

# Determination 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, however, the analysis can be challenging due to the reactivity and instability of sulfur compounds 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 a PerkinElmer Clarus® 590 GC coupled with an OI Analytical Pulsed Flame Photometric Detector (PFPD).



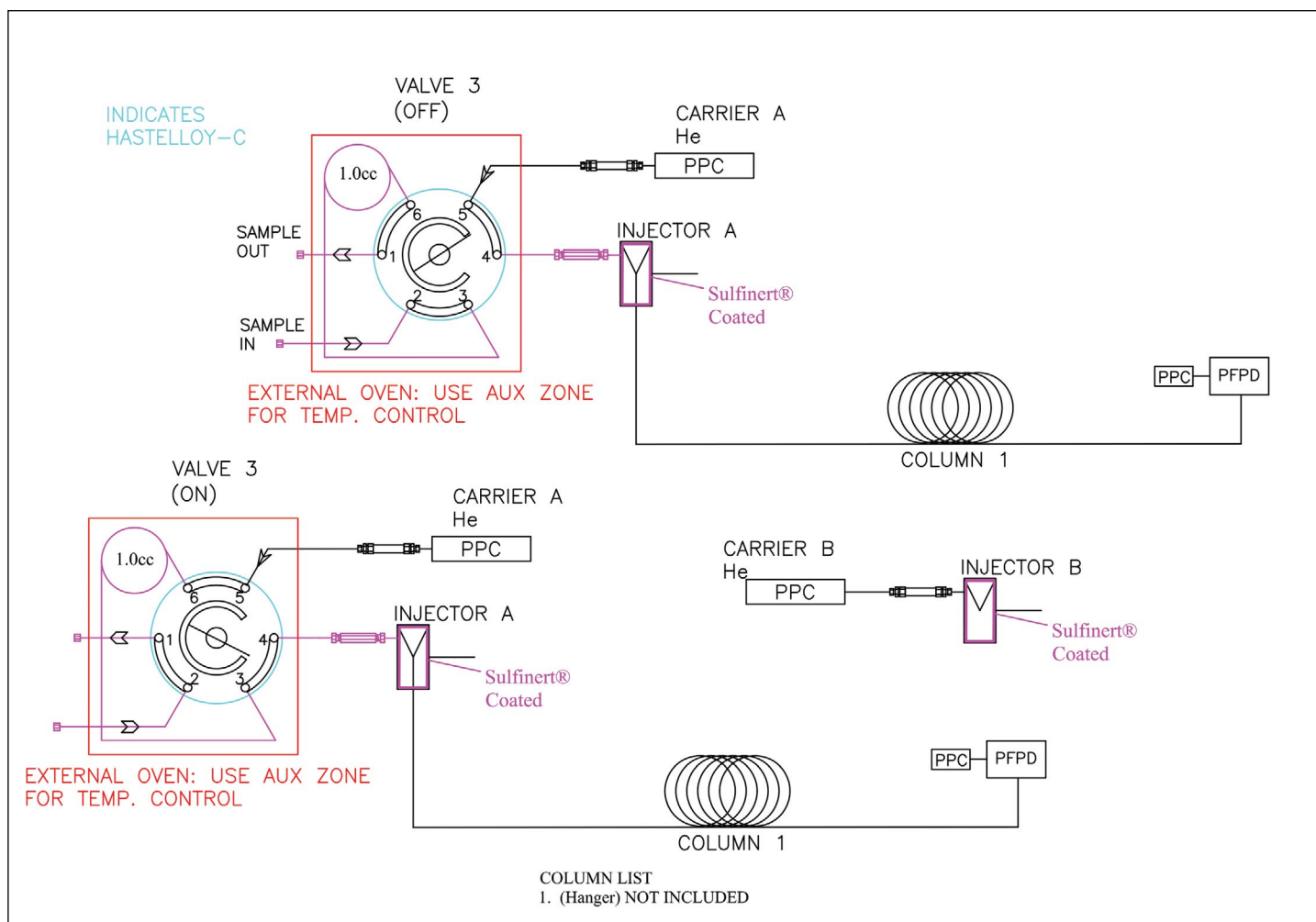
## Experimental

### System Description:

Data for this study were acquired using the PerkinElmer Clarus 590 gas chromatograph with TotalChrom® CDS, heated Hastelloy-C® six-port gas sampling valve with passivated tubing and a 1ml loop, and an OI Analytical 5383 PFPD. Standards were generated using permeation tubes and a KIN-TEK FlexStream™ standard diluter.

The PFPD was tuned for optimum sulfur response, and 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. Please see Figure 1 for the flow diagram of the PerkinElmer gas sampling system.

Figure 1. PerkinElmer Gas Sampling System



## 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 permeation oven held at a constant temperature of 40 °C. The concentrations of the compounds were varied by changing the nitrogen flow rate through the permeation oven using flows from 250 to 1500 ml/minute. A seven-point calibration was run, after which five Initial Demonstrations of Capability (IDOC) were run using a 500ml/min flow and eight Method Detection Limit (MDL)

standards were run using 2000ml/min. Thirty replicates of a natural gas sample containing an unknown composition and concentration of light sulfur compounds were also analyzed to show repeatability. 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

<b>PK1 Clarus 590 GC and OIA 5383 PFPD</b>	
KIN-TEK permeation oven	40 °C Nitrogen dilution gas Dilution gas flow rate 250 to 1500 mL/min
Permeation devices	H <sub>2</sub> S, 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	6-port GSV with 1-mL Sulfinert®-coated sample loop Automated air-actuated valve All lines Sulfinert® coated Valve oven temperature 110 °C
Inlet	200 °C split mode Split ratio 10:1 Sulfinert® coated Standard 4mm I.D. quartz liner
GC column	Agilent J&W DB - Sulfur SCD column 60-m x 0.32-mm ID x 4.20 µm Helium carrier gas, 1.2 mL/min
Oven program	40 °C for 10 min then 30 °C/min to 180°C, and hold for 10 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 <sub>2</sub> /air ratio tuned for optimum sulfur emission 6-24 msec sulfur gate with square root on (linear mode) 1-2 msec hydrocarbon gate

Samples containing natural gases, 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 2 - 9 for standard and sample chromatograms.

Figure 2. Standard at 500 ml/min

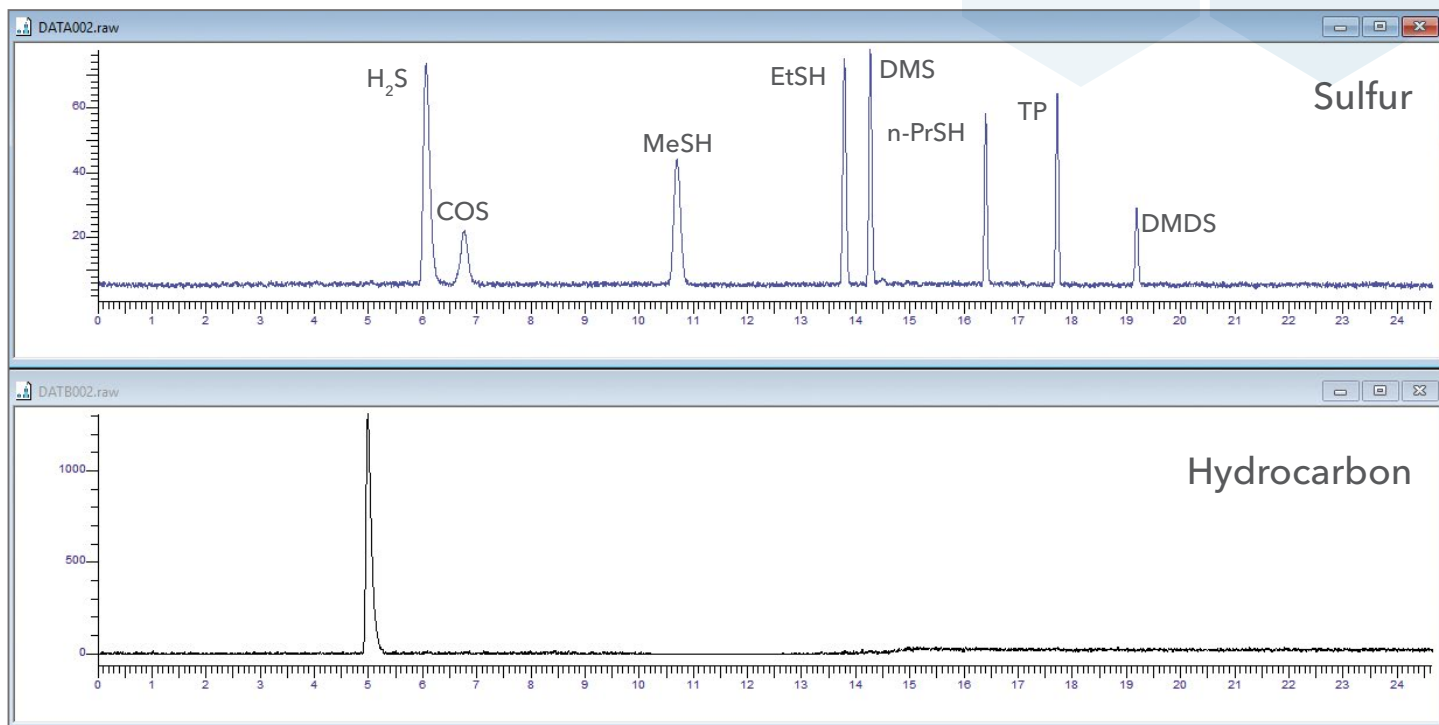


Figure 3. Sample for RSD study

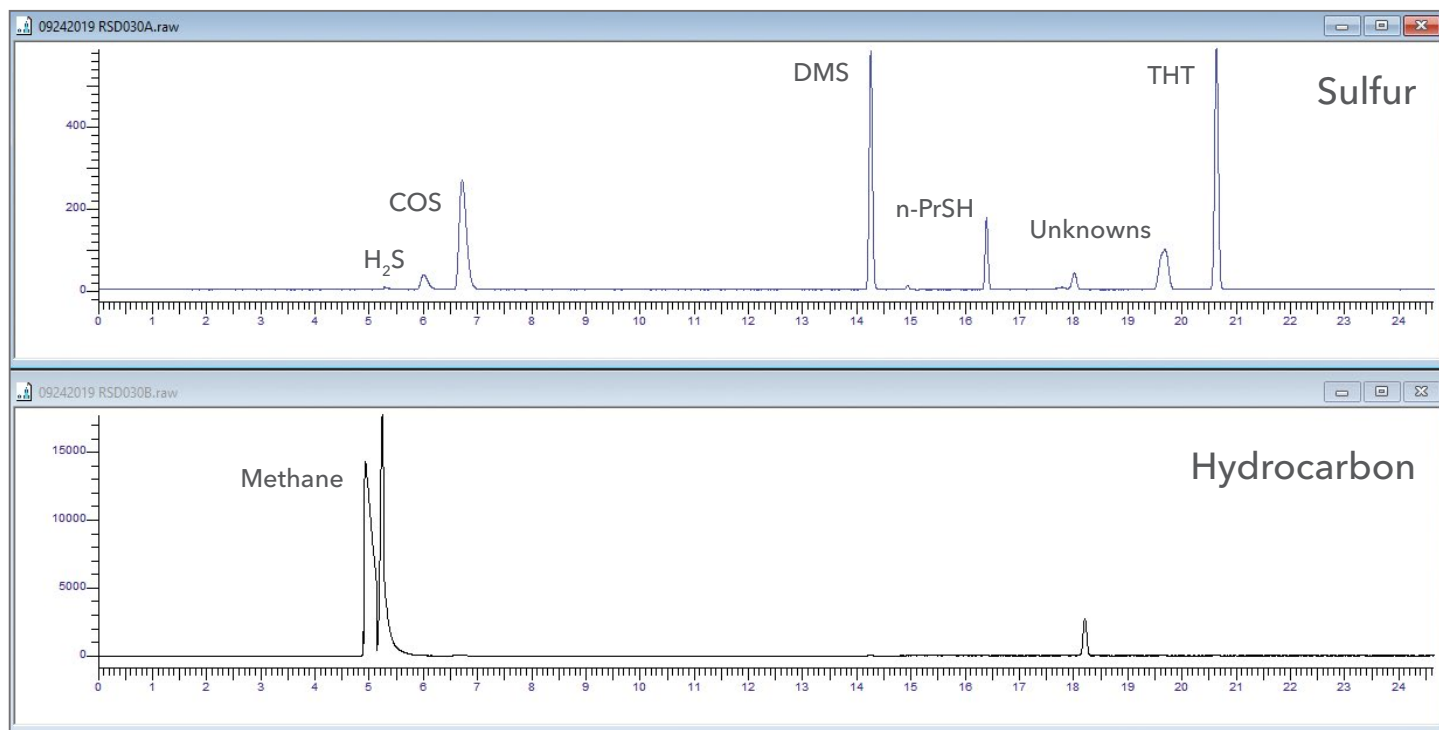


Figure 4. PerkinElmer LPG sample

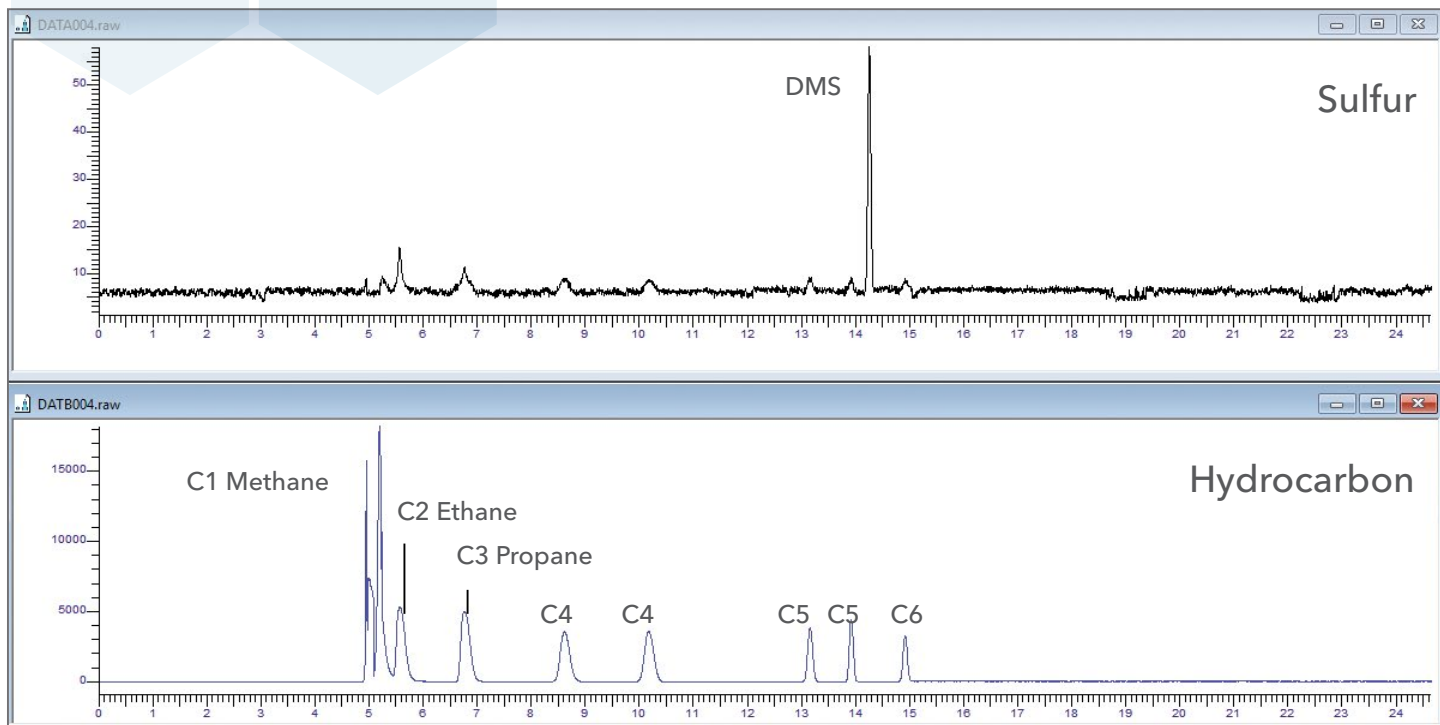


Figure 5. PerkinElmer LPG sample spike

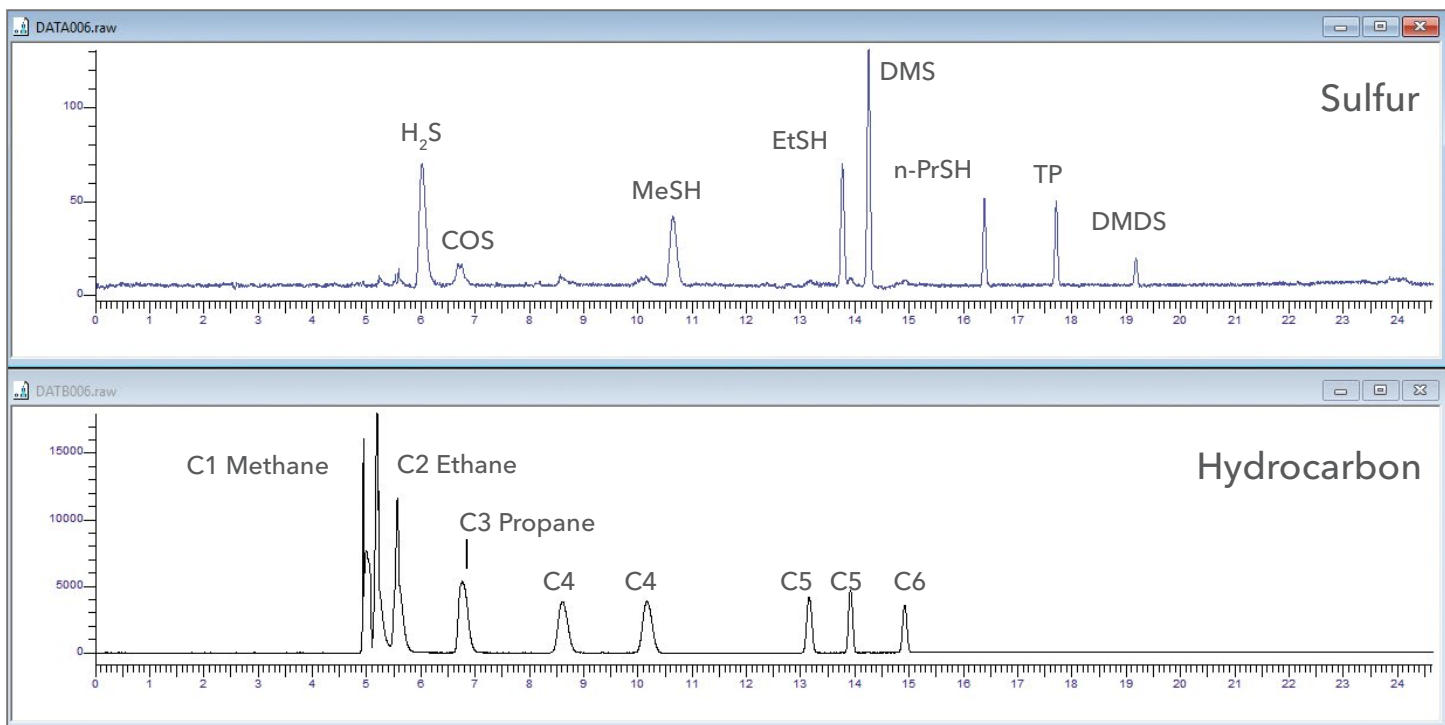


Figure 6. 25% Ethene and Ethane sample

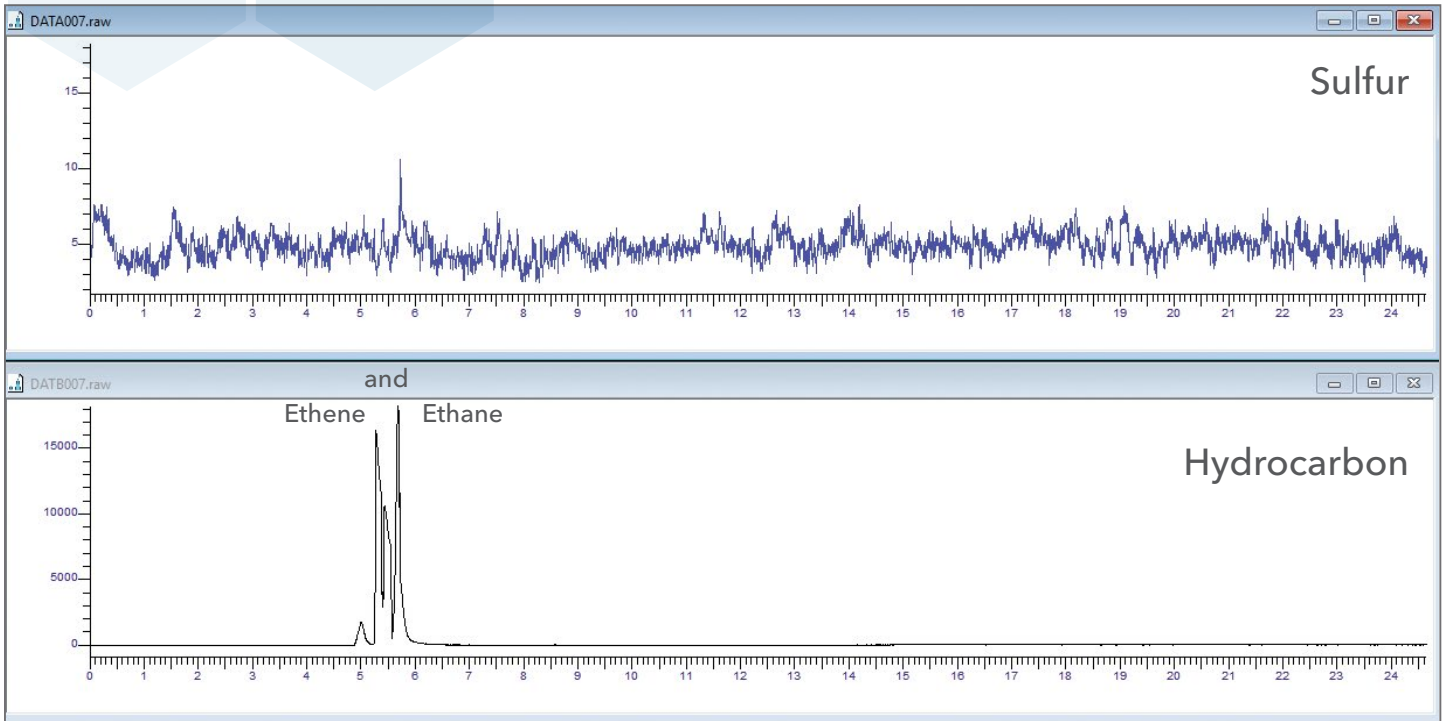


Figure 7. 25% Ethene and Ethane sample spike

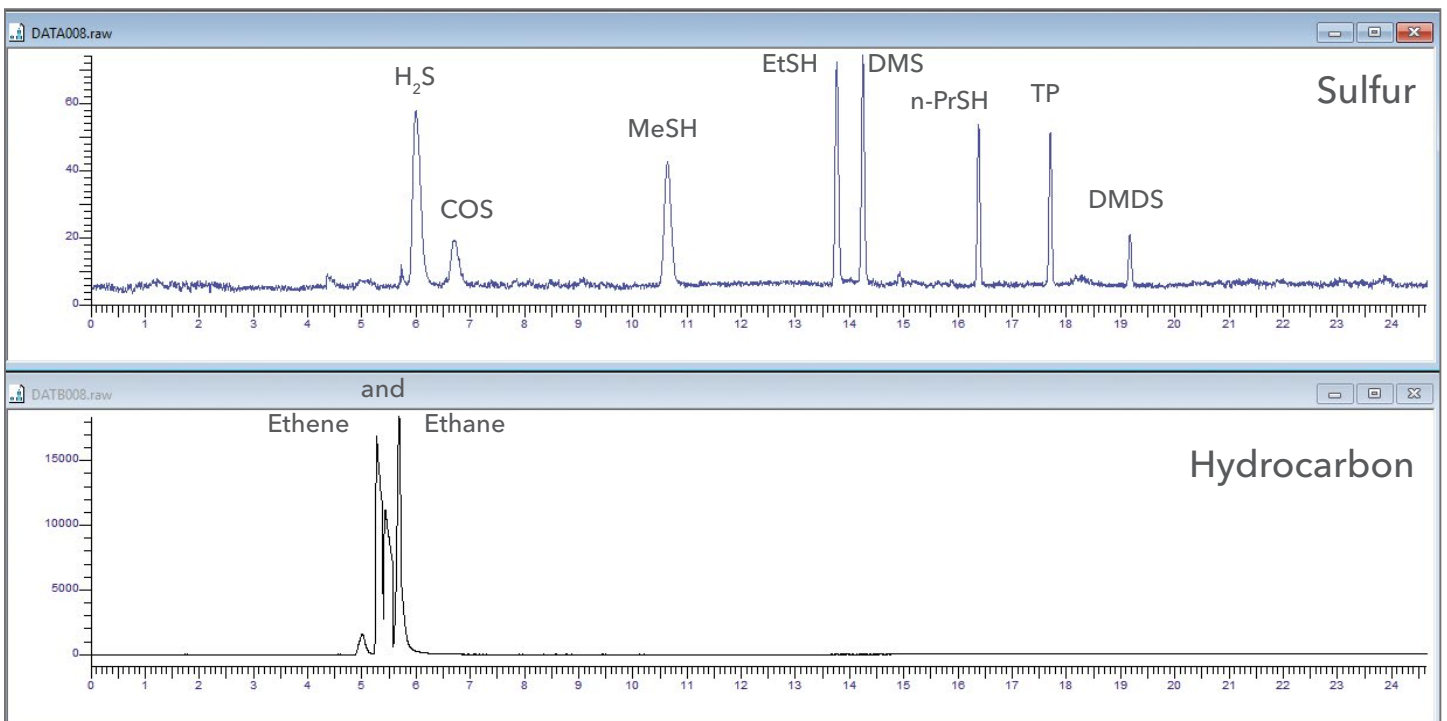


Figure 8. 25% Propene and Propane sample

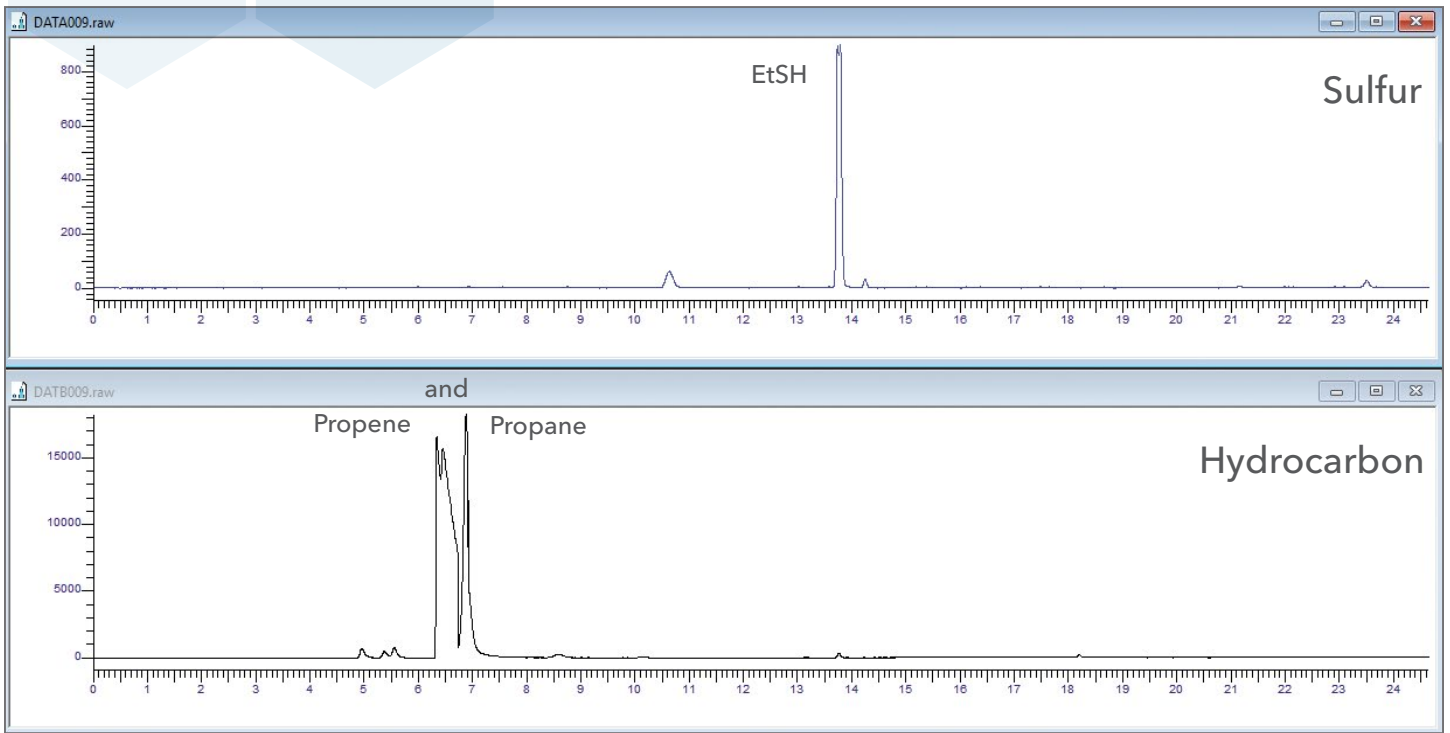
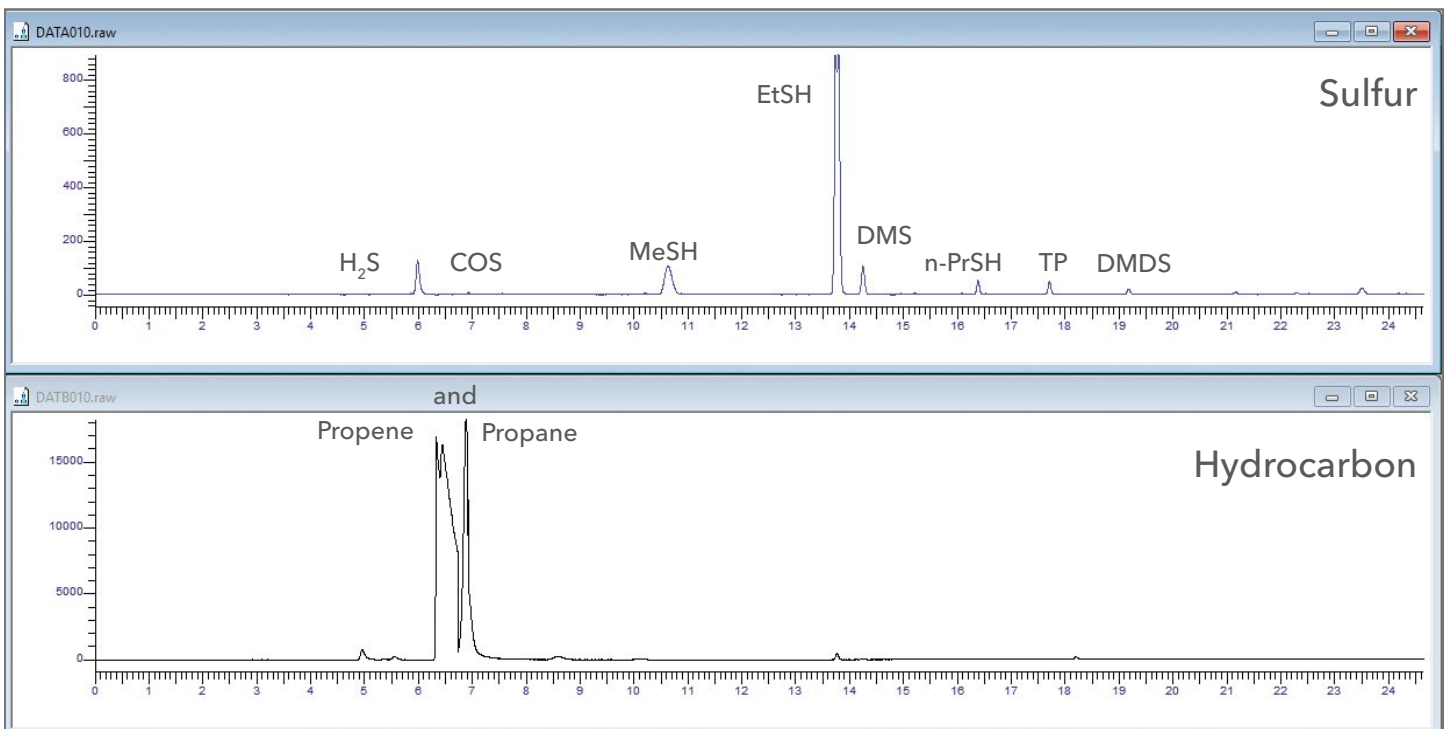


Figure 9. 25% Propene and Propane sample spike



## Results and Discussion

Calibration was easily performed using the KIN-TEK FlexStream standard diluter. Calibration criteria of greater than 0.990 were met. Repeatability, MDL, and IDOC studies also produced acceptable data as outlined in Table 2. The data showed excellent repeatability and stability using the PerkinElmer gas sampling valve. The PFPD also demonstrated great response and stability.

Table 2. Results

Compound	Cal Range (PPMV)	Retention Time	Correlation Coefficient	MDL (PPMV)	Avg Sample Amount (PPMV)	%RSD SAMPLE	IDOC Precision (% RPD)	IDOC Accuracy (% REC)
1. Hydrogen sulfide (H <sub>2</sub> S)	0.329 - 1.973	6.06	0.999	0.038	0.657	11	6.33	109.9
2. Carbonyl sulfide (COS)	0.067 - 0.401	6.76	0.991	0.045	2.993	2	11.5	105.0
3. Methanethiol (MeSH)	0.233 - 1.397	10.68	0.997	0.018	ND	N/A	2.02	102.2
4. Ethanethiol (EtSH)	0.180 - 1.082	13.78	0.999	0.032	ND	N/A	0.98	106.8
5. Dimethyl sulfide (DMS)	0.180 - 1.082	14.26	0.998	0.018	4.67	1	4.59	102.4
6. 2-Propanethiol (n-PrSH)	0.116 - 0.694	16.39	0.993	0.039	1.866	3	3.56	104.6
7. Thiophene (TP)	0.133 - 0.799	17.72	0.998	0.030	ND	N/A	2.23	102.0
8. Dimethyldisulfide (DMDS)	0.030 - 0.181	19.18	0.992	0.017	ND	N/A	10.2	107.2

ND = Non - detect      Flow range for calibration standards = 250 - 1500 ml/min      Flow for MDL standards = 2000 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. The PFPD is easier to maintain and operate compared to other sulfur detectors. The constant pulsing of the flame results in a "self-cleaning" detector, which essentially eliminates coking problems found in other detectors. As the PFPD has an equimolar response, unidentified compounds may be quantitated with confidence. Sulfur compounds of the same class should have approximately the same response factor. These unknown or uncalibrated compounds are quantitated as monosulfur species. 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 using 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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