

# Analysis of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography with Pulsed Flame Photometric Detection (PFPD)

PETROCHEMICAL SERIES



## Introduction

Accurate identification and measurement of sulfur species is critical in the petroleum industry. Natural gas and other gaseous fuels naturally contain varying amounts and classes of sulfur compounds. Even in trace amounts, sulfur can be destructive to the natural gas refining process by corroding equipment and/or inhibiting or destroying catalysts, not to mention the associated odor that may appear. Although naturally occurring sulfur can cause harm, sulfur is actually added in small amounts (1 to 4 ppmv) to natural gas as a petroleum product for safety purposes on the backend. Due to the reactivity and instability of sulfur species during sampling, reliable analysis can be challenging with improper equipment.

The Pulsed Flame Photometric Detector (PFPD) has advantages over other sulfur detectors such as unambiguous sulfur detection and selectivity against hydrocarbon matrices, increased sensitivity, and equimolar sulfur response.



Figure 1. OI Analytical 5383 PFPD

## Experimental

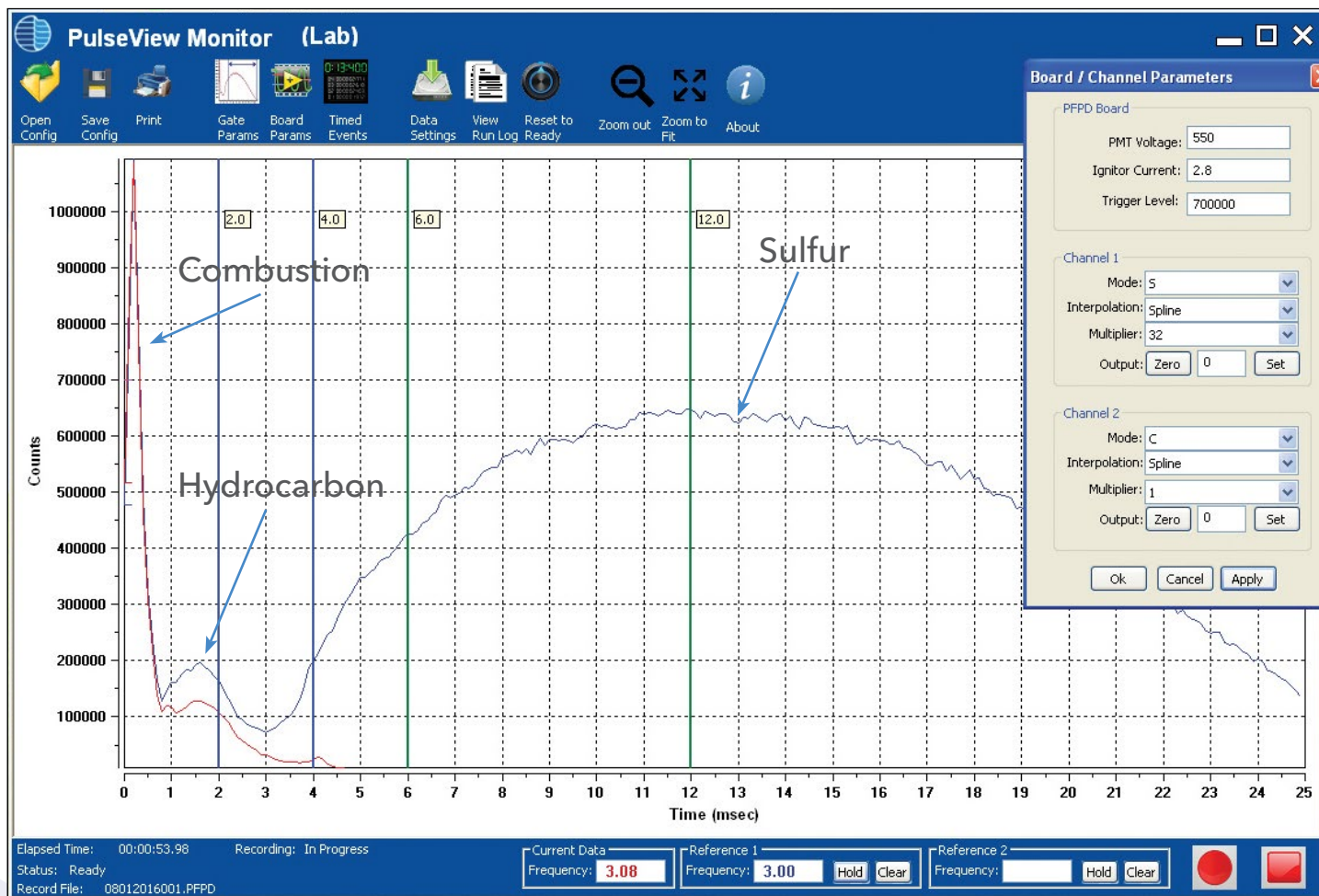
### System Description:

This application note describes the analysis of sulfur in various matrices using an Agilent 7890A GC coupled with an OI Analytical 5383 Pulsed Flame Photometric Detector (PFPD). The superior sensitivity of the 5383 PFPD makes it the instrument of choice for the analysis of sulfur and other elements. Its linear, equimolar response to sulfur allows selective measurement of individual sulfur species from low ppb to ppm levels, and total sulfur as the sum of individual peaks. The unique capability to obtain simultaneous sulfur and hydrocarbon chromatograms from a single PFPD detector sets it apart from other sulfur detection technologies. The system consists of an Agilent

gas chromatograph configured with two electronically controlled air actuated valves. The Agilent Select Low Sulfur column was used because of its unique inertness and selectivity. It handles the difficult separation of H<sub>2</sub>S from C<sub>2</sub> matrices and COS from C<sub>3</sub> very well.

The PFPD was tuned for optimum sulfur response with the sulfur emission extending out to 25ms. Please see Figure 2. It was configured for sulfur and hydrocarbon detection with the sulfur run in the linearized mode, i.e. with the square root function on. Simultaneous, mutually selective sulfur and hydrocarbon chromatograms were produced from a single detector using the dual gate capability of the PFPD.

Figure 2. Emission in PulseView Monitor



## Standard and sample analysis:

The instrument was calibrated for H<sub>2</sub>S, COS, MeSH, EtSH, DMS, n-PrSH, TP, and DMDS using permeation devices and a KIN-TEK permeation oven held at a constant temperature of 40° C. The concentrations of the compounds were varied by changing the air flow rate through the permeation oven using flows from 250 to 2500 ml/minute. A seven-point calibration was run. Five Initial Demonstrations of Capability

(IDOC) were run using a 500ml/min flow and eight Method Detection Limit (MDL) standards were run using 3000 ml/min. Standards and samples were introduced through the Sulfinert line going into the sampling valve. Please see Table 1 for Instrument Configuration and Operating Conditions.

Table 1. Instrument Configuration and Operating Conditions

| Agilent 7890A GC and OIA 5383 PFPD |   |                |             |       |             |       |             |
|------------------------------------|---|----------------|-------------|-------|-------------|-------|-------------|
| KIN-TEK permeation oven            | 40 °C<br>Air dilution gas<br>Dilution gas flow rate 250 to 2500 mL/min  |                |             |       |             |       |             |
| Permeation devices                 | H <sub>2</sub> S, MeSH, EtSH, DMS, TP devices; permeation rate = 750 ng/min at 40 °C<br>COS device; permeation rate = 190 ng/min at 35 °C<br>n-PrSH device; permeation rate = 590 ng/min at 40 °C<br>DMDS device; permeation rate = 190 ng/min 40 °C  |                |             |       |             |       |             |
| Automated injection system         | 4-port selection valve<br>6-port GSV with 1 mL Sulfinert®-coated sample loop<br>Automated air-actuated valve<br>All lines Sulfinert® coated<br>Valve oven temperature 110 °C  |                |             |       |             |       |             |
| Volatiles interface                | 200 °C<br>Split mode<br>Split ratio 10:1<br>Sulfinert® coated   |                |             |       |             |       |             |
| GC column                          | Agilent J&W Select Low Sulfur 60-m x 0.32-mm ID<br>Helium carrier gas, 1.2 mL/min   |                |             |       |             |       |             |
| Oven program                       | 40 °C for 13 min then 30 °C/min to 180°C, and hold for 7 min<br>Total run time 24.67 minutes  |                |             |       |             |       |             |
| Sulfur detection                   | Pulsed Flame Photometric Detector (PFPD) with 2-mm combustor, BG-12 filter, R1924 PMT<br>Detector base temperature 250 °C<br>H <sub>2</sub> /air ratio tuned for optimum sulfur emission<br><table border="0" style="margin-left: 20px;"> <tr> <td>H<sub>2</sub></td> <td>11.5 ml/min</td> </tr> <tr> <td>Air 1</td> <td>14.1 ml/min</td> </tr> <tr> <td>Air 2</td> <td>14.3 ml/min</td> </tr> </table><br>6-24 msec sulfur gate with square root on (linear mode)<br>1-2 msec hydrocarbon gate<br>PMT 575<br>Trigger level 800000<br>Multiplier 64 | H <sub>2</sub> | 11.5 ml/min | Air 1 | 14.1 ml/min | Air 2 | 14.3 ml/min |
| H <sub>2</sub>                     | 11.5 ml/min   |                |             |       |             |       |             |
| Air 1                              | 14.1 ml/min   |                |             |       |             |       |             |
| Air 2                              | 14.3 ml/min   |                |             |       |             |       |             |

Samples containing natural gas, ethene and ethane, and propene and propane were analyzed. The samples were also spiked to see if the hydrocarbons caused any matrix effect to the sulfur compounds. Please see figures 3 – 8 for standard and sample chromatograms.

Figure 3. Standard at 500 ml/min

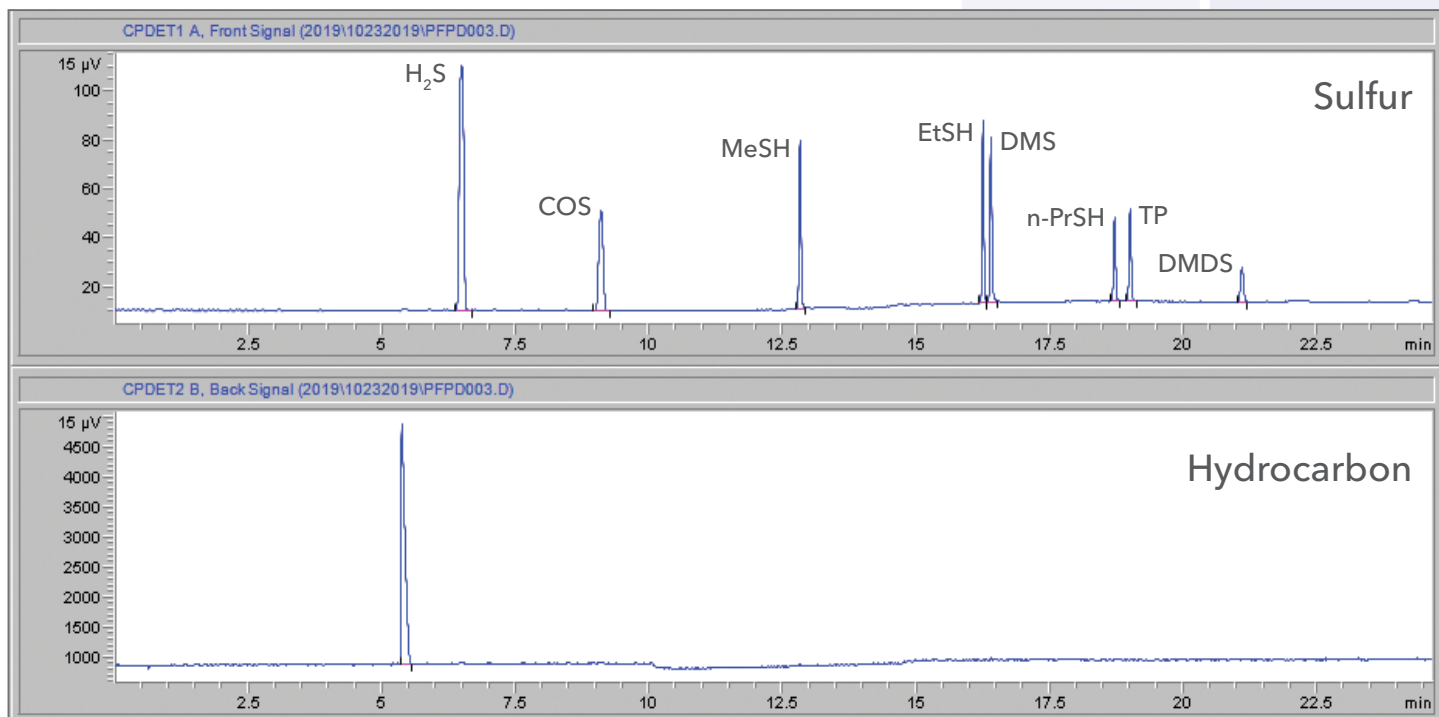


Figure 4. LPG Sample

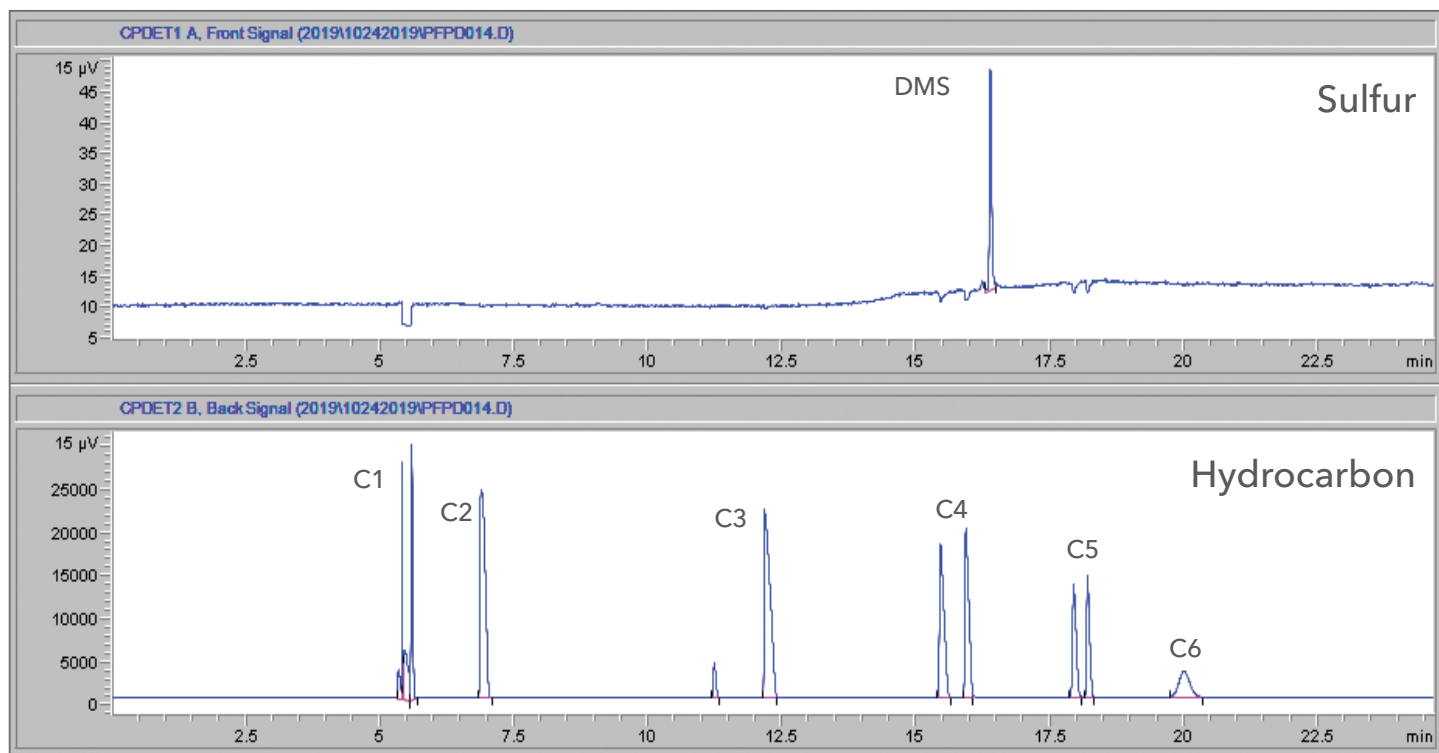


Figure 5. LPG Sample Spike

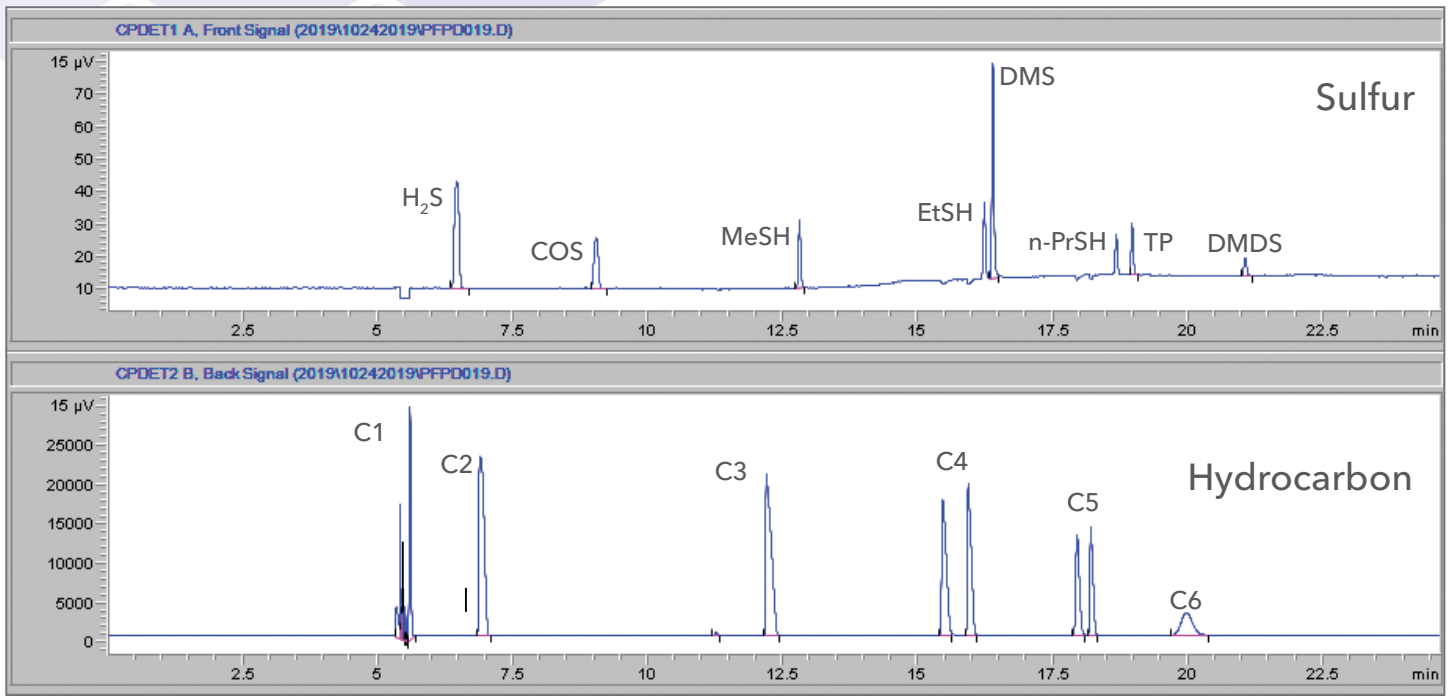


Figure 6. 25% Ethene and Ethane Sample

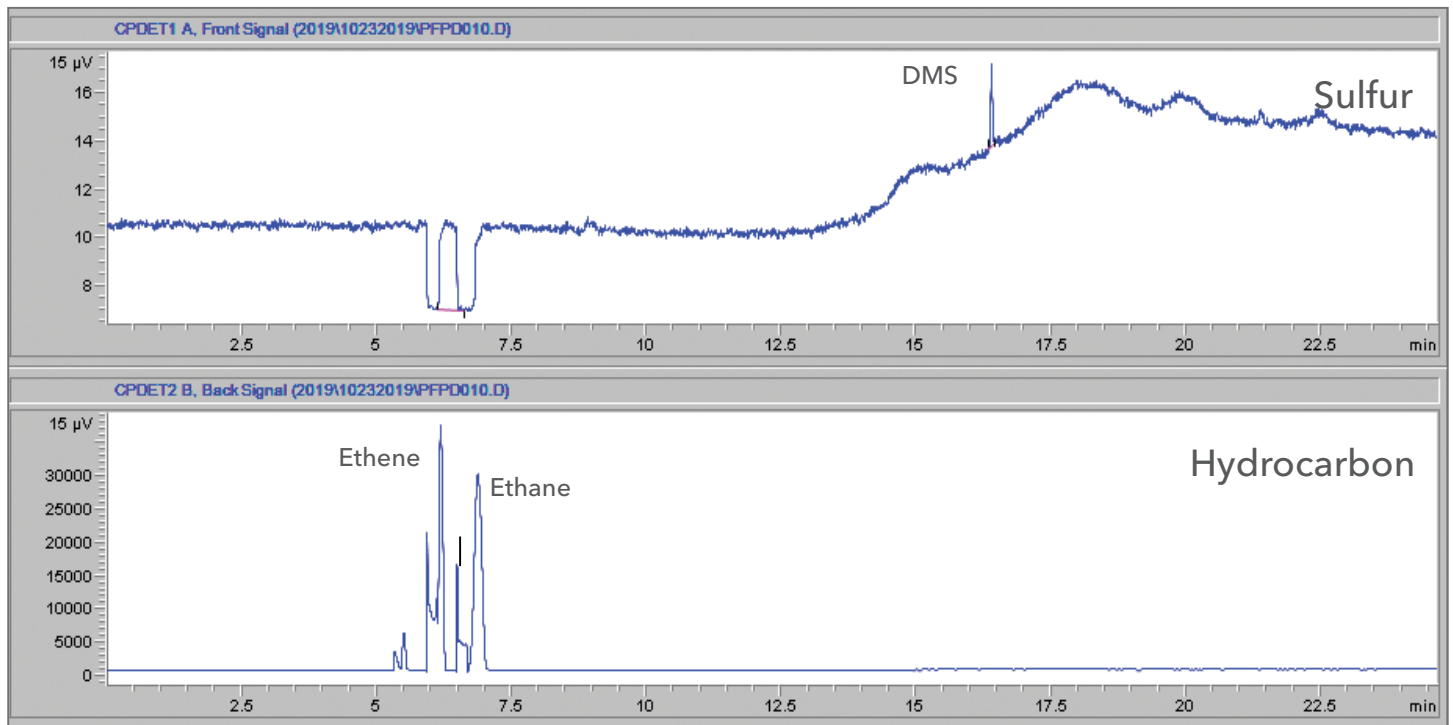


Figure 7. 25% Ethene and Ethane Sample Spike

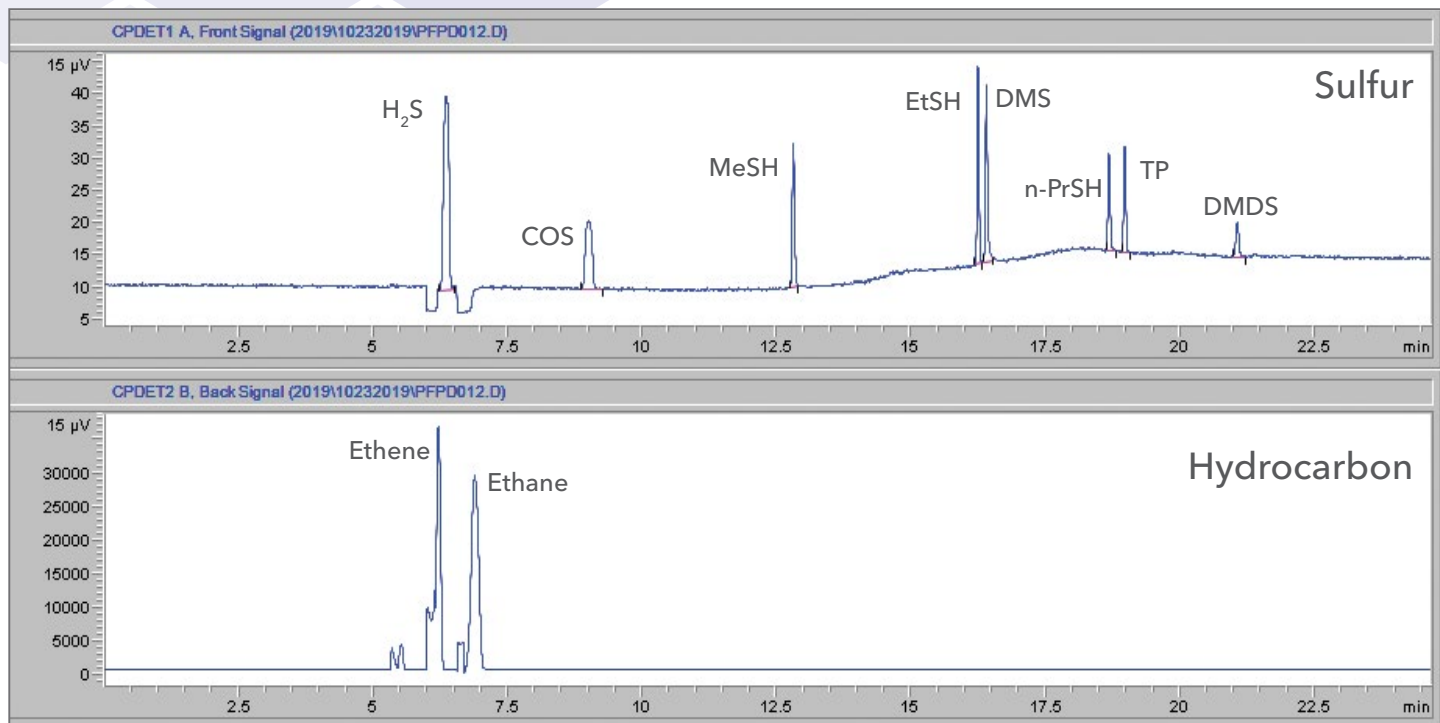


Figure 8. 25% Propene and Propane Sample

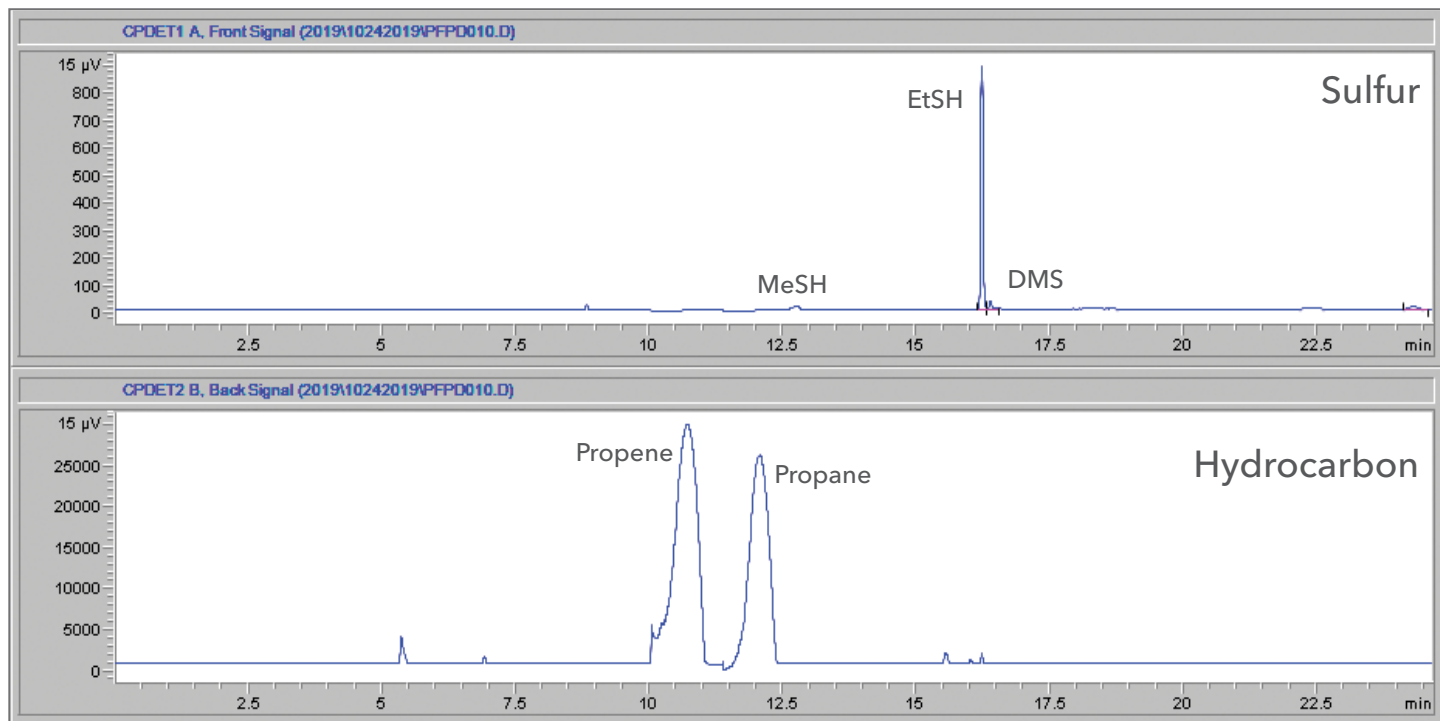
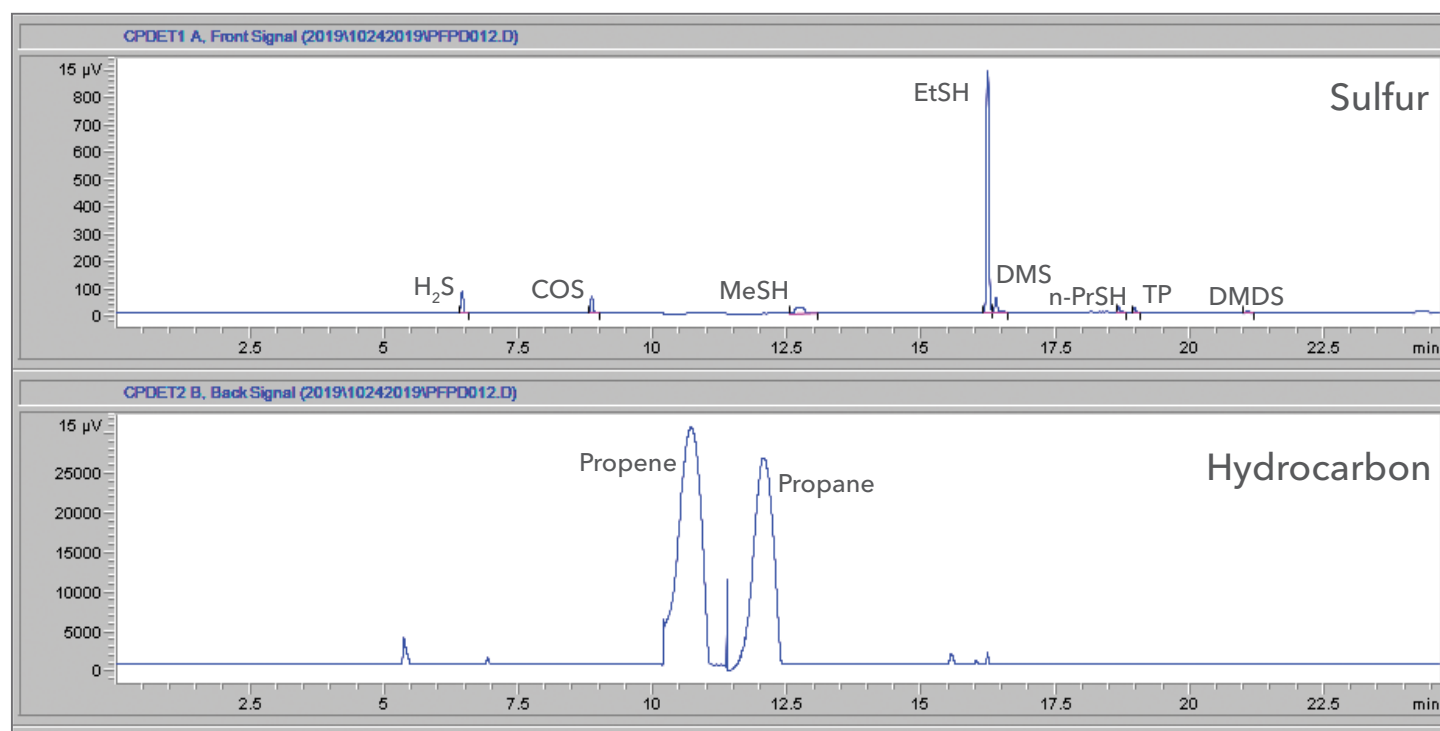


Figure 9. 25% Propene and Propane Sample Spike



### Results and Discussion

Calibration criteria of greater than 0.999 were met. MDL and IDOC studies also produced acceptable data. Please see Table 2. The data showed excellent detectivity, selectivity, and consistency. The PFPD also has great response and stability. Good separations of the sulfur compounds from matrix were achieved.

Table 2. Results

| Compound                               | Cal Range (PPMV) | Concentration at 500 ml/min | Retention Time | Correlation Coefficient | MDL (PPMV) | IDOC Precision (% RPD) | IDOC Accuracy (% REC) |
|--|------------------|-----------------------------|----------------|-------------------------|------------|------------------------|-----------------------|
| 1. Hydrogen sulfide (H <sub>2</sub> S) | 0.197-1.973      | 0.982                       | 6.51           | 0.999                   | 0.036      | 0.87                   | 98.5                  |
| 2. Carbonyl sulfide (COS)              | 0.135-1.353      | 0.674                       | 9.09           | 0.999                   | 0.008      | 1.08                   | 97.3                  |
| 3. Methanethiol (MeSH)                 | 0.140-1.397      | 0.702                       | 12.81          | 0.999                   | 0.013      | 0.85                   | 98.9                  |
| 4. Ethanethiol (EtSH)                  | 0.108-1.082      | 0.543                       | 16.34          | 0.999                   | 0.012      | 0.71                   | 101                   |
| 5. Dimethyl sulfide (DMS)              | 0.108-1.082      | 0.543                       | 16.38          | 0.999                   | 0.013      | 2.89                   | 97.3                  |
| 6. 2-Propanethiol (n-PrSH)             | 0.069-0.694      | 0.347                       | 18.70          | 0.999                   | 0.013      | 1.27                   | 103                   |
| 7. Thiophene (TP)                      | 0.080-0.799      | 0.401                       | 18.99          | 0.999                   | 0.007      | 1.60                   | 98.5                  |
| 8. Dimethyldisulfide (DMDS)            | 0.018-0.181      | 0.090                       | 21.09          | 0.999                   | 0.004      | 1.33                   | 95.1                  |

Flow range for calibration standards = 250 – 2500 ml/min    Flow for MDL standards = 3000 ml/min  
 Flow for IDOC standards = 500 ml/min

## Conclusions

The PFPD provides a fast, reliable method for analyzing sulfur compounds in a variety of matrices on any GC. Other compounds or matrices can also be analyzed with this system without having to make significant changes to the method. Ultimately, the matrix concentration can be balanced with the required sulfur sensitivity and GC split ratios or sample dilution to optimize performance for various analyses.

## Reference

ASTM D6228 - 19, "Standard Test method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection". 2019.

## Acknowledgement

Thank you to KIN-TEK Analytical, Inc. for the loan of the FlexStream™ permeation tube diluter.



OI Analytical, a Xylem brand  
1725 Brannum Lane  
Yellow Springs, OH 45387

+1.937.767.7241  
info@ysi.com  
ysi.com



[ysi.com/pfpd](https://ysi.com/pfpd)