

Analysis of Impurities in Propane/Propylene Streams Using a Pulsed-Flame Photometric Detector (PFPD)

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, of course, 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 2013¹. 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 purity². 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 propane/propylene. This whitepaper presents 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 that can detect sulfur at better than 0.1 ppmv.

Experimental

The OI Analytical S-PRO System (Figure 1) equipped with the 5383 PFPD was used for this application. This system consists of a custom-configured gas chromatograph with two electronically controlled air-actuated valves for sulfur analysis in gas phase samples. The Agilent Low Sulfur Select column was used because it handles the difficult separation of H_2S from C_2 matrices and COS from C_3 matrices very well.

Instrument operating conditions are shown in Table 1. The PFPD was tuned for optimum sulfur response. It was configured for sulfur and hydrocarbon detection with sulfur run in the linearized mode, i.e., with the square root function on. Simultaneous, mutually selective sulfur and hydrocarbon chromatograms are produced from a single detector using the dual time gate capability of the PFPD. The instrument was calibrated for H_2S , COS , and $MeSH$ 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 nitrogen flow rate through the permeation oven. The calibration range for H_2S was 0.083 to 1.881 ppmv, for COS it was 0.093 to 2.083 ppmv, and for $MeSH$ 0.032 to 0.719 ppmv. Gas samples were introduced via the sample inlet of the S-PRO sample pathway. See Figures 2 and 3 for examples of standard chromatograms.



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

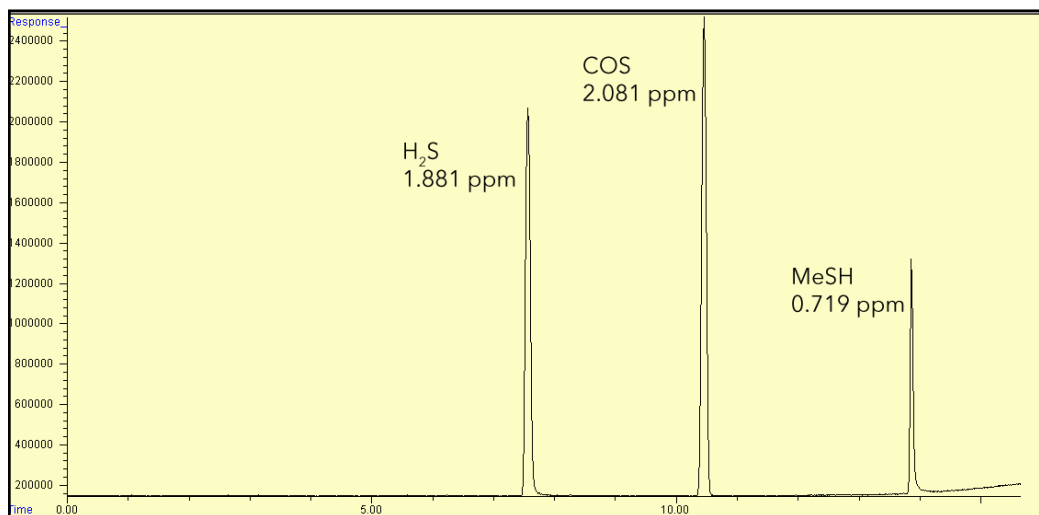


Figure 2. High Standard

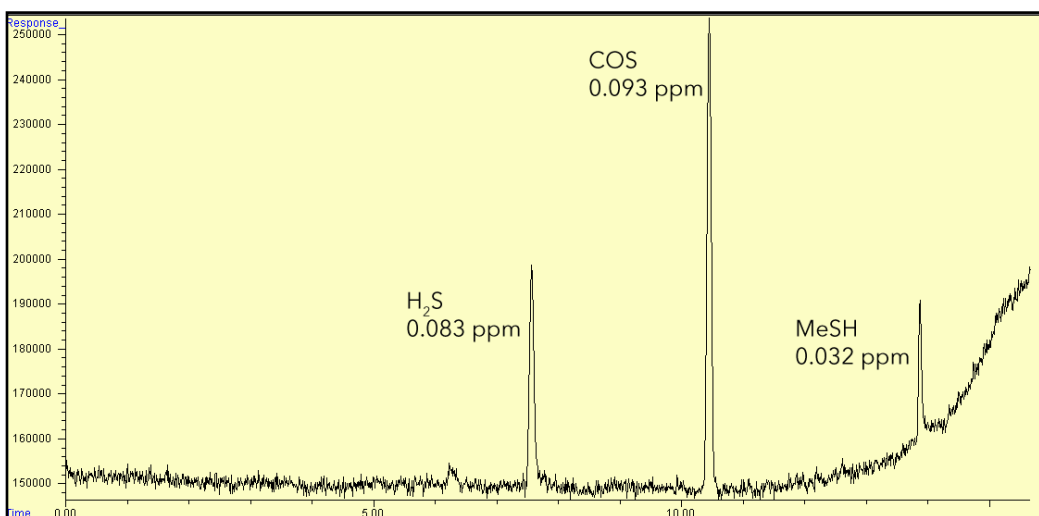


Figure 3. Low Standard

Table 1. Instrument Configuration and Operating Conditions

S-PRO Select GC System	
Permeation Oven	35 °C
	Nitrogen dilution gas
	Dilution gas flow rate 200 - 4500 mL/min
Permeation Devices	H ₂ S wafer device; permeation rate = 809 ng/min at 40 °C
	COS wafer device; permeation rate = 1586 ng/min at 40 °C
	MeSH wafer device; permeation rate = 441 ng/min at 40 °C
Automated Injection System	4-port selection valve
	6-port GSV with 1-mL Sulfinert®-coated sample loop
	Automated, air-actuated valves
	All lines Sulfinert coated
	Valve oven temperature 110 °C

Volatiles Interface	200 °C
	Split mode
	Split ratio 10:1
	Sulfinert coated
GC Column	Agilent J&W Select Low Sulfur Column
	60-m x 0.32-mm ID
	Helium carrier gas, 1.2 mL/min
Oven Program (Agilent 7890A)	40 °C for 10 min
	30 °C/min to 180 °C
	Hold for 0.5 min*
	Total run time 15.2 min
Sulfur Detection	Pulsed Flame Photometric Detector (PFPD)
	2-mm combustor, BG-12 filter, R1924 PMT
	Detector base temperature 250 °C
	H ₂ /air ratio tuned for optimum sulfur emission
	6-24 msec sulfur gate (linear mode; square root on)
	1-2 msec hydrocarbon gate

*Oven hold time may be extended to include later eluting compounds.

Results and Discussion

Calibration

A ten-point calibration was analyzed and the Agilent GC Chemstation Open Lab data system was used to generate calibration curves. Linearity was established for the three compounds with a correlation coefficient of 0.999. See Figure 4.

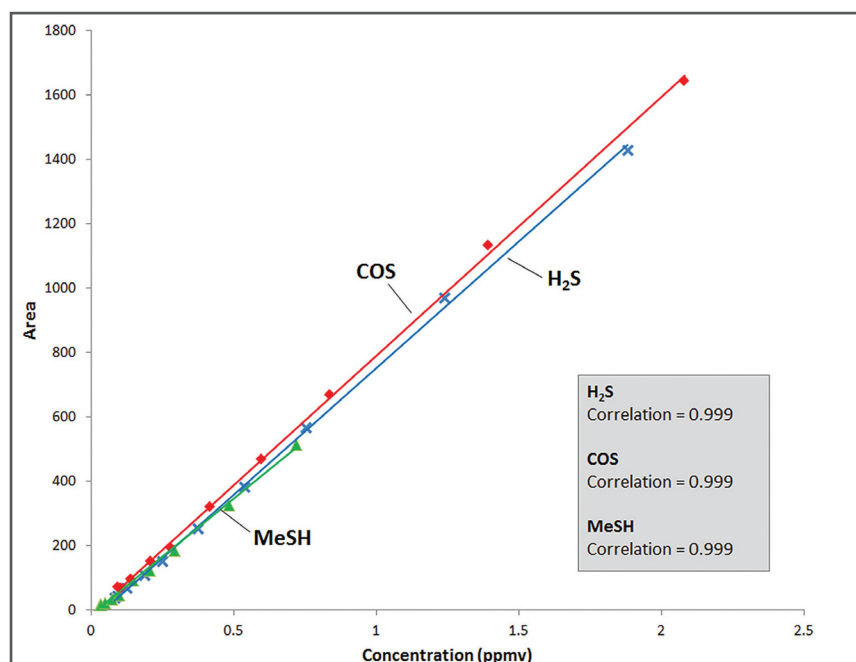


Figure 4. Calibrations

System Stability

A repeatability study was performed over a two-week period with 110 replicate injections of standards. Fairly low %RSDs exemplify the stability of the PFPD and the GC system. See Table 2.

Table 2. Repeatability Study for Sulfur Compounds

Compound Name	Concentration ppmv in Nitrogen	%RSD
H ₂ S	0.188	10.96
COS	0.209	4.31
MeSH	0.072	8.81

Samples

Manufactured samples containing various sulfur compounds in propylene/propane, ethylene/ethane, and methane matrices were analyzed. Sulfur compounds were easily separated from the propylene/propane and methane matrices. The separation of H₂S from the C₂ matrix is more difficult because H₂S elutes between ethylene and ethane. When analyzing for some samples there is a balance between reporting levels desired and getting results without matrix interference. Co-elutions must be monitored as matrices and split ratios are changed. See Figures 5-10.

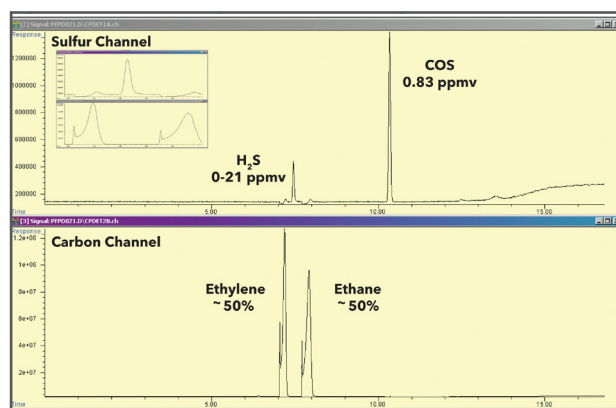


Figure 5. Sulfur in Ethylene/Ethane (10 split)

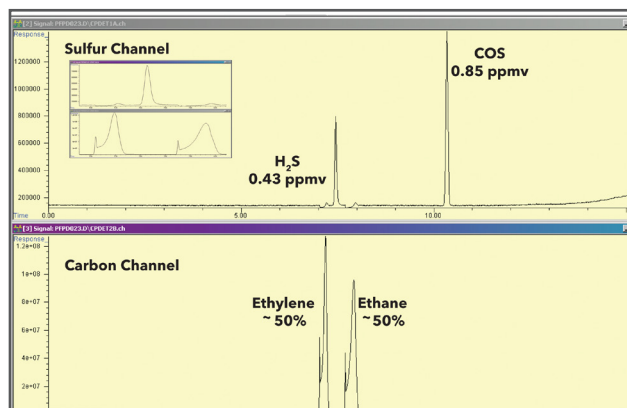


Figure 6. Sulfur in Ethylene/Ethane (10 split)

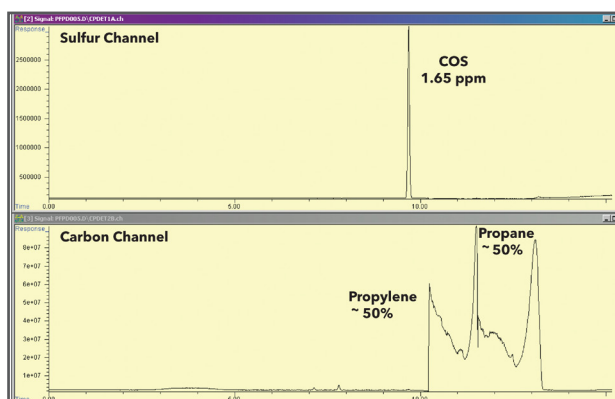


Figure 7. Sulfur in Propylene/Propane (10 split)

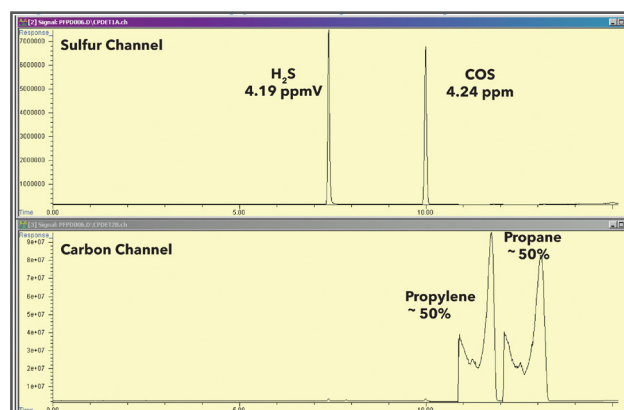


Figure 8. Sulfur in Propylene/Propane (20 split)

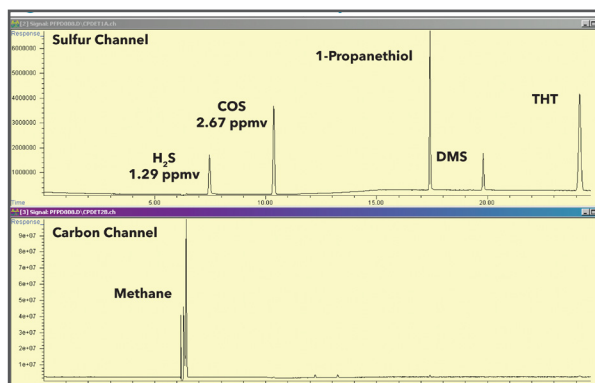


Figure 9. Sulfur in Natural Gas (20 split)

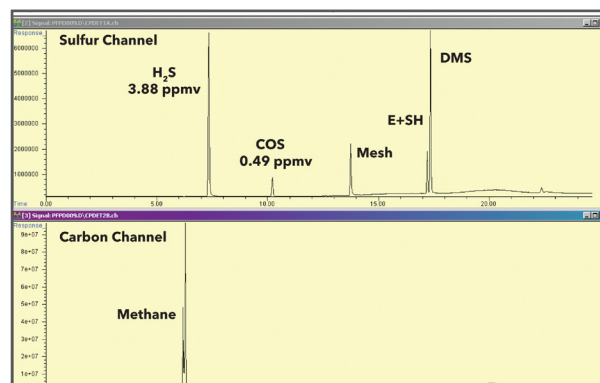


Figure 10. Sulfur in Methane (100 split)

Conclusion

The OI Analytical S-Pro GC System with 5383 PFPD coupled with Agilent Select Low Sulfur column provides a fast and reliable method for analyzing H_2S and COS, as well as other sulfur compounds, in a variety of matrices. This system can be used to analyze the lighter sulfur compounds in a variety of matrices without having to make significant changes to the chromatographic conditions. Ultimately, the matrix concentration can be balanced with the required sulfur sensitivity and GC split ratios to optimize performance for various analyses.

References

1. Market Study: Polypropylene (3rd Edition), Ceresana December, 2014.
2. ASTM Standard D6228-10 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.

Acknowledgements

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