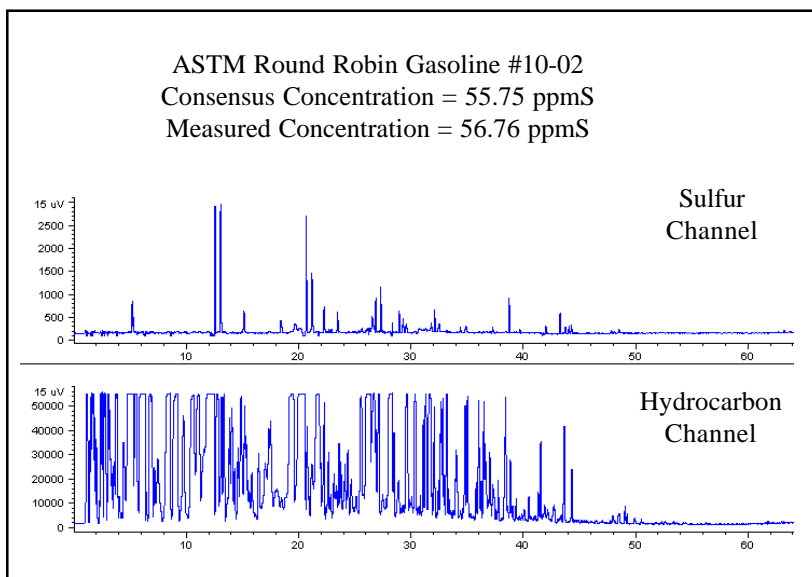


Figure 8. PFPD Chromatogram of ASTM Round Robin Gasoline #10-02 with a Consensus Concentration of 55.75 ppm Total Sulfur. Calculated Concentration was 56.76 ppm Total Sulfur (~102% of the Consensus Value).

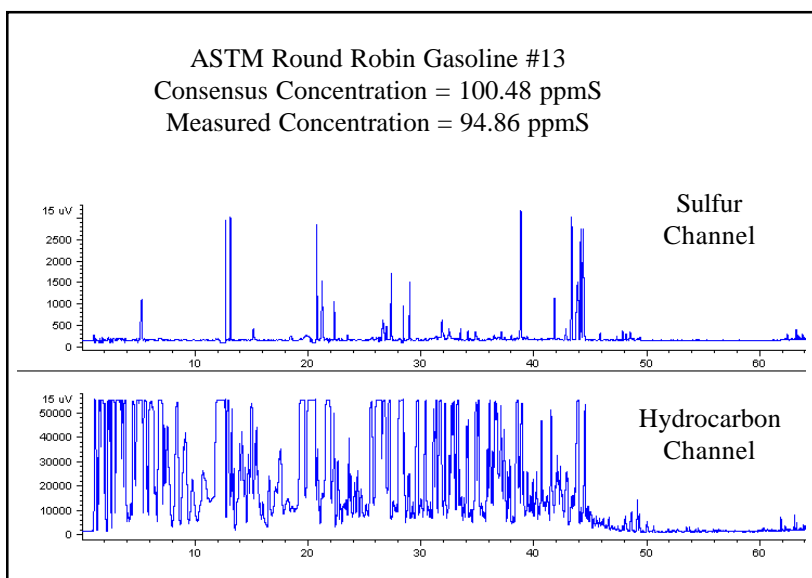


Figure 9. PFPD Chromatogram of ASTM Round Robin Gasoline #13 with a Consensus Concentration of 100.48 ppm Total Sulfur. Calculated Concentration was 94.86 ppm Total Sulfur (~94% of the Consensus Value).

### **Total Sulfur in Unrefined and Refined Gasolines**

Two unknown gasolines expected to contain low- to mid-level total sulfur concentrations were analyzed on the PFPD, and their concentrations were calculated using the RF from ASTM Round Robin Gasoline #11 (with consensus concentration of 31.63 ppm total sulfur). The results of these analyses are shown in Figures 10 and 11. The first sample, an unrefined gasoline, was expected to have a total sulfur concentration of about 50 ppm; the concentration calculated using the reference matrix RF was 42.2 ppm total sulfur. The second sample, the refined gasoline, had been found in the past to have a total sulfur concentration in the range of 9 to 15 ppm. The calculated concentration in this sample was 12.6 ppm total sulfur. These data were acquired using 1- $\mu$ L injections, a 9:1 split ratio, a DB-5MS capillary column, and a ramped oven program.

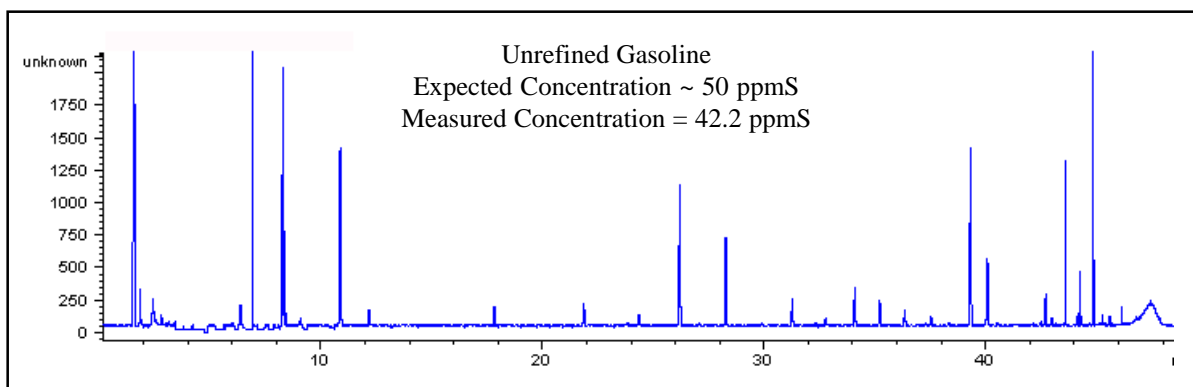


Figure 10. PFPD Sulfur Chromatogram of an Unrefined Gasoline with a Concentration of 42.2 ppm Total Sulfur

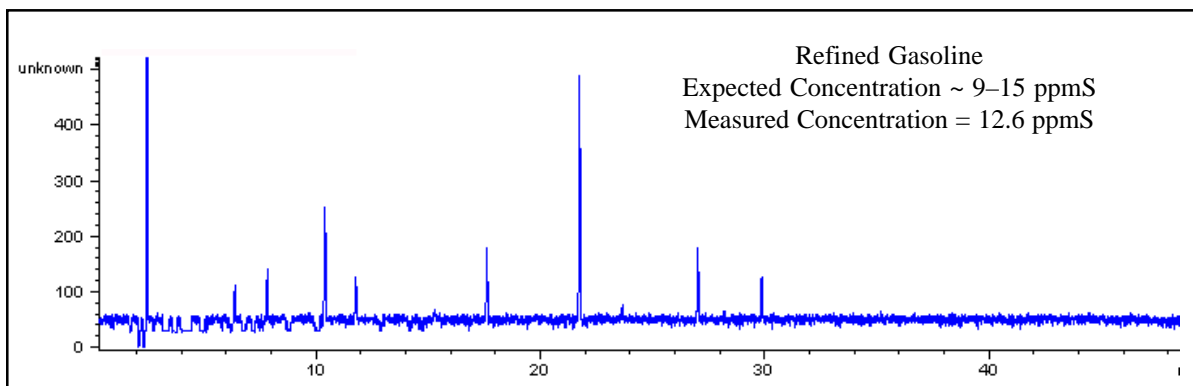


Figure 11. PFPD Sulfur Chromatogram of a Refined Gasoline with a Concentration of 12.6 ppm Total Sulfur. Total Sulfur Concentrations from this Sample and the One Shown in Figure 10 were Both Calculated Using a Gasoline Reference Matrix with a Consensus Concentration of 31.63 ppm Total Sulfur.

### Total Sulfur in a Low-Level Gasoline

A refined gasoline known to contain approximately 5 ppm total sulfur was analyzed on the PFPD; the resulting chromatogram is shown in Figure 12. The peak pattern generated by the OI Analytical PFPD is similar to a chromatogram of the same sample obtained using a sulfur chemiluminescence detector (SCD) (Figure 13) but with an improvement in chromatographic resolution. As expected with the injection of neat gasoline, there was a high hydrocarbon mass on column (due to the low 10:1 split ratio) co-eluting with the sulfur components of interest. The intensity of the hydrocarbon co-elution is illustrated by the monitoring of a second carbon channel in addition to the sulfur channel. As can be seen from the two simultaneous PFPD chromatograms, there was negligible contribution to the sulfur signal from the high hydrocarbon background.

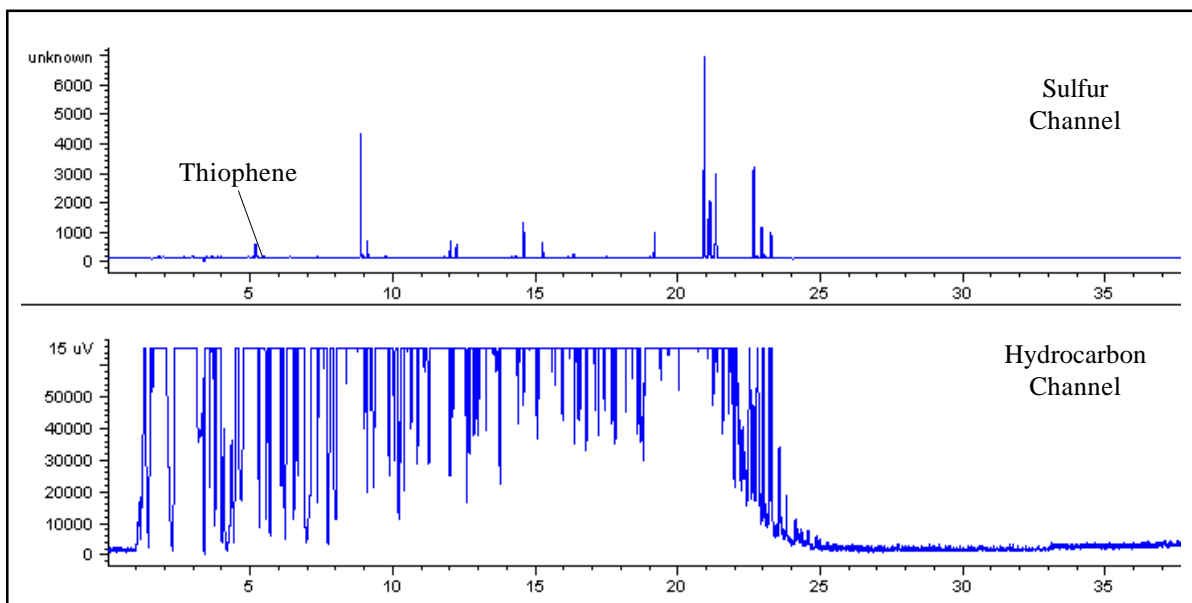


Figure 12. PFPD Chromatogram of a Gasoline Sample Containing 5 ppm Total Sulfur

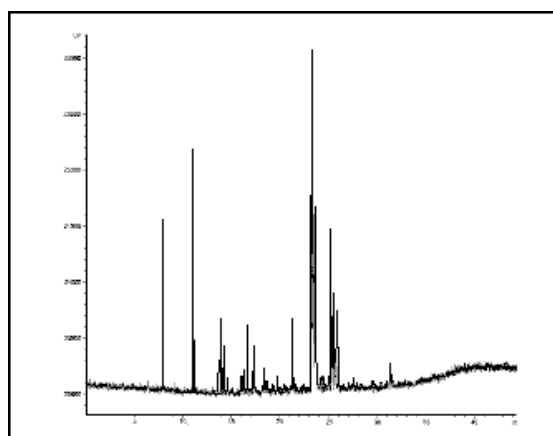


Figure 13. Sulfur Chemiluminescence Chromatogram of the Same Sample. Note the Difference in Chromatographic Resolution and Overall Decrease in Sulfur Sensitivity Indicated by the S/N Ratio.



### Total Sulfur in LCO and Crude Oil

Figures 14 and 15 demonstrate the detection and quantitation of total sulfur in light cycle oil (LCO) and crude oil samples, respectively. Both samples had a significant distribution of the high molecular weight sulfur compounds, as indicated by their relatively late elution profiles. The distribution of hydrocarbons in the LCO is shown in the bottom trace of Figure 14, illustrating how the PFPD can be used to monitor and chart potential interferences. In this sample, there was virtually no interference from the hydrocarbon. Both the LCO and the crude oil were analyzed using a PFPD configured with a 2-mm combustor and a BG-12 optical filter, 1- $\mu$ L injections, a 10:1 split ratio, and an HP-1 capillary column. Both samples were determined to have a total sulfur concentration exceeding 500 ppm using a reference material for calibration.

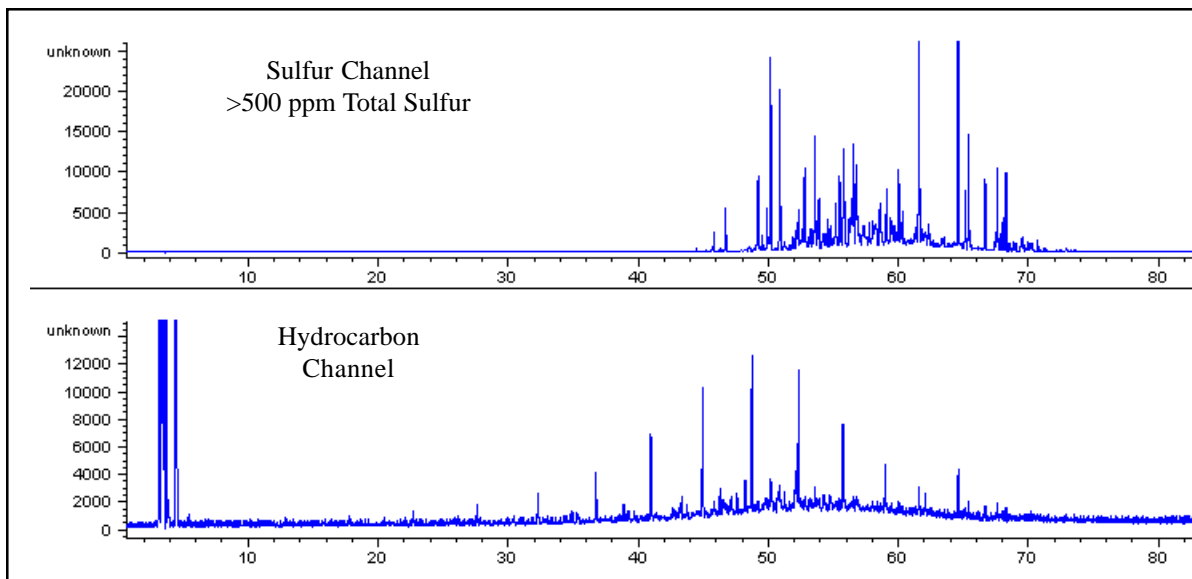


Figure 14. PFPD Chromatogram of Light Cycle Oil (LCO) with a Total Sulfur Concentration in Excess of 500 ppm. Note the Lack of any Interference from the Hydrocarbons in the Sulfur Channel.

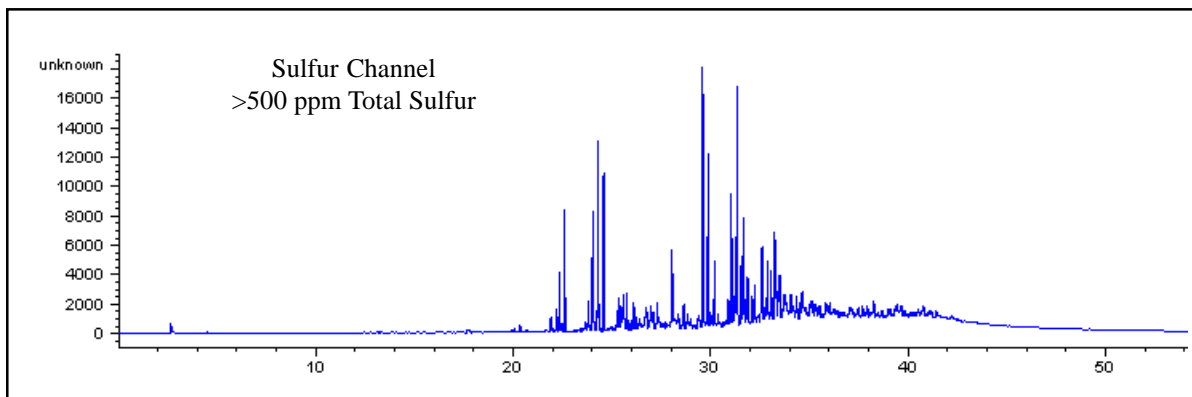


Figure 15. PFPD Chromatogram of a Crude Oil with a Total Sulfur Concentration in Excess of 500 ppm. The Total Sulfur Concentration in this Sample and the One Shown in Figure 14 were Estimated Using a Gasoline Reference Matrix.

### **Total Sulfur in an Unknown Petrochemical Product**

Figure 16 shows the PFPD sulfur and hydrocarbon chromatograms resulting from the analysis of an unknown petrochemical product determined to contain 350 ppm total sulfur. Historically, this sample had been found to contain between 350–450 ppm total sulfur. The data were acquired with a PFPD configured and optimized for sulfur with a 3-mm combustor, using a 1- $\mu$ L injection split 75:1, a Restek Rtx-35MS capillary column, and a very slow GC oven program.

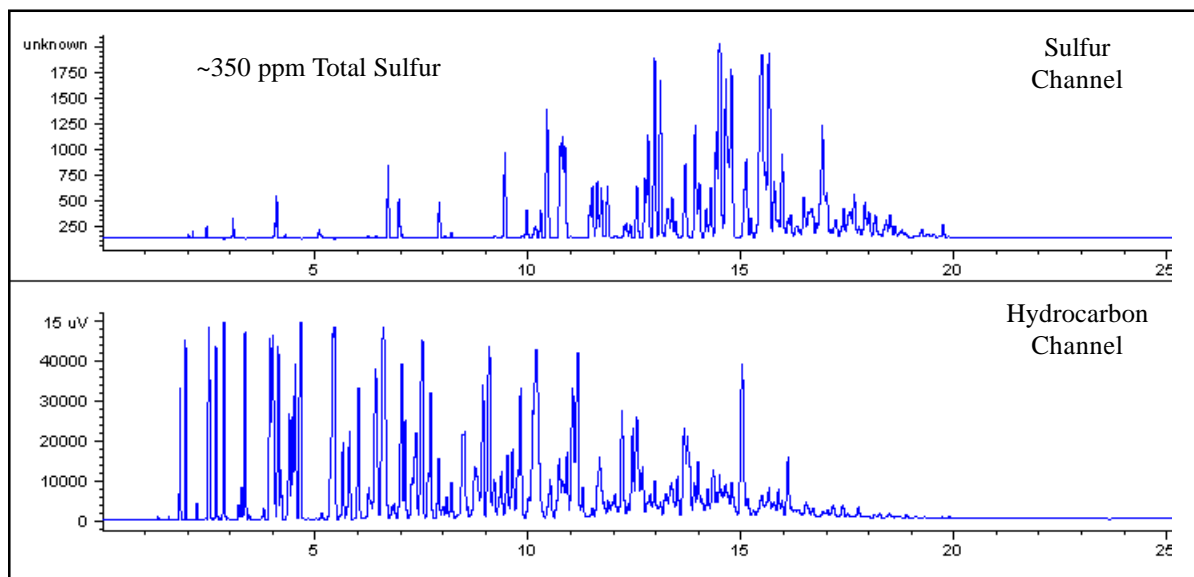


Figure 16. PFPD Chromatogram of an Unknown Petrochemical Product with a Concentration of 350 ppm Total Sulfur

### **Total Sulfur in Cresylic Acid Using an Internal Standard**

An alternate procedure for calculating total sulfur concentration is to spike the sample with a known concentration of an internal standard and use the RF from that peak to determine the overall total sulfur concentration in the sample. This procedure is illustrated in Figure 17. The sample, cresylic acid, was spiked with 20 ppm sulfur as thiophenol, a compound not expected to be naturally occurring in this matrix. The concentration of two specific peaks of interest, benzothiophene and diphenyldisulfide (DPDS), were determined to be 35 ppm sulfur and 56.7 ppm sulfur, respectively, and the total sulfur concentration was 270 ppm. These data were acquired on a PFPD configured and optimized for sulfur determination with a 3-mm combustor and a BG-12 optical filter. Analyses were done using a 0.2- $\mu$ L injection and a 50:1 split ratio.

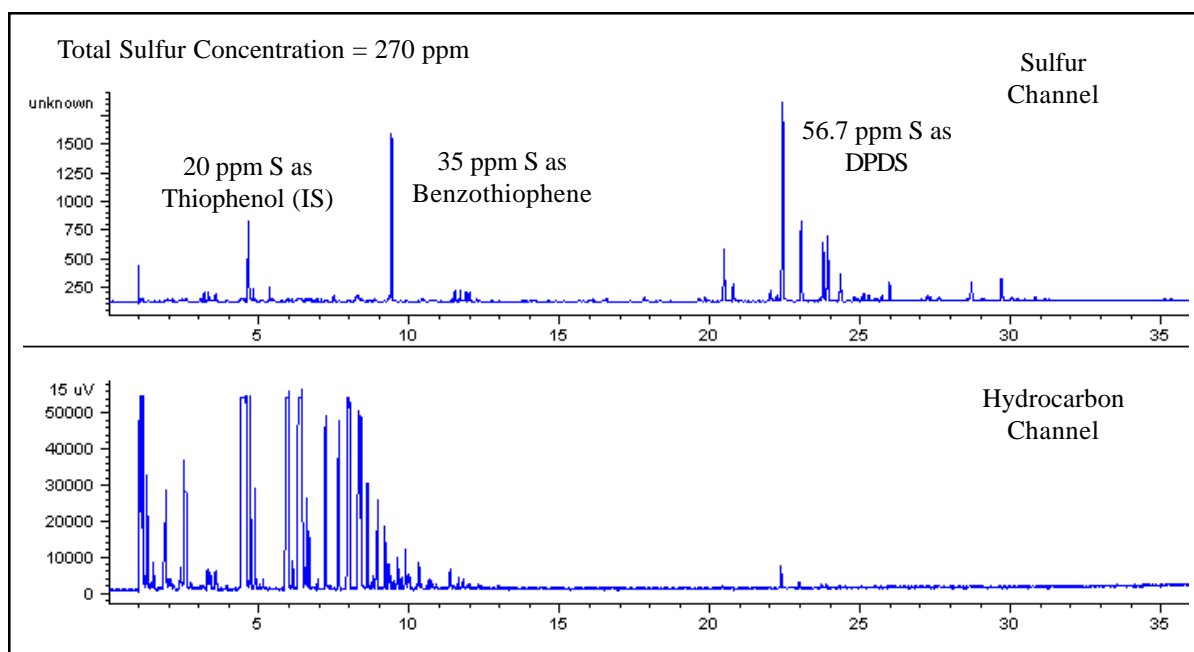


Figure 17 PFPD Chromatogram of Cresylic Acid. Sulfur Content of Two Specific Peaks of Interest, as well as the Overall Total Sulfur Concentration were Calculated Using Thiophenol as an Internal Standard

### **Conclusion**

The PFPD can be used to determine the total sulfur content in a wide variety of petrochemical products at concentrations ranging from very low (e.g., <5 ppm S) to very high (e.g., >500 ppm S). Sub-ppm measurements are easily performed for specific compound identification. The PFPD's inherent equimolar response for sulfur allows for 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. This information can be very useful for refineries and chemical manufacturers to analyze and optimize changes to the refining process. Although slight 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.

### **Acknowledgement**

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