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Application Note
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# Analysis of Impurities in Ethylene/Ethane and Propylene/Propane Streams Using a Pulsed Flame Photometric Detector (PFPD)

PETROCHEMICAL SERIES

## Introduction

Some of the key processes in the petrochemical industry are conversions of high-grade ethylene ($C_2$) and propane/propylene ($C_3$) feedstocks into end products (polyethylene, polypropylene) and intermediates such as 1-butene. These are the building blocks for plastics and a wide range of products, and are a large industry, with 55 million metric tons of polypropylene produced in 2013.[1] Unfortunately, even trace levels of sulfur species $H_2S$ and COS, which are often entrained in $C_2$ and $C_3$ feedstocks, corrode pipes and equipment, inhibit or damage catalyst beds, and lower product yield and purity. The need for a fast, reliable analysis method for $H_2S$ and COS in both $C_2$ and $C_3$ feedstocks is obvious, but sulfur in $C_2$ and $C_3$ is a difficult application, owing to the poor separation of the impurities from the matrix when coupled with the quenching of the PFPD detector signal by the matrix carbon. Reactivity of the sulfur species, especially $H_2S$ with all surfaces in the calibration and analytical system, adds additional complexity to this application. We present here a fast, reliable and robust method for the analysis of sulfur contaminants in $C_2$ and $C_3$ feedstocks that makes use of an automated gas loop injection system, separation by gas chromatography, and pulsed flame photometric detection (PFPD) that can detect sulfur at better than 0.1 ppmv.


Figure 1. OI Analytical S-Pro Select GC System with 5383 PFPD

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## Experimentation

Instrument operating conditions are shown in Table 1. The PFPD was tuned for optimum sulfur response and was run in the Linearized Mode (square root on). The instrument was calibrated for $H_2S$ and COS using certified wafer-type permeation devices and a permeation oven held at a constant temperature of 35 °C. The concentrations of the compounds were varied by changing the helium flow through the permeation oven. The calibration range for $H_2S$ was 0.17 to 6.60 ppm and for COS was 0.39 to 15.48 ppm. Gas samples and standards were introduced into the system through the gas sample inlet adjacent to the permeation oven.

Table 1. S-Pro Select GC System Configuration

| | S-Pro Select GC System |
|---|---|
| Permeation Oven | 35 ˚C<br>Helium dilution gas<br>Dilution gas flow rate 5 to 200 mL/min |
| Permeation Devices | $H_2S$ wafer device; permeation rate = 45 ng/min at 35 ˚C<br>COS wafer device; permeation rate = 190 ng/min at 35 ˚C |
| Automated Injection Systems | 4-port selection valve<br>6-port GSV with 1-mL Sulfinert®-coated sample loop<br>Automated, air-actuated valves<br>All lines Sulfinert® coated<br>Valve oven temperature 110 ˚C |
| Volatiles Interface | 200 ˚C<br>Split mode<br>Split ratio 40:1<br>Sulfinert® coated |
| GC Column | Agilent J&W Select Low Sulfur Column<br>60-m x 0.32-mm ID<br>Helium carrier gas, 1.2 mL/min |
| Oven Program | 40 ˚C for 10 min*<br>30 ˚C/min to 185 ˚C<br>Hold for 0.5 min<br>Total run time 15.3 min |
| Sulfur Detection | Pulsed Flame Photometric Detector (PFPD)<br>2-mm combustor, BG-12 filter, R1924 PMT<br>Detector base temperature 250 ˚C<br>$H_2$/air ratio tuned for optimum sulfur emission<br>6-24 msec sulfur gate (linear mode)<br>1-3 msec hydrocarbon gate<br>Square Root on |

* If only propylene/propane matrix is being analyzed the initial oven temperature may be changed to 60 ˚C.

## Results & Discussion

### Calibration

An eight point calibration was analyzed. Figures 1 and 2 illustrate the calibration curves and linearity for the two compounds.

**Figure 1. $H_2S$ Calibration**

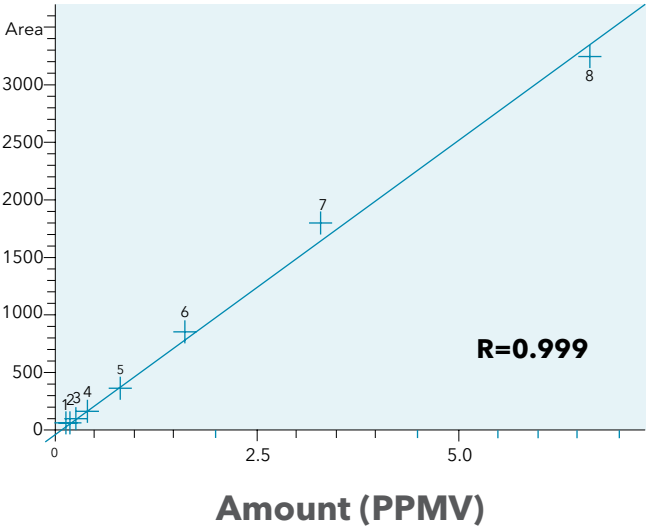
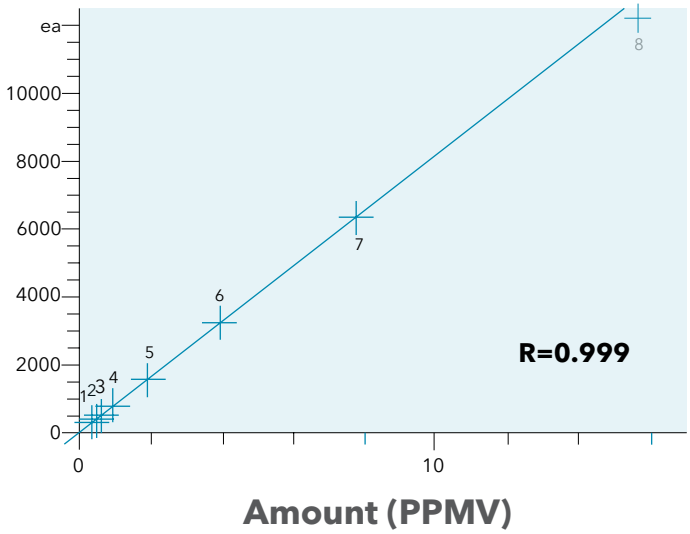



**Figure 2. COS Calibration**




### Method Detection Limit Study

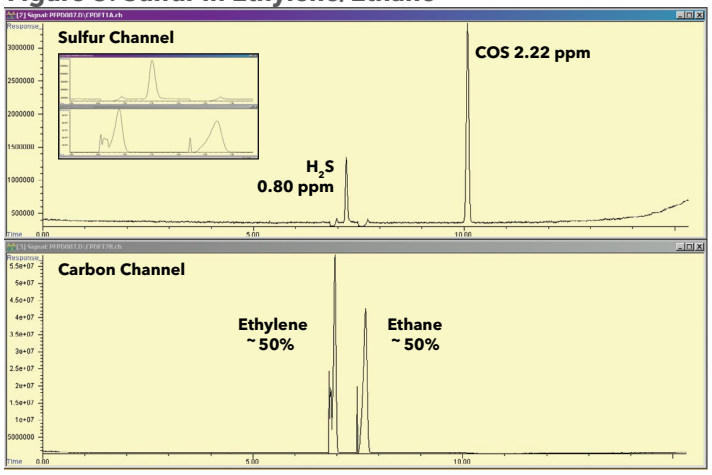
Seven injections of 0.17 ppmv $H_2S$ and 0.39 ppmv COS were injected using a 160:1 split which yielded 0.0425 ppm $H_2S$ and 0.0975 ppm COS. The calculated MDL for $H_2S$ was 0.013 ppm and 0.019 ppm for COS.

Sample and standards containing $H_2S$ and COS in propane/propylene, ethylene/ethane and natural gas were analyzed. See Figures 3 - 8.

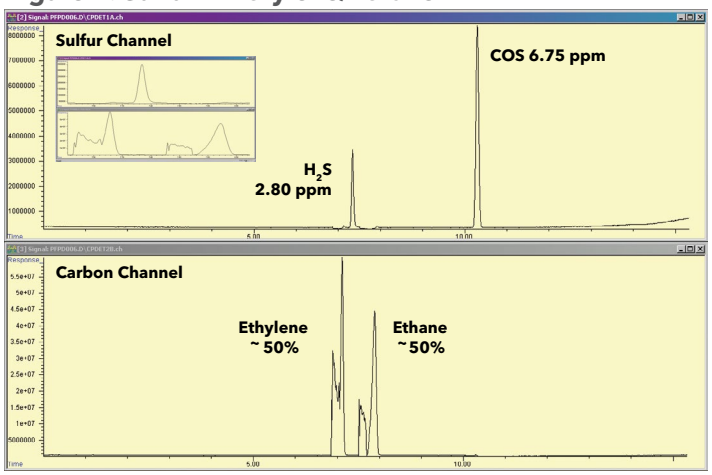
### System Stability

A gas standard was analyzed, then six injections of refinery gas samples were injected followed by another injection of the gas standard. The % deviation for $H_2S$ was 3.1% and for COS was 2.2%.

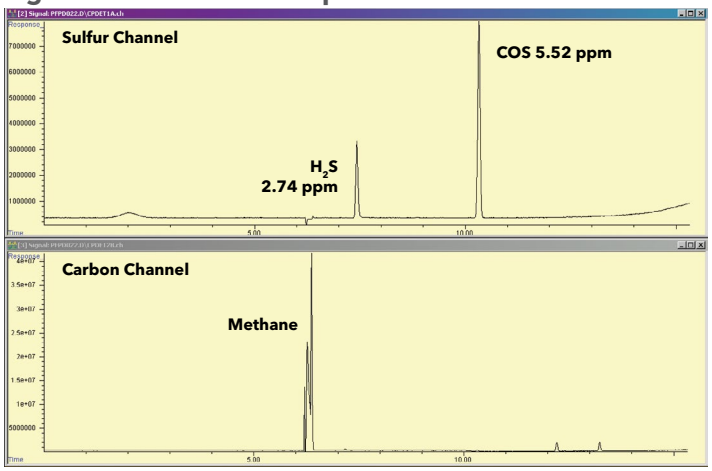
## Figure 3: Sulfur in Ethylene/Ethane



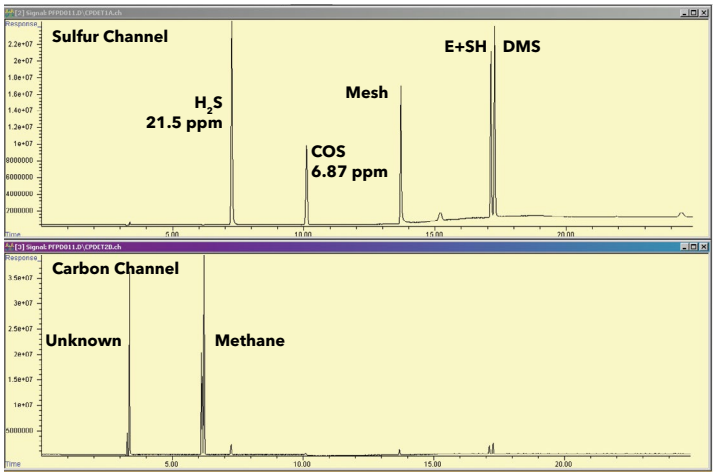

## Figure 4: Sulfur in Ethylene/Ethane




## Figure 5: Natural Gas Sample #1

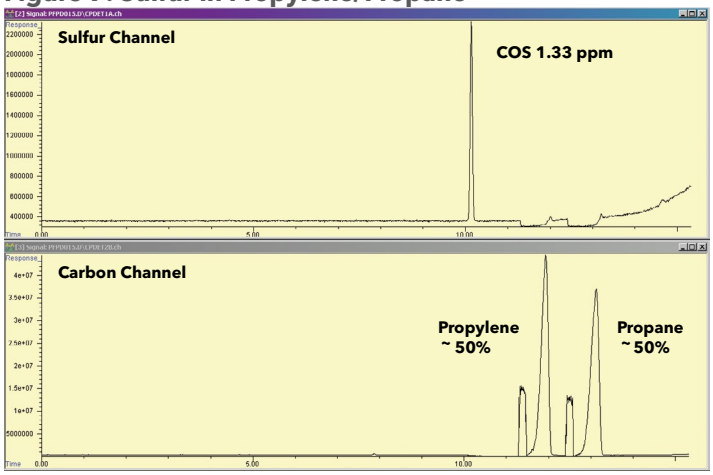



## Figure 6: Natural Gas Sample #2

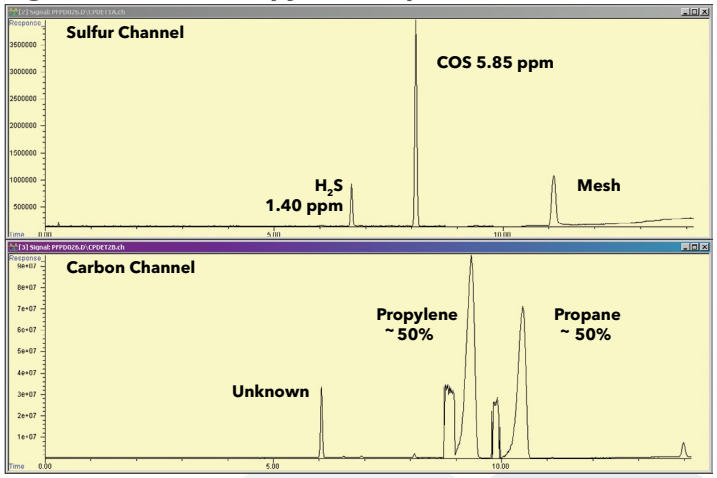



**Note: Final GC time was extended.**

## Figure 7: Sulfur in Propylene/Propane




## Figure 8: Sulfur in Propylene/Propane



## Results and Conclusions

The OI Analytical S-PRO Select GC System with PFPD coupled with the Agilent Select Low Sulfur column provides a fast and reliable method for the analysis of $H_2S$ and COS in both $C_2$ and $C_3$ matrices. Calibration is easily performed using permeation devices. The inert sample pathway can be checked using gas standards to ensure that sample results are accurate.

The Agilent Low Sulfur column does a reasonable job of separating the $H_2S$ peak from the ethylene matrix peak (in this 50/50 mixture of ethylene/ethane) to avoid co-elution and potential quenching in the PFPD by this matrix peak. Further investigations are anticipated to determine what % level of the ethylene matrix peak will result in excessive co-elutions of the $H_2S$ on the ethylene peak due to significant broadening of this hydrocarbon peak as the concentration is increased from a 50/50 mixture.



## References

1. Ceresana, Market Study: Polypropylene, 3rd edition, Dec. 2014.

2. ASTM International, ASTM D-6228 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection.

3. OI Analytical Application Note, Fast Determination of Impurities in Propane-Propylene Streams Using a Pulsed Flame Photometric Detector (PFPD) and a New Capillary PLOT Column, 2011.

## Acknowledgements

Thank you to DCG Partnership in Pearland, Texas for providing support and cylinders containing various concentrations of matrix and sulfur.

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