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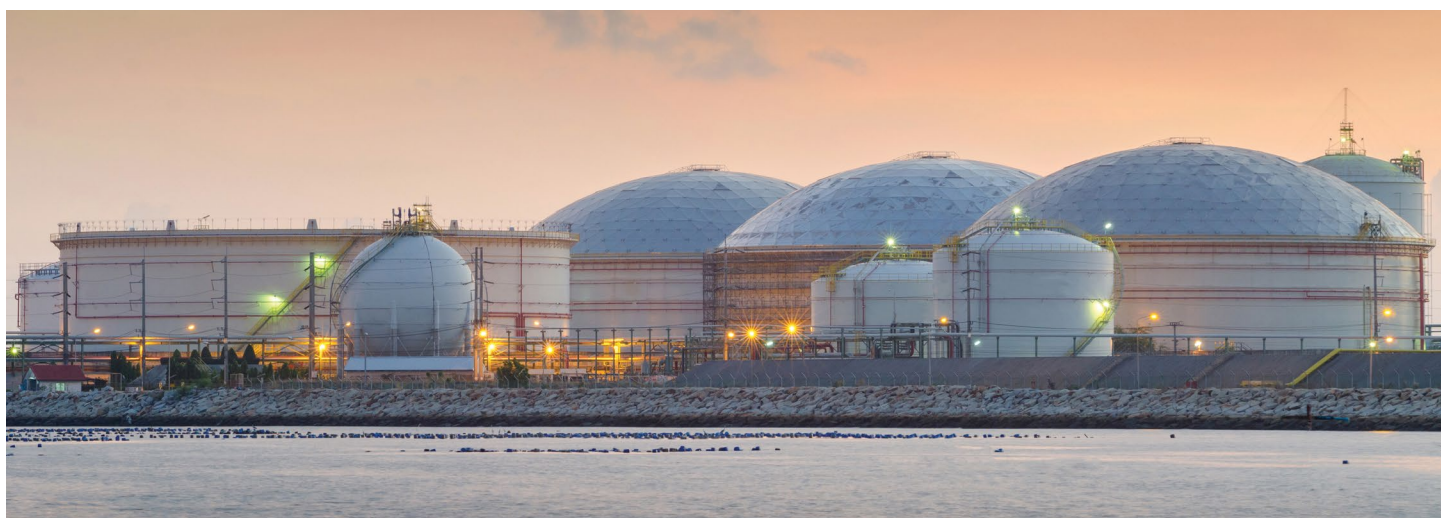 Analysis of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Pulsed Flame Photometric Detection

PETROCHEMICAL SERIES

Introduction

Natural gas and other gaseous fuels naturally contain varying amounts and classes of sulfur compounds, which can be odorous, corrosive to equipment, and inhibit or destroy catalysts used in gas processing. Even trace amounts of sulfur can be destructive to processing. Sulfur is also added in small amounts, 1 to 4 ppmv, to natural gas and other petroleum products for safety purposes. Accurate identification and measurement of sulfur species is critical in the petroleum industry. The analysis of sulfur can be challenging due to their reactivity and instability during sampling and analysis. 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. This application note will describe the analysis of sulfur in various matrices using an Agilent 7890A GC coupled with an OI Analytical 5383 Pulsed Flame Photometric Detector (PFPD).

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

Experimental

System Description:

The OI Analytical S-PRO Select System equipped with a 5383 PFPD was used for this application. 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 a custom-configured Agilent gas chromatograph 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 H2S from C2 matrices and COS from C3 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
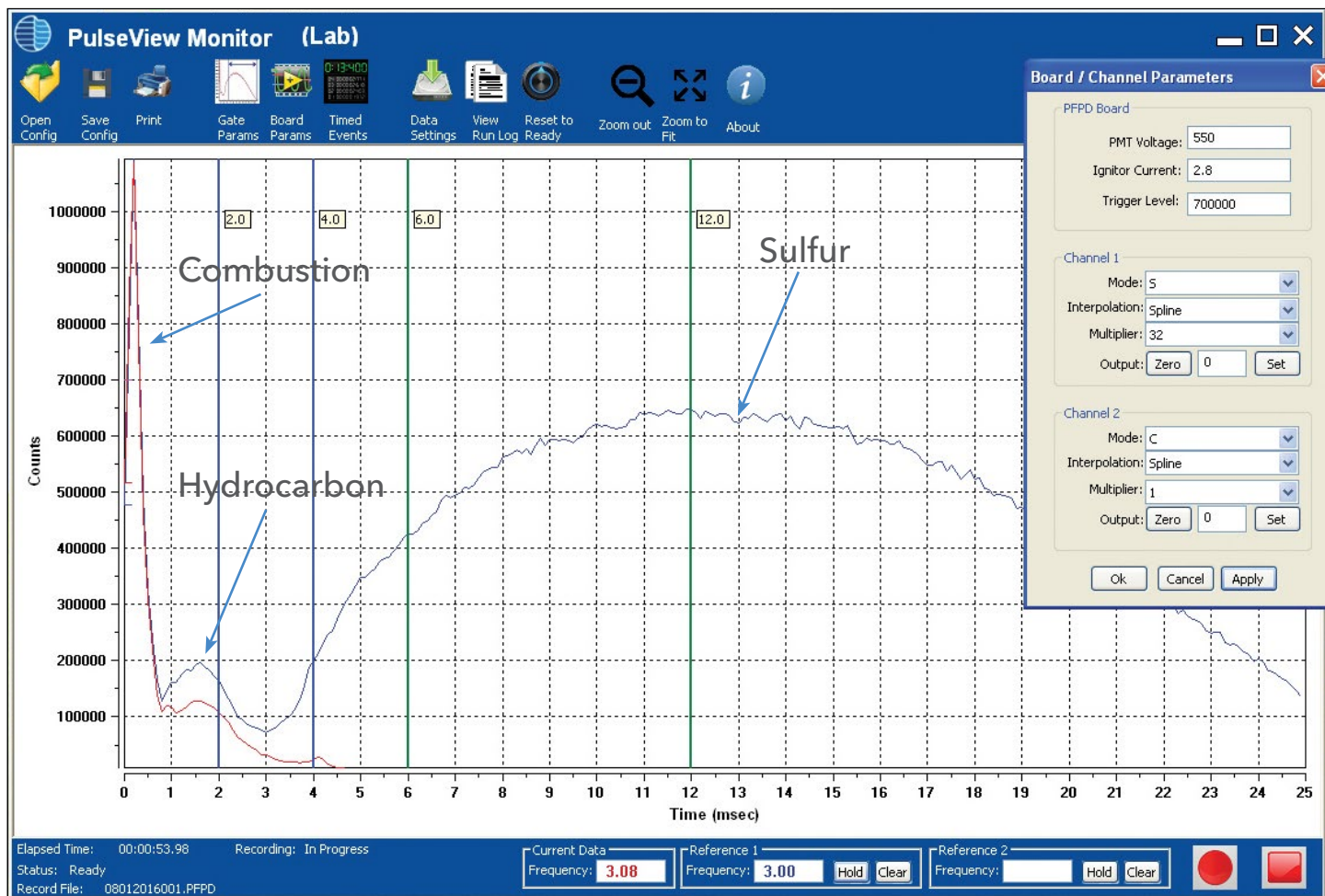
Standard and sample analysis:

The instrument was calibrated for H2S, 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 Air dilution gas Dilution gas flow rate 250 to 2500 mL/min
Permeation devices	H_2S, MeSH, EtSH, DMS, TP devices; permeation rate = 750 ng/min at 40 °C COS device; permeation rate = 190 ng/min at 35 °C n-PrSH device; permeation rate = 590 ng/min at 40 °C DMDS device; permeation rate = 190 ng/min 40 °C
Automated injection system	4-port selection valve 6-port GSV with 1 mL Sulfinert®-coated sample loop Automated air-actuated valve 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 60-m x 0.32-mm ID 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 Total run time 24.67 minutes

Sulfur detection	Pulsed Flame Photometric Detector (PFPD) with 2-mm combustor, BG-12 filter, R1924 PMT
	Detector base temperature 250 °C
	H_2/air ratio tuned for optimum sulfur emission
	    H_2 11.5 ml/min
	    Air 1 14.1 ml/min
	    Air 2 14.3 ml/min
	
	6-24 msec sulfur gate with square root on (linear mode)
	1-2 msec hydrocarbon gate
	PMT 575
	Trigger level 800000
	Multiplier 64

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.

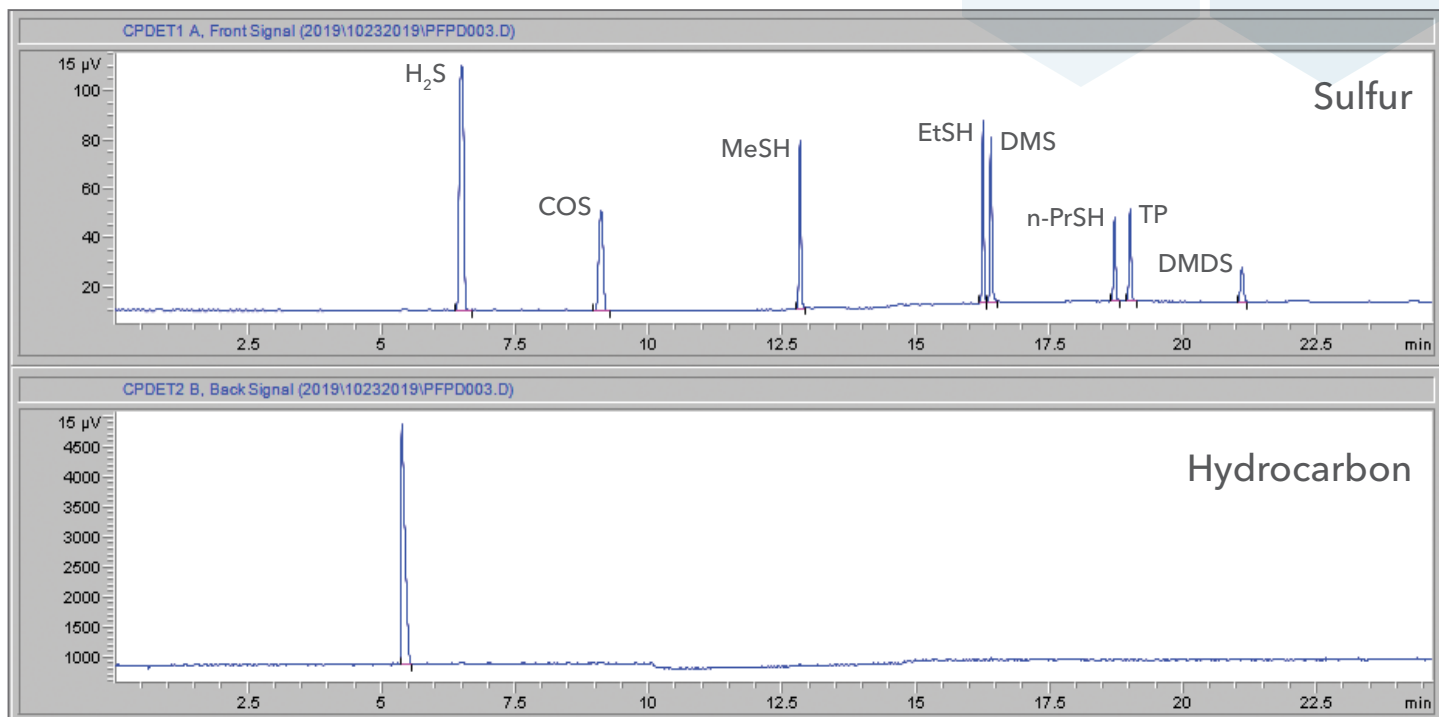Figure 3. Standard at 500 ml/min
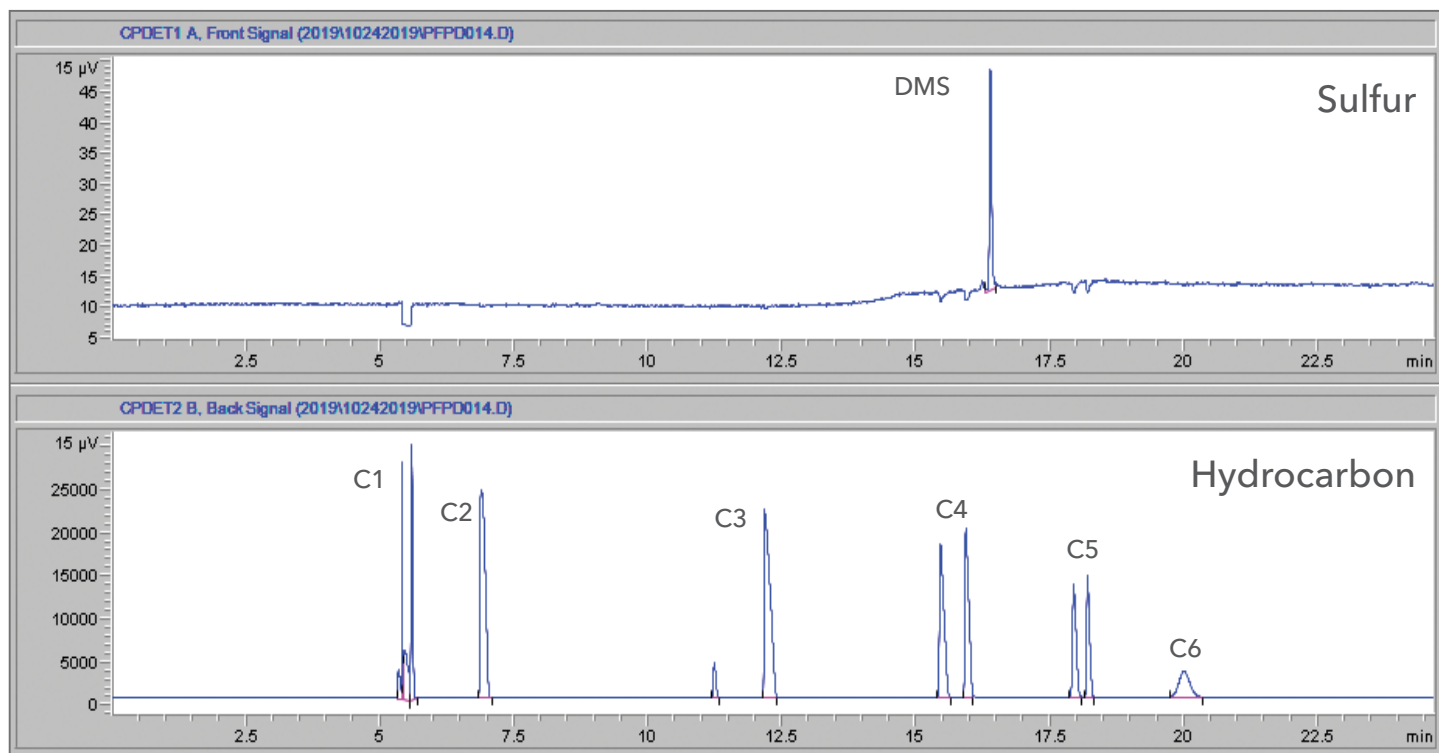

Figure 4. LPG Sample

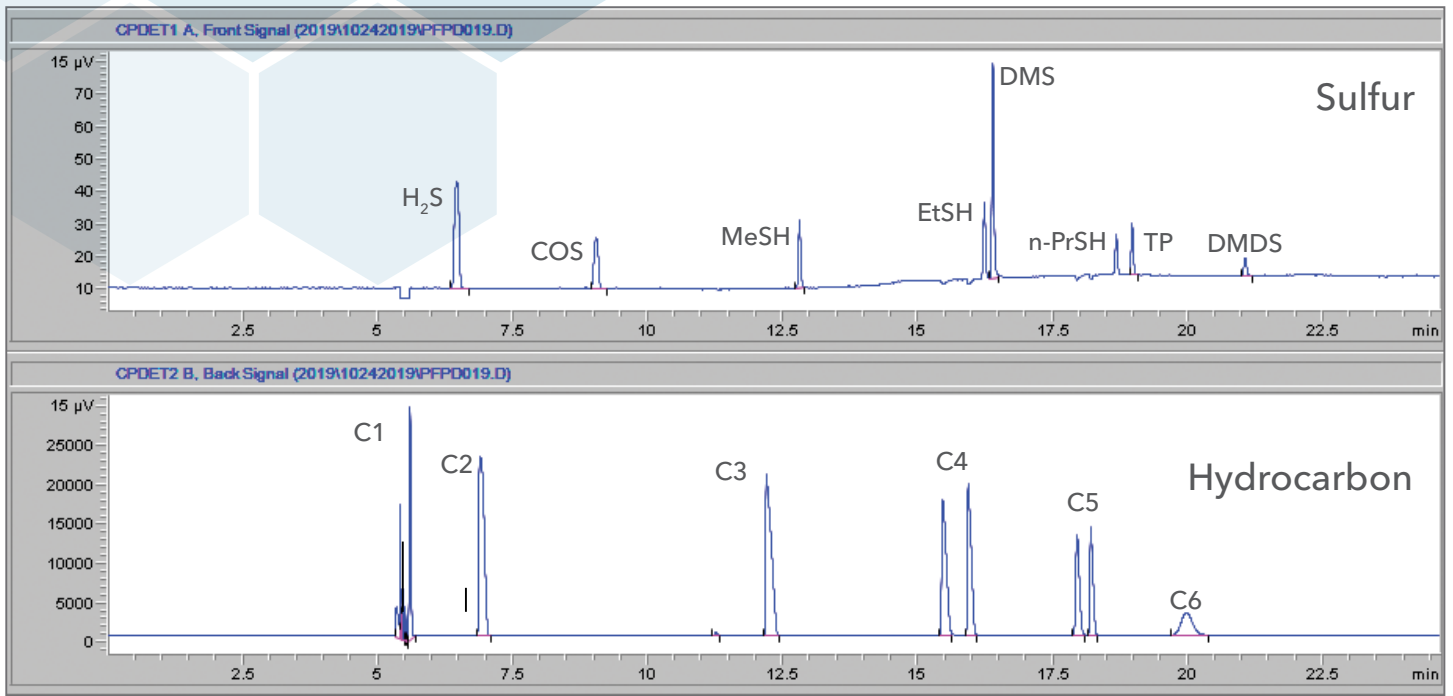Figure 5. LPG Sample Spike
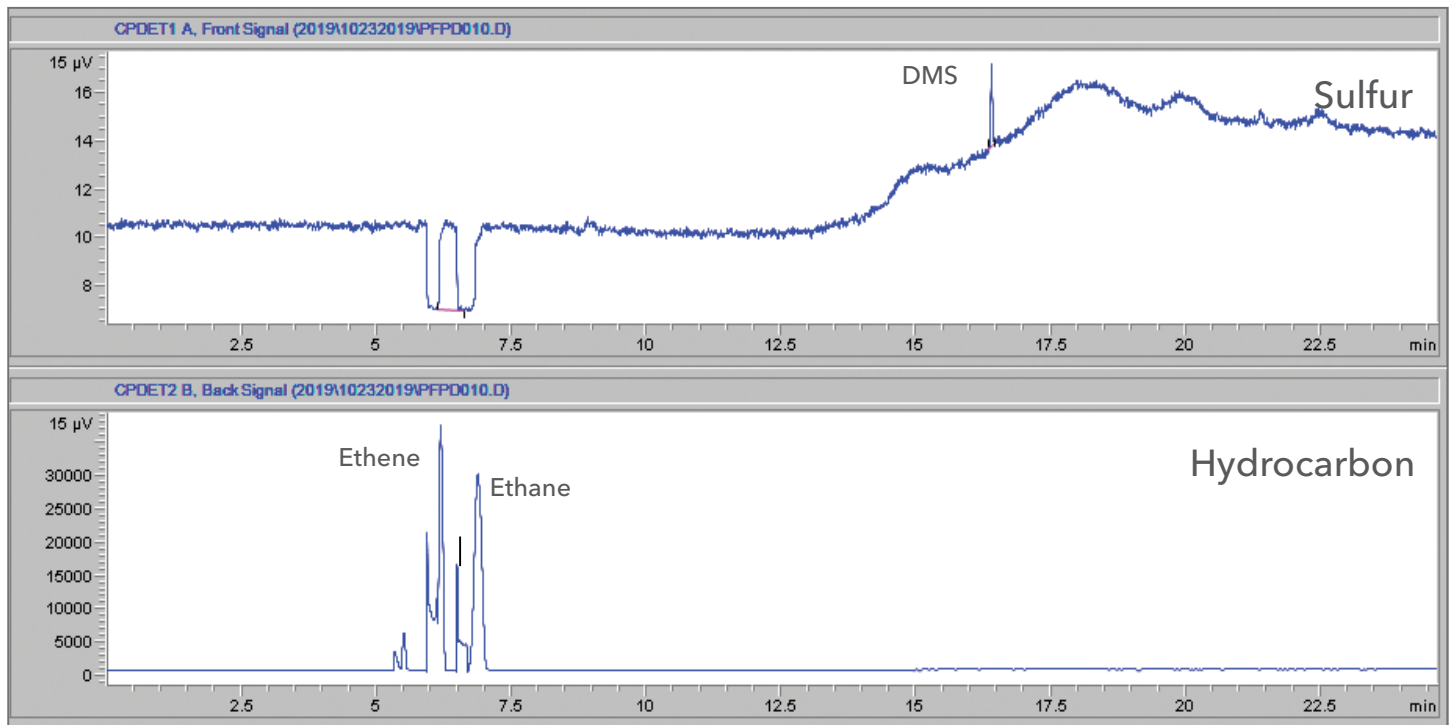

Figure 6. 25% Ethene and Ethane Sample

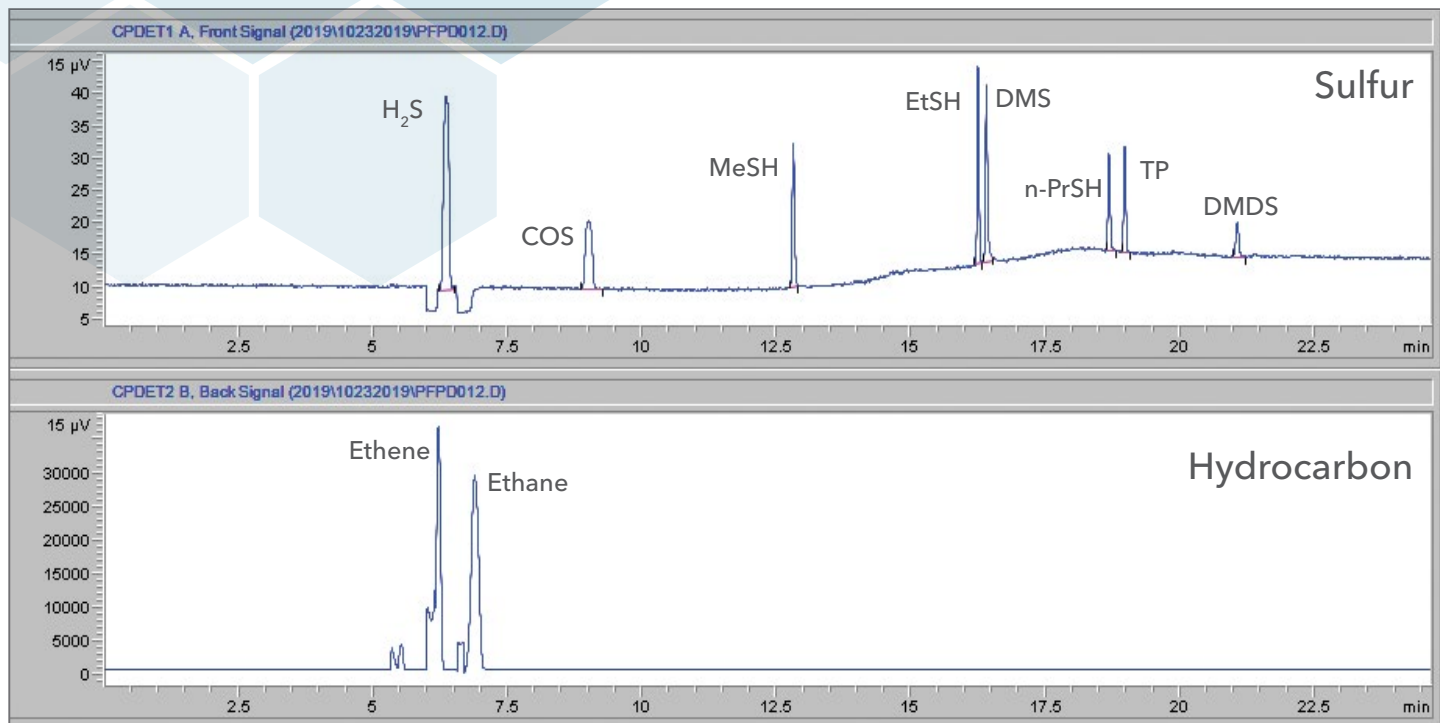Figure 7. 25% Ethene and Ethane Sample Spike

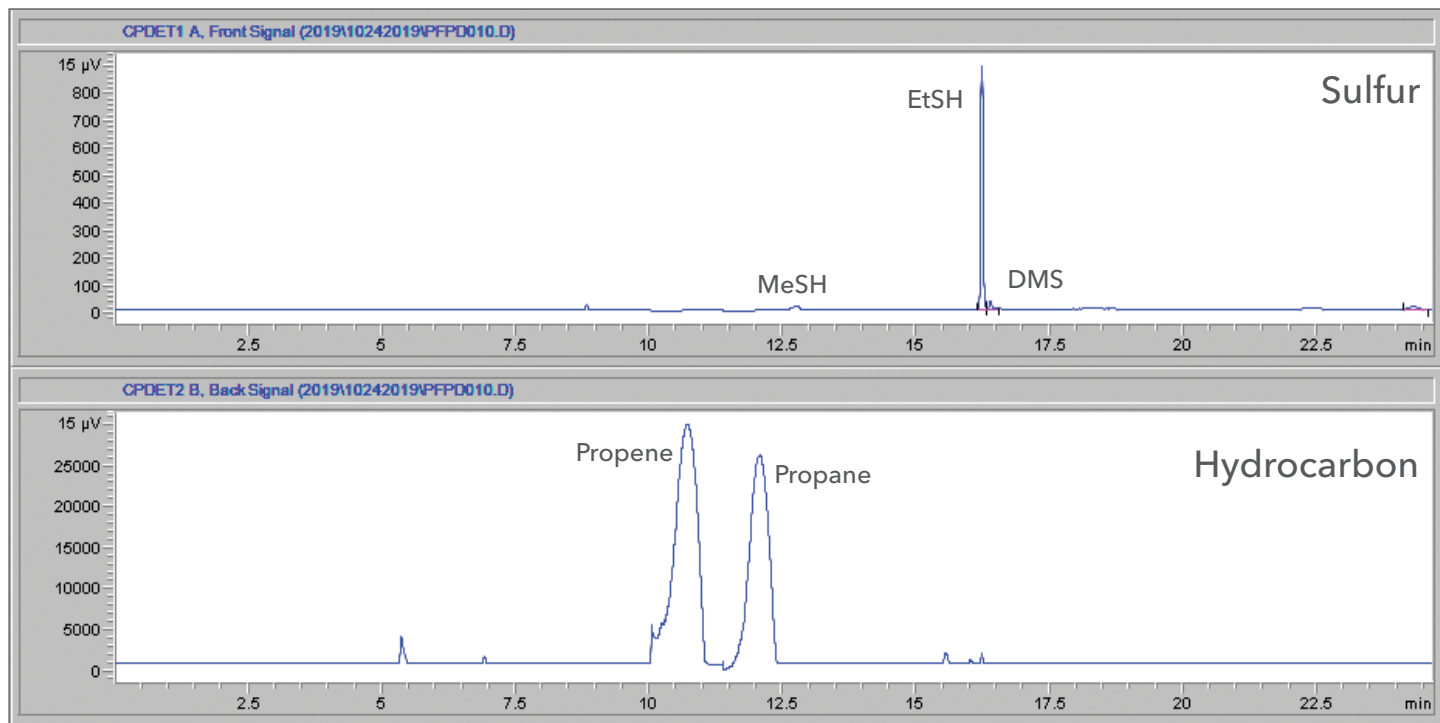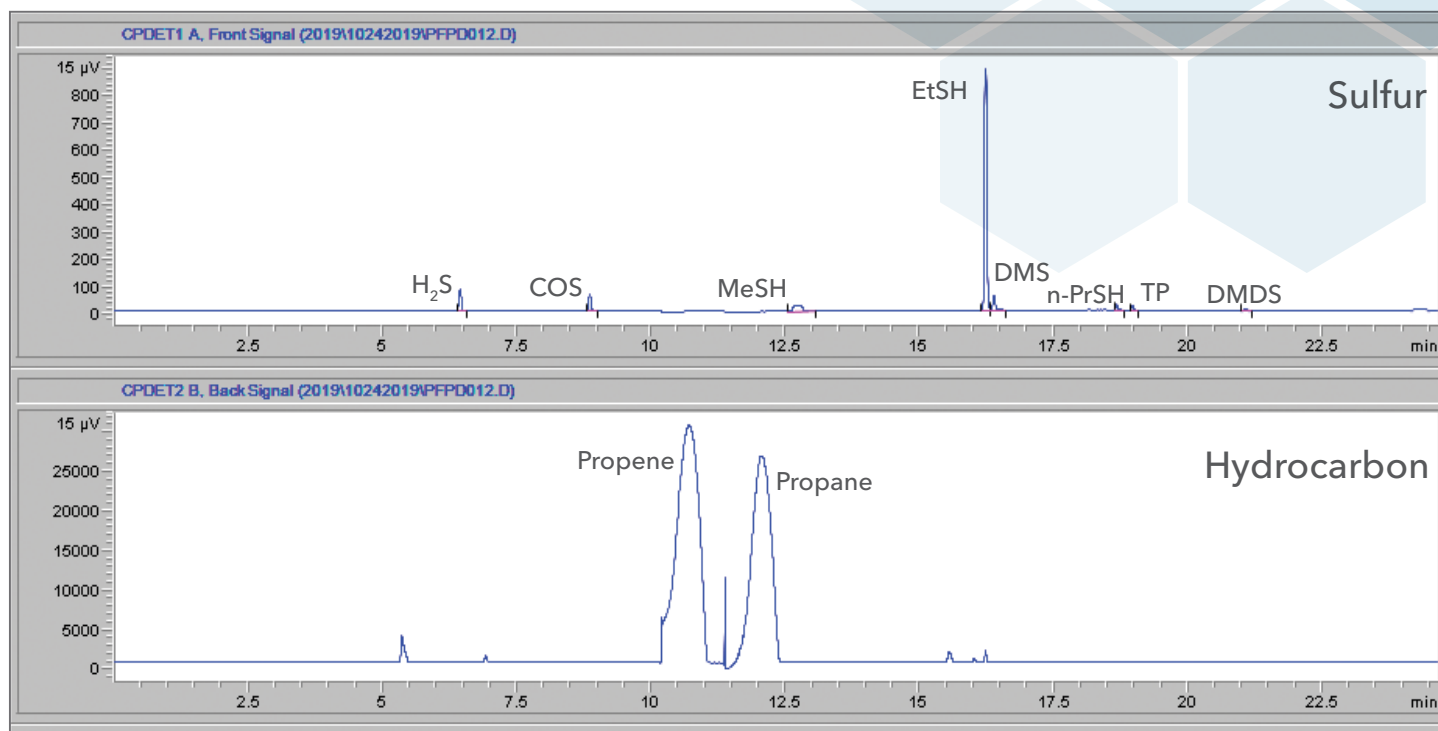Figure 8. 25% Propene and Propane Sample

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$_2$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 instrumentation used provides a fast, reliable method for analyzing sulfur compounds in a variety of matrices. 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

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OI Analytical, a Xylem brand
PO Box 9010
College Station, TX 77842-9010

+1.979.690.1711
oi-info@xyleminc.com
oico.com

oico.com/Petroleum