Determination of Sulfur in Natural Gas by ASTM Method D 6228-11 Using a Pulsed Flame Photometric Detector (PFPD)

Introduction

Natural gas and other gaseous fuels contain varying amounts and types of sulfur compounds, which can be corrosive to equipment and can inhibit or destroy catalysts used in gas processing. In addition, small amounts of sulfur odorants are added to natural gas and other liquefied petroleum gases (LPGs) for safety purposes. Accurate measurement of the levels of these sulfur species is essential to ensure proper processing and to monitor odorant levels for public safety.

Determination of sulfur in gaseous fuels is done almost exclusively by gas chromatography (GC) with a sulfur-selective detector. There are several ASTM Standard Test Methods written for this purpose, and although the operating conditions are similar, the principal difference between the methods is the type of selective detector used to detect and quantify the sulfur species.

The advantages that the Pulsed Flame Photometric Detector (PFPD) has over the other sulfur-selective detectors include unambiguous sulfur recognition and selectivity against hydrocarbon matrices, increased sensitivity, and equimolar sulfur response. The PFPD also exhibits long-term stability with little or no maintenance, and can operate for months or even years on the same calibration curve with no change in response factors.

This application note illustrates how the PFPD is used for determination of volatile sulfur species in natural gas and other gaseous fuels using ASTM Method D 6228-11, "Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection".[1]

System Description

All data for this study 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, and compound detection and quantitation with the PFPD.

Figure 1. The OI Analytical SPRO-Select is designed to detect and quantify low-concentration 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 it 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.

Chromatography

Any capillary GC column can be used that will separate the sulfur species from the natural gas matrix. This study illustrates the use of two commercially available capillary PLOT columns, the Agilent J&W Select Low Sulfur column (used in the SPRO-Select GC system) and the Agilent GS-GasPro column (used in the S-PRO 3200 GC system).

Detection

The SPRO-Select 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.

Experimental

All instrument operating conditions are shown in Table 1. A 1-mL aliquot of each sample was introduced onto the analytical column using a gas sampling loop, an air-actuated valve, and a 50:1 split ratio. The PFPD was configured and optimized for a trace-level sulfur detection. Each of the capillary columns tested required different oven ramping programs; they are listed separately in Table 1.

Table. 1. Instrument Configuration and Operating Conditions

GC Operating Conditions		
Permeation Oven	40 °C Helium dilution gas Dilution gas flow rate 5 to 200 mL/minute	
Automated Injection System	4-port selection valve (sample or standard) 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	
Sulfur Detection	Pulsed Flame Photometric Detector (PFPD) 2-mm combustor, BG-12 filter, R1924 PMT 200 °C H_2/air ratio tuned for optimum sulfur emission SULFUR: 6-24 msec sulfur gate, Square Root ON HYDROCARBON: 1-3 msec hydrocarbon gate, Square Root OFF	
Chromatography		
GC Column	S-PRO 3200 System Column #1 Agilent GS-GasPro PLOT column 30-m x 0.32-mm ID Helium carrier gas, 2 mL/minute	SPRO-Select System Column #2 CP8575 Agilent J&W Select Low Sulfur PLOT column 60-m x 0.32 mm ID Helium carrier gas, 2 mL/minute
Oven Program	60 °C for 2 minutes 20 °C/minute to 260 °C Hold for 5 minutes Total run time 17 minutes	50 °C for 5 minutes 5 °C/minute to 200 °C Hold for 0.1 minute Total run time 35.1 minutes

Results and Discussion

Two natural gas samples were blended for this project and provided by DCG Partnership (Pearland, TX). Both natural gas samples contained five sulfur compounds at concentrations ranging from 3 to 6 ppmv, and one or more representative hydrocarbons that are typically found in different grades of natural gas. The composition of the blended natural gas samples are shown in Table 2.

Table. 2. Composition of Blended Natural Gas Samples

Compound	Sample #1 Repeatability Study	Sample #2 Chromatography with Matrix Present
COS	3.45 ppmv	3.57 ppmv
H_2S	4.83 ppmv	3.06 ppmv
Dimethyl Sulfide (DMS)	4.11 ppmv	3.81 ppmv
1-Propanethiol	5.92 ppmv	4.45 ppmv
Tetrahydraothiophene (THT)	4.46 ppmv	4.15 ppmv
n-Pentane	-	0.253%
n-Butane	-	0.253%
Propane	-	0.508%
Ethane UHP	-	0.506%
Methane UHP	Balance	Balance

Calibration

The instrument was calibrated for H_2S and COS using certified wafer-type permeation devices and the permeation oven. Details of the permeation oven conditions and calibration standards are described in detail in OI Application Note 3672.[2] The concentration of H_2S in the test mixtures was confirmed using the response factor (RF) from the H_2S wafer device, and the concentration of all other sulfur compounds were verified using the RF generated by the COS wafer device. The calculated concentrations of the sulfur compounds were within ±4% of the reported concentrations in both blends.

Repeatability

Sample #1 (five sulfur compounds in UHP methane) was analyzed 20 times on each analytical column to demonstrate repeatability. The gas sample loop and sampling lines were flushed with helium between replicates to simulate real world sampling conditions. The relative standard deviation (RSD) for the 20 replicate injections ranged from 1.2 to 3.3% on the GS-GasPro column, and from 1.5 to 2.5% on the CP8575 Agilent J&W Select Low Sulfur column. The results are tabulated in Tables 3 and 4. Overlaid chromatograms in Figures 2 and 3 further illustrate the stability and repeatability of the system

Table 3. Twenty Replicate Analyses of Sulfur Compounds in Methane on the GS-GasPro Column (Column #1)

Compound Name	COS	H$_2$S	DMS	1-Propanethiol	THT
Retention Time (minutes)	3.25	3.56	10.33	10.52	13.44
Concentration (ppmv in methane)	3.45	4.83	4.11	5.92	4.46
Peak Area Counts					
Run 1	3165	2686	2745	2471	2177
Run 2	3199	2638	2763	2492	2240
Run 3	3150	2635	2772	2451	2167
Run 4	3170	2590	2766	2442	2186
Run 5	3160	2605	2747	2450	2145
Run 6	3126	2561	2705	2398	2171
Run 7	3105	2514	2751	2430	2214
Run 8	3176	2578	2778	2424	2243
Run 9	3129	2438	2738	2404	2226
Run 10	3200	2586	2842	2495	2331
Run 11	3154	2568	2800	2469	2314
Run 12	3132	2450	2759	2417	2243
Run 13	3246	2580	2809	2497	2359
Run 14	3210	2508	2793	2435	2346
Run 15	3215	2505	2741	2409	2296
Run 16	3155	2481	2722	2396	2272
Run17	3136	2458	2695	2388	2373
Run 18	3135	2496	2792	2406	2341
Run 19	3110	2424	2766	2368	2342
Run 20	3150	2485	2492	2404	2366
Average Area Counts	*3161*	*2539*	*2749*	*2432*	*2268*
Standard Deviation	*37*	*74*	*70*	*38*	*76*
%RSD	*1.2*	*2.9*	*2.5*	*1.5*	*3.3*

Table 4. Twenty Replicates Analyses of Sulfur Compounds in Methane on the Agilent J&W Select Low Sulfur Column (Column #2)

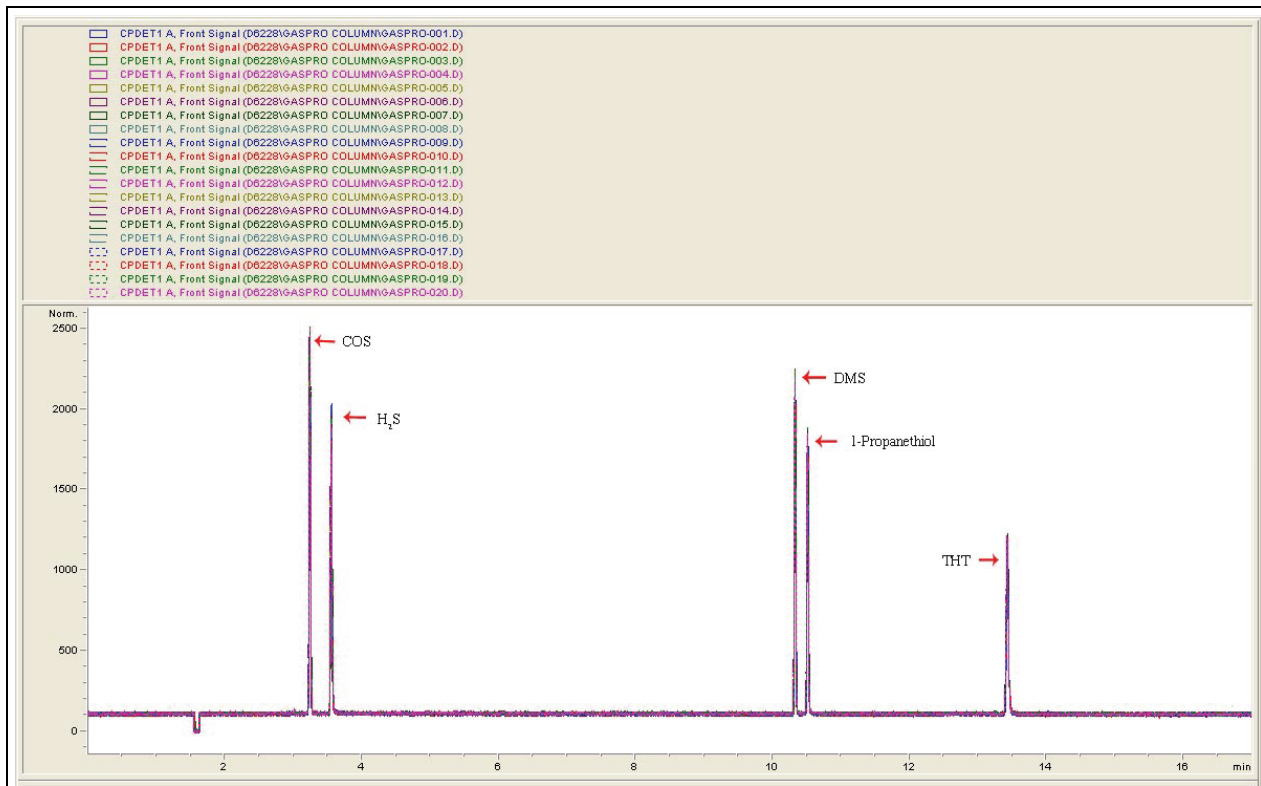| Compound Name	H$_2$S	COS	DMS	1-Propanethiol	THT
Retention Time (minutes)	4.49	5.95	16.52	23.52	30.55
Concentration (ppmv in methane)	4.83	3.45	4.11	5.92	4.46
Peak Area Counts					
Run 1	3350	3981	3648	2814	4470
Run 2	3225	4127	3967	2956	4734
Run 3	3301	4165	3965	3041	4705
Run 4	3326	4130	3973	2936	4679
Run 5	3357	4184	3963	2921	4717
Run 6	3272	4164	3983	2914	4695
Run 7	3324	4176	4000	2954	4734
Run 8	3169	4128	3944	2881	4658
Run 9	3260	4185	3982	2933	4702
Run 10	3302	4217	3990	2917	4744
Run 11	3108	3849	3808	2933	4800
Run 12	3418	4020	3902	2990	4760
Run 13	3369	4061	3923	2854	4746
Run 14	3351	4111	3933	2967	4704
Run 15	3373	4066	3906	2977	4800
Run 16	3336	4124	3932	2926	4648
Run17	3394	4080	3905	2942	4685
Run 18	3184	4146	3955	2981	4663
Run 19	3260	4173	4009	2854	4691
Run 20	3375	4106	3920	2841	4670
Average Area Counts	3303	4110	3930	2927	4700
Standard Deviation	82	85	81	56	69
%RSD	2.5	2.1	2.0	1.9	1.5

Figure 2. Overlaid Chromatograms from 20 replicate injections of Sample #1 onto the GS-GasPro column (Column #1)
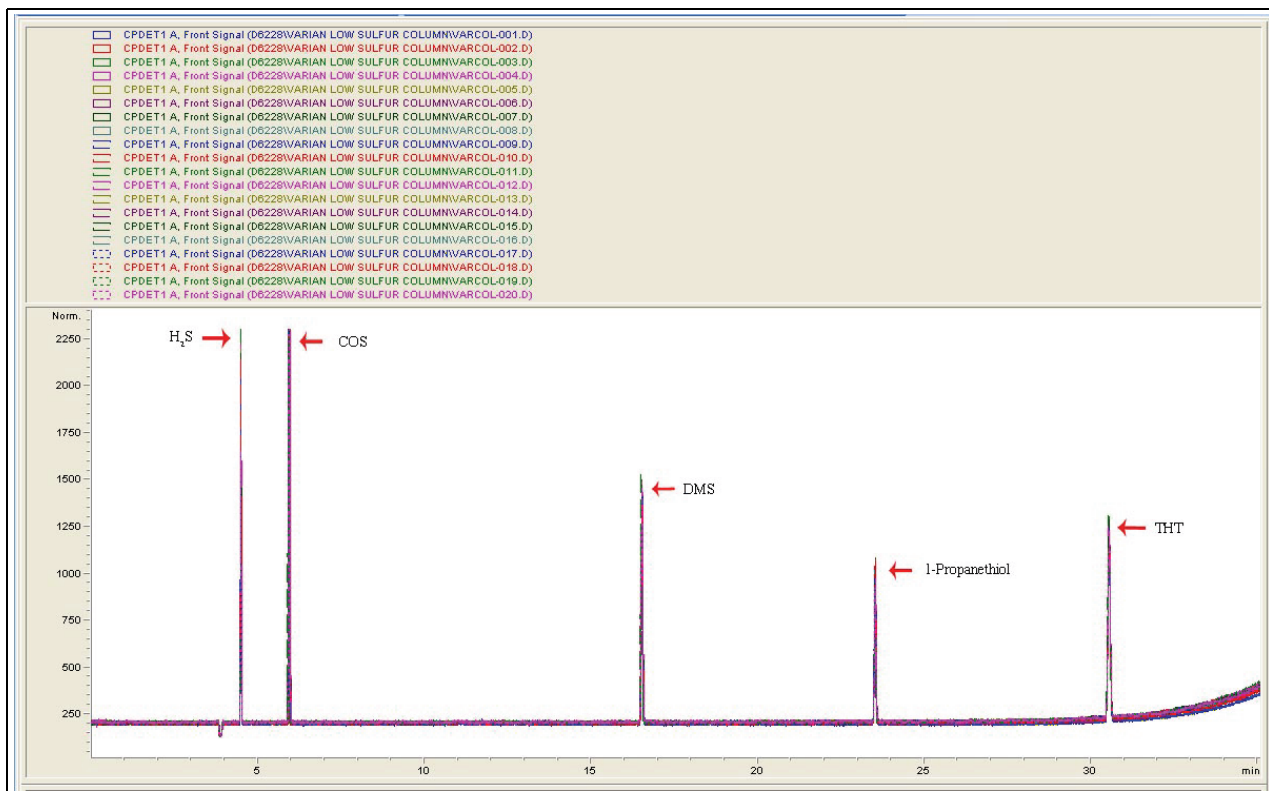

Figure 3. Overlaid chromatograms from 20 replicate injections of Sample #1 onto the CP8575 Agilent J&W Select Low Sulfur column (Column #2)

Chromatography

Any capillary column that can provide adequate separation of the target sulfur compounds can be used with the PFPD for ASTM Method D 6228-11. The two columns used in this study were chosen because of their superior peak shape, excellent sensitivity for sulfur compounds, retention time repeatability, and overall stability when used with this method.

The PFPD is capable of outputting two simultaneous GC signals. For this study, the first signal was assigned to sulfur using a 6 to 24 msec gate, and the second signal was assigned to hydrocarbons using a 1 to 3 msec gate. This configuration produced two simultaneous and mutually selective chromatograms, one for sulfur compounds and one for the hydrocarbon profile. Figures 4 and 5 illustrate the sulfur and hydrocarbon chromatograms for Sample #2 on each of the selected columns.
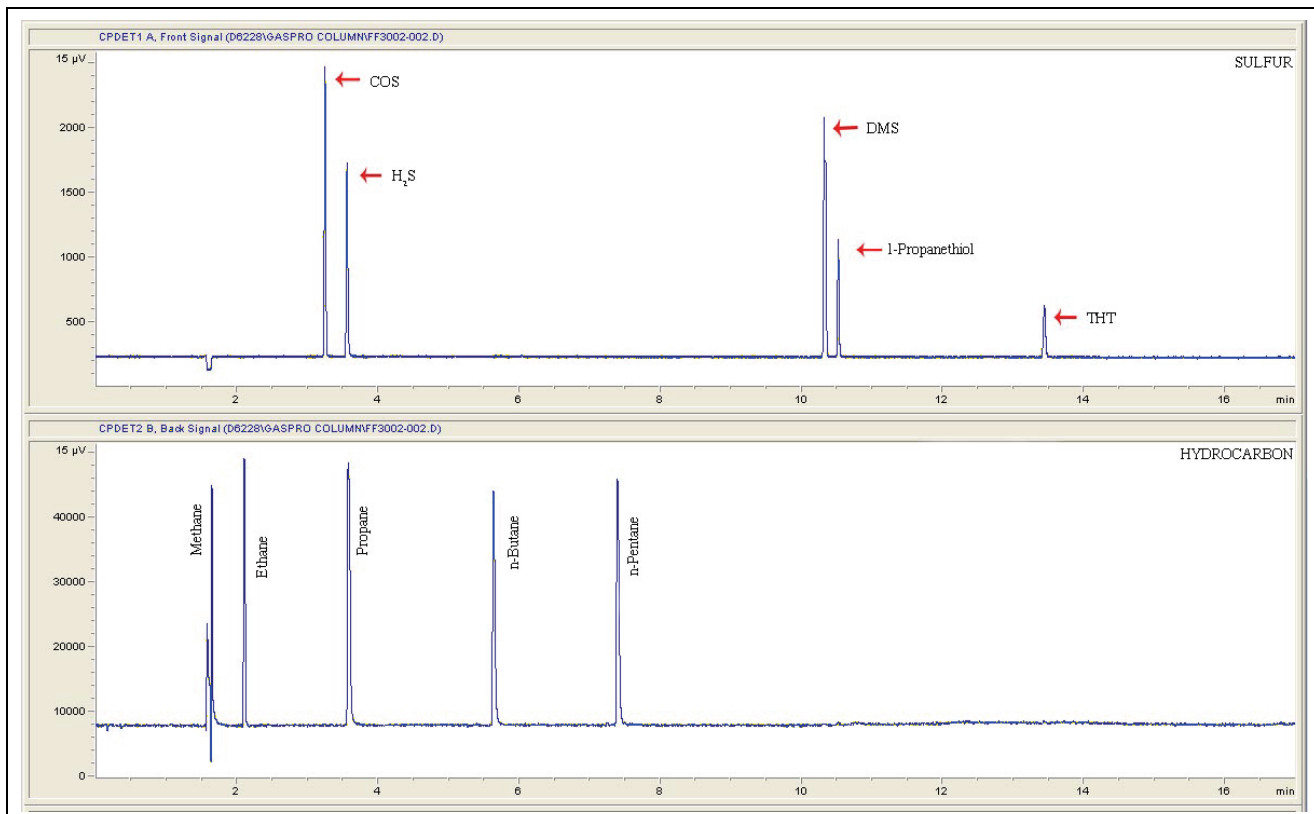

Figure 4. Simultaneous sulfur and hydrocarbon chromatograms of a blended natural gas (Sample #2) acquired using the OI Analytical S-PRO 3200 and conditions shown for column #1 (GasPro).
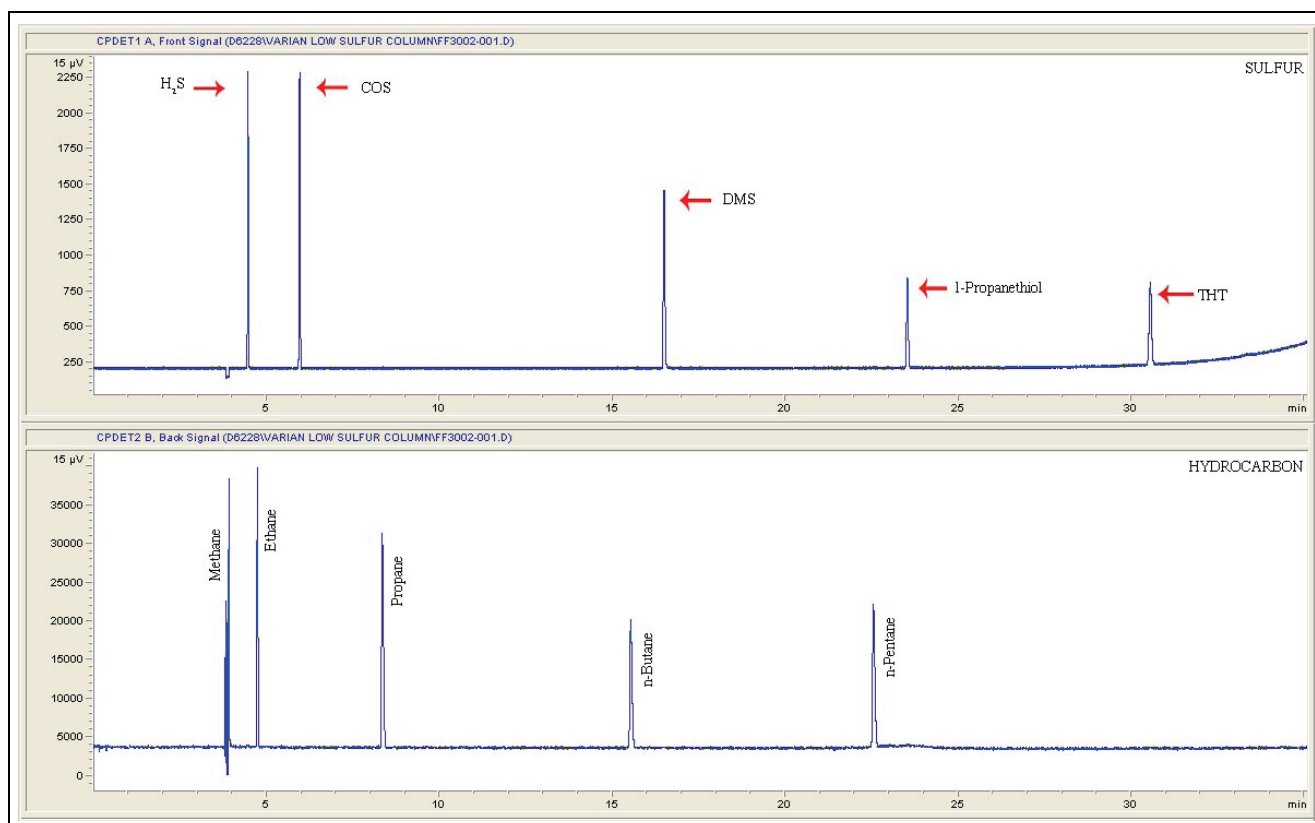
Figure 5. Simultaneous sulfur and hydrocarbon chromatograms of a blended natural gas (Sample #2) acquired using the OI Analytical SPRO-Select and conditions shown for column #2 (Agilent J&W Select Low Sulfur).

Summary and Conclusion

The SPRO-Select system can be used to detect and quantitate sulfur species in natural gas using ASTM Method D 6228-11 with a high level of precision and accuracy, meeting all of the method requirements. Two commercially available analytical columns are shown to yield reproducible chromatograms with symmetric peak shape and chromatographic resolution of the sulfur and hydrocarbon peaks of interest.

References

1. ASTM Standard D 6228 "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

2. Fast Determination of Impurities in Propane-Propylene Streams Using a Pulsed Flame Photometric Detector (PFPD) and a New Capillary PLOT Column, OI Analytical Application Note #36720910.

Acknowledgement

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