O·I·Analytical

Application Note 36720111

Fast Determination of Impurities in Propane-Propylene Streams Using a Pulsed Flame Photometric Detector (PFPD) and a New Capillary PLOT Column

Keywords

Pulsed Flame Photometric
　　Detector (PFPD)
Carbonyl Sulfide (COS)
SPRO-Select
PLOT Column
Propane-propylene matrix

Introduction

High grade ethylene and propylene feedstocks are used in production of a variety of fine chemicals and end products. Determination of low-level sulfur impurities, such as H_2S and COS, in the feed is important because they can corrode equipment, poison catalysts during production, and affect polymer yield.

Analysis of volatile sulfur compounds in light hydrocarbon streams is traditionally done by gas chromatography (GC) with sulfur-selective detection, and is generally very successful for most feedstocks. However, with a propane-propylene feed, most available GC columns will not separate the impurities from the C3 matrix, will irreversibly absorb H_2S, or result in poor peak shape for the sulfur compounds. Some solutions require additional equipment for heart-cutting or even two analytical lines with two detectors.

A turn-key system is now available, which is based on the Pulsed Flame Photometric Detector (PFPD)[1] and a new capillary PLOT column[2]. The column provides complete baseline separation of the volatile sulfur impurities from the propane-propylene matrix, sharp, symmetric peak shape, and excellent response for H_2S. The PFPD provides unambiguous sulfur detection with long-term stability and minimal maintenance.

System Description

All data were acquired using the OI Analytical SPRO-Select System shown in Figure 1. The SPRO-Select is a fully integrated GC system based on the Agilent 7890 GC that incorporates calibration, QA/QC capability, automated sample introduction, baseline separation of the C3 matrix from the target compounds, and compound detection and quantitation.

Presented at the 2011 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy Atlanta, Georgia, March 13–18, 2011

Figure 1. The OI Analytical SPRO-Select is designed to detect and quantify sulfur species in gas-phase samples.

Sample Introduction

An automated air-actuated 4-port sample selection valve is programmed to select either the analytical sample or the calibration standard generated by the integrated permeation oven. The sample is introduced into the analytical system using a 6-port valve and a 1-mL gas sample loop. The sample is then introduced onto the GC column through the OI split/splitless volatiles interface optimized for low-volume injections. The entire sample pathway resides inside a heated valve oven, and is treated with Sulfinert® surface coating to minimize adsorption of sulfur on system surfaces.

OI Volatiles Interface

The OI volatiles interface is designed specifically for introducing low-concentration gas samples at varying split ratios from a gas sampling valve. The temperature of the heated inlet, the carrier gas flow for the column, and the split ratios are controlled directly through the 7890 keypad or via ChemStation. The column installs quickly and easily from inside the GC oven.

Permeation Oven

The permeation oven is fully integrated into the system with temperature and dilution gas flow rate controlled through the 7890 keypad or ChemStation. The oven accommodates up to five individual permeation devices and is used to generate gas-phase analytical standards at point-of-use for either automated calibration or sequenced introduction of QA/QC check standards. A pure compound is sealed inside a permeation device (tube or wafer) and diffuses across the permeable membrane at a defined rate for a given temperature. All permeation devices are supplied with a certificate stating the precise permeation rate and uncertainty range at a given reference temperature. The permeation oven is held at a constant temperature to produce a constant diffusion rate. A precise flow rate of dilution gas, controlled using the AUX EPC flow control module, is passed through the oven and across the permeation device; the result is an accurate gas standard always available at point-of-use without the need for expensive standards in cylinders.

Detection

The SPRO-Select system is configured with the OI Analytical Pulsed Flame Photometric Detector (PFPD) for detection and quantitation of individual sulfur compounds. The linear, equimolar response is used to generate a single response factor for sulfur, which is then used to quantify the sulfur content in both known and unknown sulfur species. When configured for sulfur detection, the PFPD produces simultaneous, mutually selective sulfur and hydrocarbon chromatograms from a single detector. The constant pulsing of the flame results in a self-cleaning detector with long term stability, virtually no coking, and minimal maintenance requirements.

Chromatography

Baseline separation of the sulfur contaminants from the matrix is achieved using the CP8575 Agilent J&W Select Low Sulfur PLOT column. Unlike other PLOT columns, this new column completely separates the H_2S and COS sulfur species from the propane-propylene matrix allowing for unambiguous, low-level identification and quantitation without interference from the C3 hydrocarbons.

Experimental

All instrument operating conditions are shown in Table 1. The instrument was calibrated for H_2S and COS using certified wafer-type permeation devices. The permeation oven was held at a constant temperature of 40 °C, and the concentration of H_2S and COS were varied by changing the dilution gas flow rate through the permeation oven. Ten replicate injections were made for each calibration point to confirm that the gas flow rate and new concentration had reached equilibrium for each level, and the average peak area was used to generate a linear calibration curve. The calibration ranges for H_2S and COS were 0.14 to 5.60 ppmv and 0.39 to 7.80 ppmv, respectively. A mid-point standard with H_2S at 1.40 ppmv and COS at 3.90 ppmv was generated for the long-term stability study. Details of the permeation oven conditions and calibration standards are shown in Table 2.

Table 1. Instrument Configuration and Operating Conditions

SPRO-Select GC System	
Permeation Oven	40 °C Helium dilution gas Dilution gas flow rate 5 to 200 mL/minute
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 50:1 Sulfinert® coated
GC Column	CP 8575 Agilent J&W Select Low Sulfur PLOT Column 60-m x 0.32-mm ID Helium carrier gas, 2 mL/minute
Oven Program	65 °C for 6.5 minutes 10 °C/minute to 185 °C Hold for one minute Total run time 19.5 minutes
Sulfur Detection	Pulsed Flame Photometric Detector (PFPD) 2-mm combustor, BG-12 filter, R1924 PMT Detector base temperature 200 °C H_2/air ratio tuned for optimum sulfur emission 6-24 msec sulfur gate (linear mode) 1-3 msec hydrocarbon gate

Table 2. Generation of Analytical Standards

Standards Generation	Permeation Oven	
Permeation Devices	H_2S wafer device, permeation rate = 17.8 ng/minute	
	COS wafer device, permeation rate = 87.6 ng/minute	
Dilution Gas	Helium	
Reference Temperature	30 °C	
Permeation Oven Temperature	40 °C	
Valve Oven Temperature	110 °C	
Volume of Sample Loop	1 mL	
Dilution Gas Flow Rate (mL/minute)	**H_2S Concentration (ppmv)**	**COS Concentration (ppmv)**
Calibration Standards		
200	0.14	0.39
100	0.28	0.78
50	0.56	1.56
25	1.12	3.12
10	2.80	7.80
5	5.60	Out of range, not used
Long-Term Repeatability Standards		
20	1.40	3.90

Results and Discussion

All analytical results are summarized in Table 3.

Table 3. Analytical Results Obtained with the SPRO-Select GC System

Parameter Measured	H_2S Result	COS Result
Analytical Standards		
Calibration Linearity	Range 0.14 to 5.60 ppmv $R^2 = 0.9999$	Range 0.39 to 7.80 $R^2 = 0.9996$
Long-Term Repeatability n = 2,400	Peak Response RSD = 3.7%	Peak Response RSD = 1.6%
Signal-To-Noise	Concentration = 0.14 ppmv S/N = 4	Concentration = 0.39 ppmv S/N = 16
Estimated Minimum Detectable Concentration	0.14 ppmv with 50:1 0.03 ppmv with 10:1	0.10 ppmv with 50:1 0.02 ppmv with 10:1

Calibration

The 6-point calibration curve for H_2S covered a range from 0.14 to 5.60 ppmv, and had a linear correlation coefficient (R^2) of 0.9999. The calibration curve for COS covered a range from 0.39 to 7.80 ppmv, with an R^2 value of 0.9996. Each point on the curves represents the average of 10 replicate injections; the relative standard deviation (RSD) for each set of replicates was under 5%. Figures 2 and 3 illustrate the calibration curves and linear R^2 values for the two analytes.
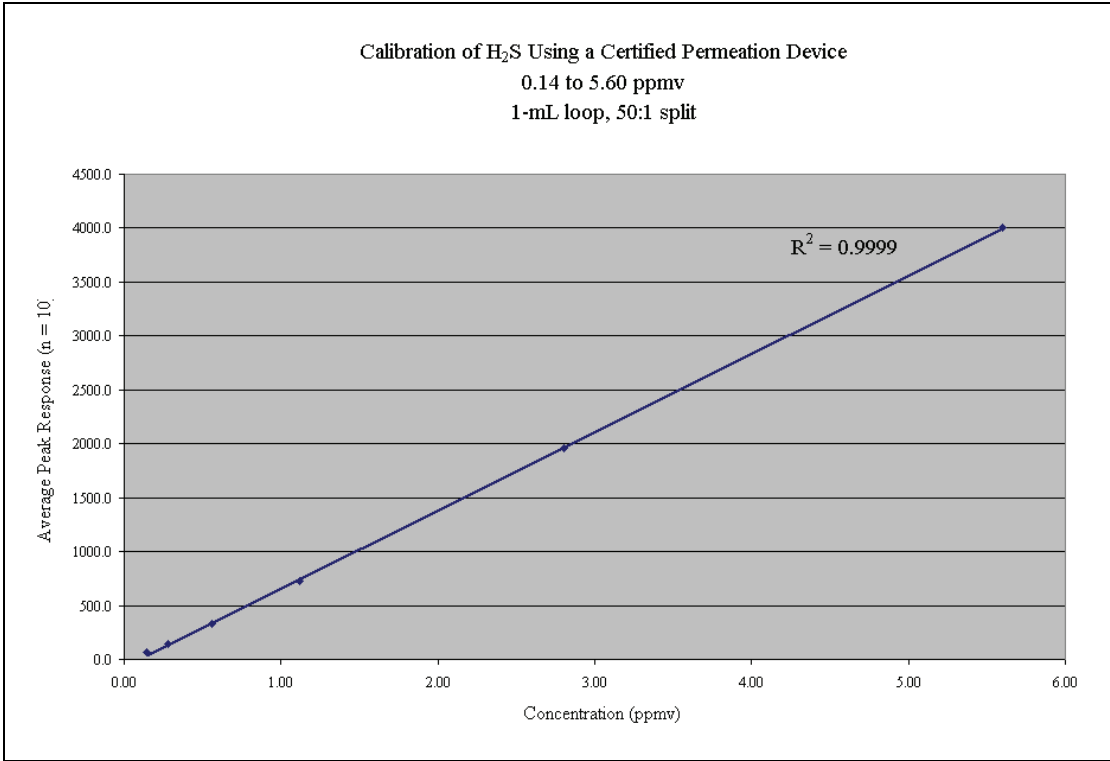
Figure 2. Calibration of H$_2$S using a certified wafer-type permeation device and the permeation oven
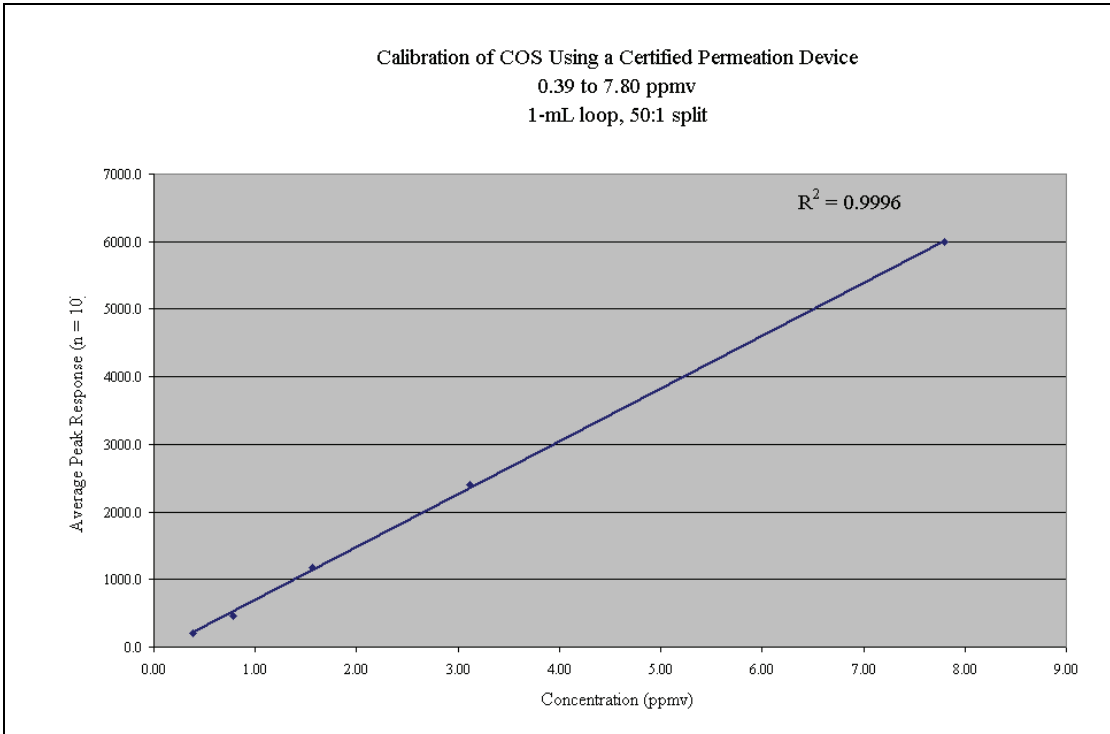

Figure 3. Calibration of COS using a certified wafer-type permeation device and the permeation oven

Long-Term Stability

A long-term stability study was done by making continuous sequential injections of a mid-level standard over a period of approximately two months, roughly 2,400 injections. Every 10th injection, about 240 data points were plotted to illustrate the system's stability over time. The RSD for H_2S and COS for all 2,400 analyses were 3.7% and 1.6%, respectively. Figure 4 is a chart of every 10th data point collected over the two-month period, and illustrates the long-term stability of the system. In Figure 5, chromatograms from approximately every 100th analysis (21 chromatograms) are overlaid to demonstrate the consistency in peak shape, retention time, and baseline stability.

Figure 4. Chart of every 10th data point collected over two-month test period, illustrating the long-term stability of the system
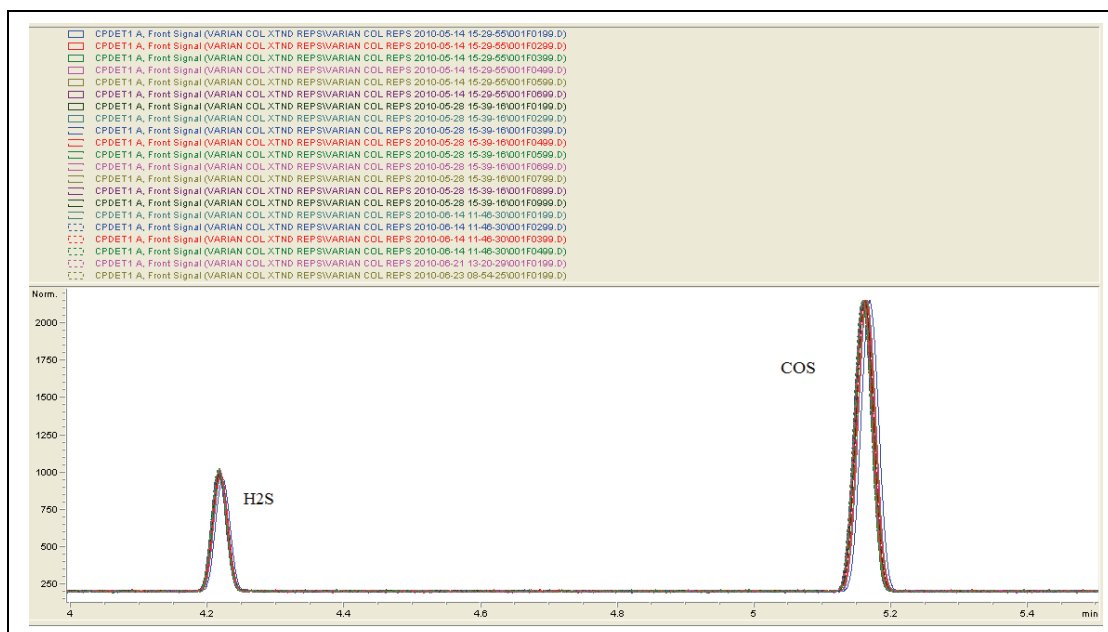
Figure 5. Chromatograms from approximately every 100th analysis overlaid, demonstrating consistency in peak shape, retention time, and baseline stability

During this period, the detector air and hydrogen gas tanks each has to be changed once, and on one occasion, the entire system lost power during an electrical storm. As soon as the gas or power was restored, the sequence was restarted immediately and data collection resumed without delay. No other maintenance or operator intervention was required over the extended test period.

Estimated Minimum Detectable Calibration

A signal-to-noise ratio was calculated for H_2S and COS using the peak height from a representative analysis of the low-level calibration standards, acquired using a 1-mL loop and a 50:1 split ratio. The minimum detectable concentration for each analyte was then estimated based on a signal-to-noise ratio of 4:1 and a split ratio of 10:1. The estimated minimum detectable concentrations for H_2S and COS were 0.03 ppmv and 0.02 ppmv, respectively, and are consistent with the levels reported by Agilent. These results are summarized in Table 3.

Analyte Separation from C3 Matrix

Three compressed gas cylinders containing unknown concentrations of H_2S and COS in different proportions of propane and propylene were used to demonstrate baseline separation of the sulfur compounds from the C3 matrix mix. Analyte concentrations were calculated based on the original calibration curves. Composition of the individual tanks is shown in Table 4, and chromatograms illustrating baseline separation of the target compounds from the C3 matrix are shown in Figures 6, 7, and 8.

Table 4. Composition of Tanks

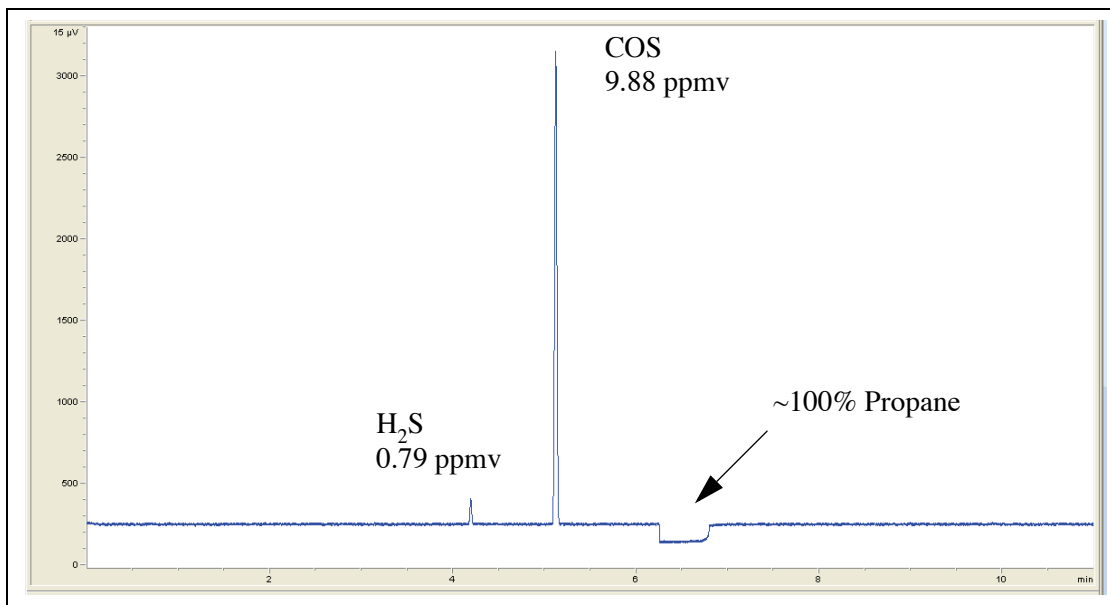| Parameter Measured	H$_2$S Result	COS Result
Calculated Concentration in Unknown Samples		
Tank #3002 100% Propane	0.79 ppmv	9.88 ppmv
Tank #3007 1% Propylene 99% Propane Trace C2	ND	9.49 ppmv
Tank #3012 77% Propylene 23% Propane	0.17 ppmv	8.23 ppmv

Figure 6. Tank #3002 contained H$_2$S at 0.79 ppmv and COS at 9.88 ppmv, and the balance was 100% propane. The COS was baseline separated from the propane by one full minute.
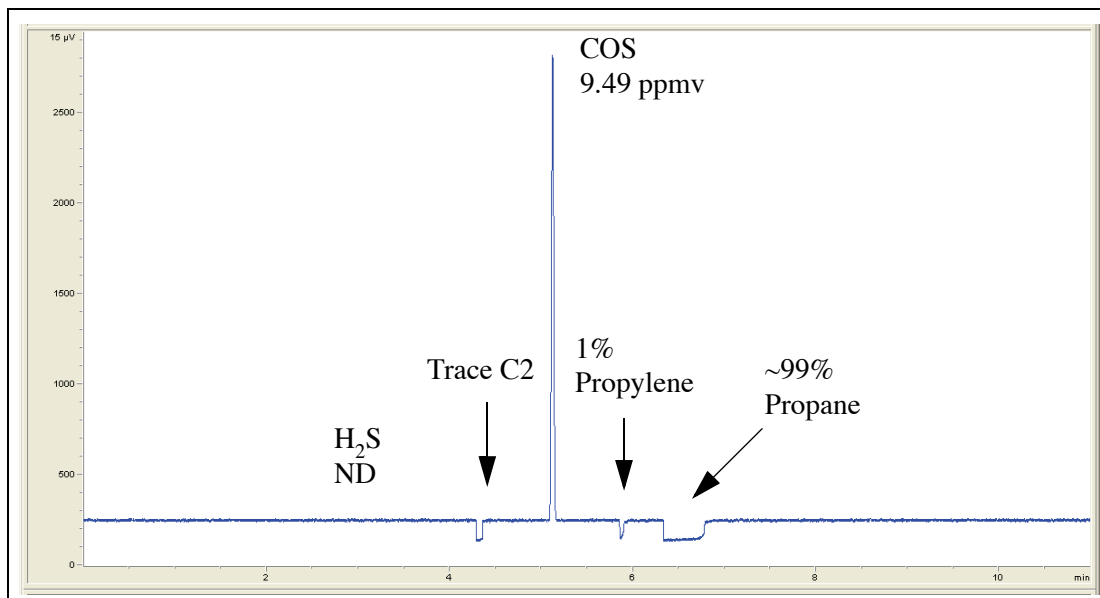
Figure 7. Tank #3007 contained 9.49 ppmv COS and no detectable H_2S. The 1% propylene and 99% propane were fully separated from the COS, as was a trace amount of C2.
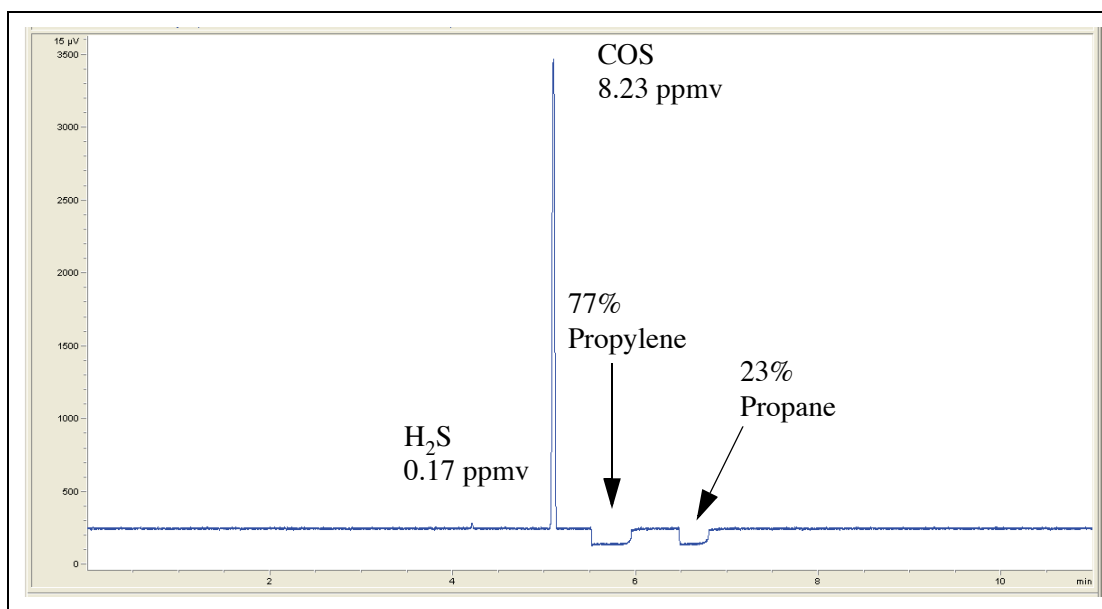

Figure 8. Tank #3012 contained 8.23 ppmv COS and a trace amount of H_2S at 0.17 ppmv. The matrix consisted of 77% propylene, which eluted before the 23% propane and was still completely baseline separated from the sulfur compounds.

Summary and Conclusions

The OI Analytical SPRO-Select system is a simple, turn-key solution for fast analysis of sulfur in propane-propylene feedstock using a Pulsed Flame Photometric Detector (PFPD) and a new capillary PLOT column. The new column provides complete baseline separation of the volatile sulfur impurities from the C3 propane-propylene matrix, good symmetric peak shape, and exhibits excellent response for H_2S. Certified permeation devices were used to generate analytical standards at point-of-use for calibration and stability testing. The PFPD remained stable over the two-month test period, in spite of temporary interruptions in operation. Minimum detectable concentrations of the sulfur compounds are estimated to be approximately 20 to 30 ppbv.

References

1. Amirav, A., Pulsed Flame Detector Method and Apparatus. U.S. Patent 5,153,673, Israel Patent 95617, Europe Patent 0475250, and Japan Patent 2759854.

2. CP 8575 Agilent J&W Select Low Sulfur PLOT Column.

Acknowledgement

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