Dual-Channel Gas Chromatographic System for the Determination of Low-Level Sulfur in Hydrocarbon Gases

Application

Hydrocarbon Processing

Authors

Roger L. Firor and Bruce D. Quimby
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

A 6890N equipped with dual flame photometric detectors is described for the analysis of ppb level volatile sulfur compounds in a variety of hydrocarbons using thick film DB-1 and GS-GasPro columns. Enhanced performance flame photometric detectors are employed that can achieve detection of sulfur compounds below 20 ppb. Examples of arsine and phosphine analysis with the same hardware are also discussed.

Introduction

Gas chromatography with sulfur selective detection is finding widespread application in many segments of the petroleum, petrochemical, and specialty chemical industries. Demand for low-level sulfur detection will increase in the future in response to more stringent regulations and tighter quality control.

Sulfur compounds can be significant poisons for various catalytic processes involved in hydrocarbon conversion. Monitoring these low-level poisons can lead to considerable saving in terms of improved yields, increased catalyst lifetime, and higher quality products. In looking at the future of fuel cells, fuel contaminants can adversely affect performance of fuel cell systems and fuel processors that are powered by natural gas or other fossil fuels. Finally, environmental regulatory issues in certain regions will continue, necessitating the need to monitor fuel impurities.

A common problem with many gas chromatographic sulfur selective detectors is hydrocarbon interference, especially from co-elution. The measurement challenge is acute when the interfering hydrocarbon comprises the majority of the sample, as in the analysis of impurities in ethylene and propylene, or sulfur in natural gas [1, 2]. In most cases, an accurate determination of the sulfur compound is difficult or not possible even with highly selective sulfur detectors. However, the use of a dual-channel system employing two very different separation columns (in terms of selectivity) largely avoids the interference problem. The configuration is shown in Figure 1. Sulfur compounds that have a severe interference on one column are likely to be separated from that interference on the other column. By assuring that a given sulfur compound will be separated on at least one of the columns, the system can use a reliable, stable, and relatively inexpensive flame photometric detector (FPD) for detection. If the hydrocarbons can be chromatographically separated from the sulfur compounds of interest, enhanced FPDs can quantitate sulfur to less than 20 ppb.

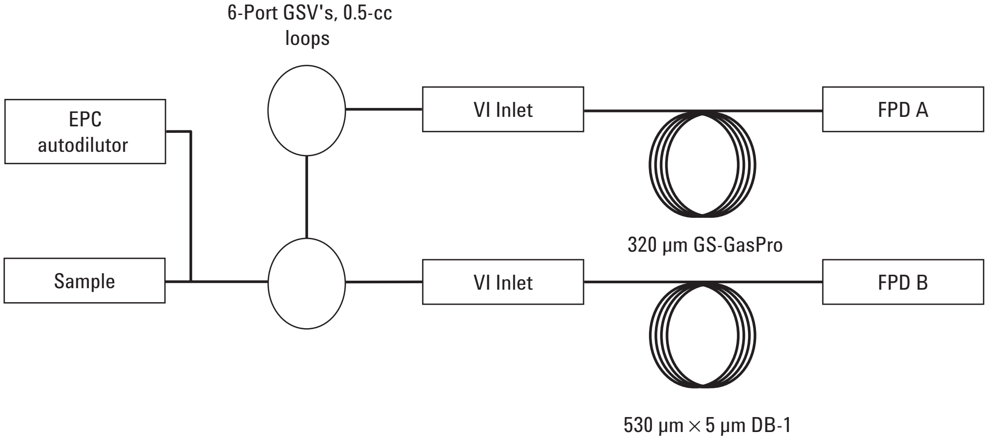

Figure 1. System configuration on the Agilent 6890N. Valves (plumbed in series) are Hastelloy C and all plumbing is Silcosteel® or Sulfinert™ treated.

Experimental

Selection of the appropriate capillary column is often key to the solution of a particular analysis problem, and this is especially true for this system. Four columns are employed (two for any given analysis) as described in Table 1.

Table 1. Recommended Column Combinations by Application

Applications	Column set
Natural gas, fuel cell gases	60 m × 530 µm × 5.0 µm DB-1 30 m × 320 µm GS-GasPro
Ethylene, propylene, C4 streams	105 m × 530 µm × 5.0 µm DB-1 60 m × 320 µm GS-GasPro

Recommended GC oven programs are 40 °C (5 min) to 290 °C (5 min) at 25 °C/min for natural gas, fuel cell gases and ethylene, and 35 °C (7 min) to 290 °C (5 min) at 20 °C/min for propylene. Somewhat lower detection limits can be achieved for sulfur in a propylene stream by employing cryo oven programs such as: –35 °C (7 min) to 290 °C (5 min) at 20 °C/min. Split ratios, as set in the GC method, vary from 0.5:1 to 2:1.

Each valve was interfaced to a specialized inert (Silcosteel treated) volatiles interface for accurate sample introduction at low split ratios into a capillary column. Due to the tendency for organosulfur compounds (especially H_2S) to adsorb to metal surfaces, great care must be used in selecting and constructing the chromatographic sample introduction system. The sample loop, tubing, and inlet are either Sulfinert or Silcosteel treated for inertness.

A factory modified FPD, with enhanced sensitivity, was used for each channel. The FPD is optimized for the analysis of trace sulfur gases, arsine, and phosphine in gaseous samples. See Table 2 for appropriate gas flow settings. These detectors achieve detection limits that are roughly four times better than standard. The sensitivity advantage is illustrated in Figure 2, where standard and modified FPDs are compared using a standard calibration blend. Minimum detection level (MDL) calculated on methyl mercaptan using linearized data and the 60 m DB-1 column is better than 15 ppb.

Table 2. FPD Gas Flow Settings

Analysis	Gas	Flow rate (mL/min)
Sulfur	Air	60
	Hydrogen	50
	Makeup	58
Arsine	Air	150
	Hydrogen	50
	Makeup	100
Phosphine	Air	110
	Hydrogen	150
	Makeup	58

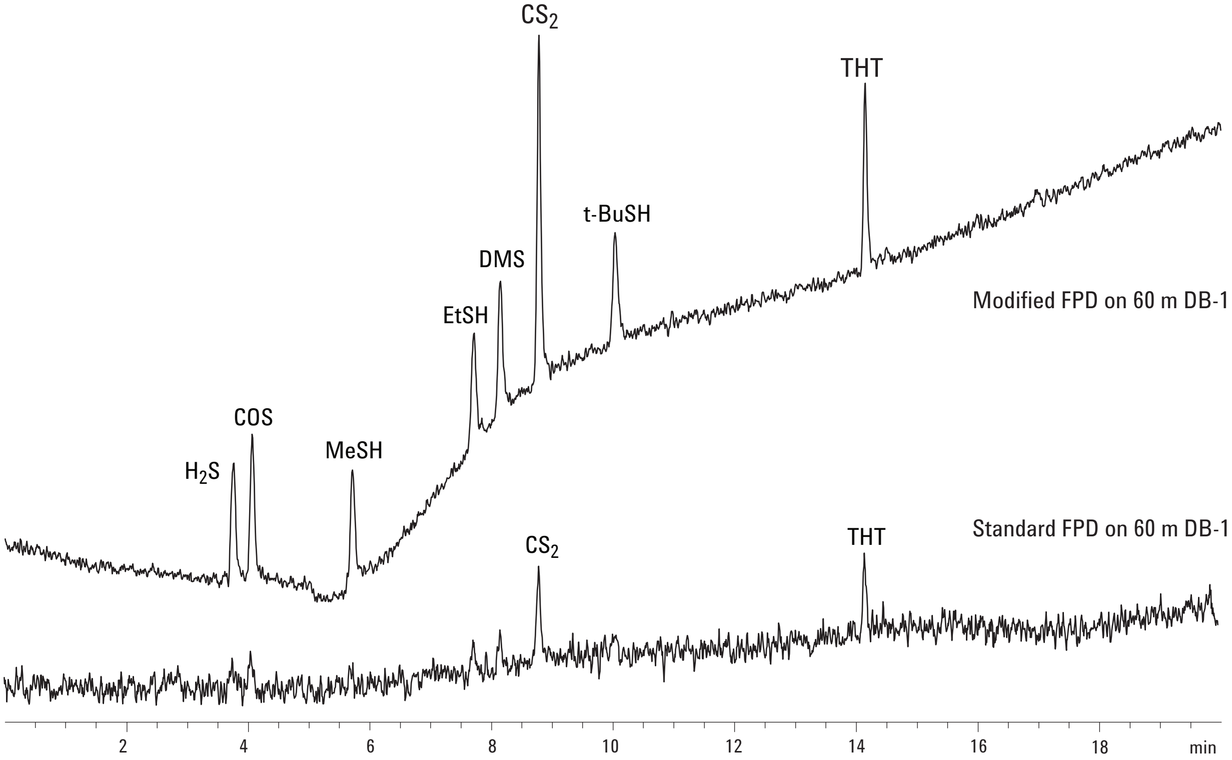

Figure 2. **Sensitivity comparison of standard and enhanced FPDs. Concentrations are 33 ppb per component (v/v) in helium.**

Due to the use of all available heated zones on the 6890N GC for either inlet or detector heating, the 6-port sample valves are not actively heated. This does not pose a problem for the light gaseous streams studied in this work. However, if desired, the valves can be heated by an auxiliary stand-alone temperature controller (Agilent model 19265B). The system is designed only for gaseous samples containing significant concentrations of hydrocarbons of C_6 or below.

Discussion

Channel 1 employs the GS-GasPro column, using a unique bonded PLOT technology, where COS is separated from C_2 and C_3 hydrocarbons, allowing measurement at trace levels. However, H_2S and the C_3s coelute. Channel 2 uses a thick film DB-1 column where H_2S is well separated from C_2s and C_3s, making low-level measurements of this sulfur impurity possible. COS and C_3s will coelute on this column. In summary, using a dual-column approach with the unique separation capabilities of GS-GasPro and thick film DB-1, both COS and H_2S can be measured in one chromatographic analysis at low ppb levels regardless of the concentrations of light hydrocarbons present in the sample. The elution order difference between the two columns is illustrated in Figure 3.

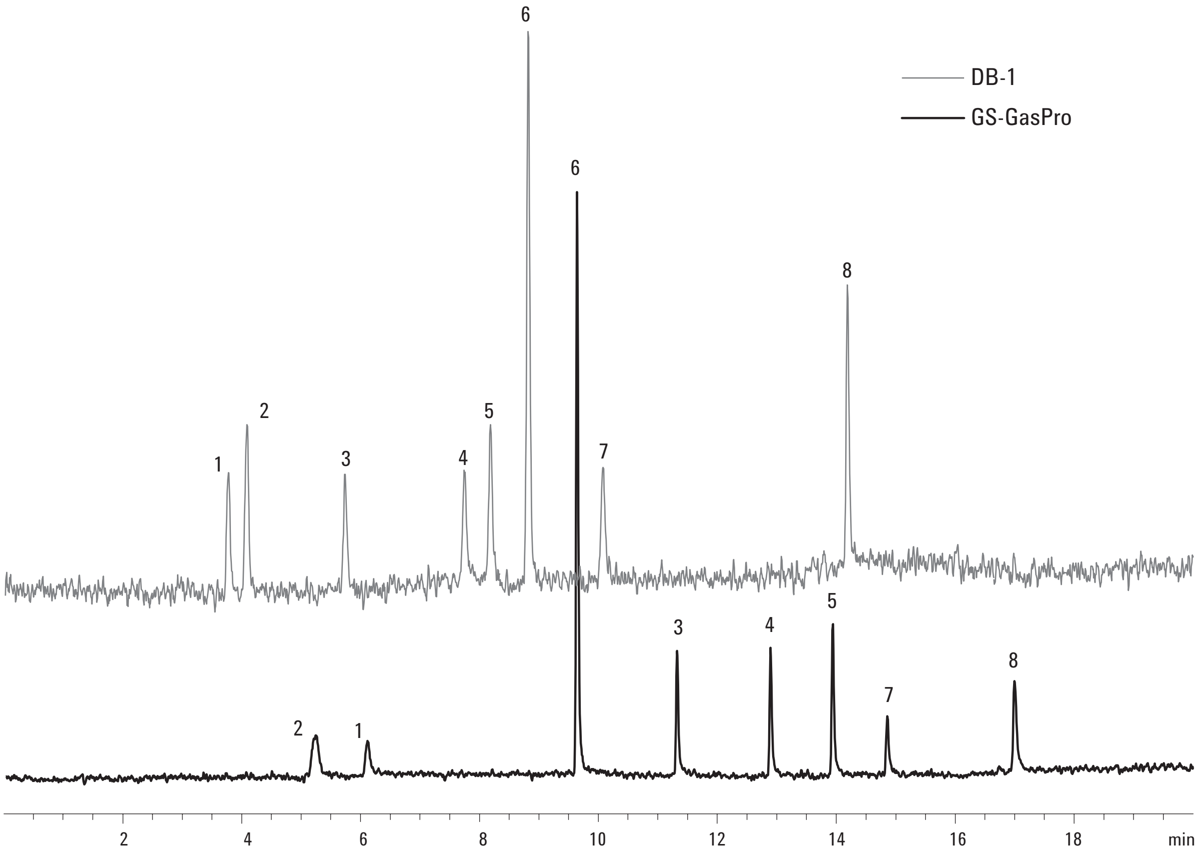

Figure 3. **The dual-column advantage. Sulfur mix at 90 ppb per component in helium. 1. H_2S, 2. COS, 3. MeSH, 4. EtSH, 5. DMS, 6. CS_2, 7. t-BuSH, 8. THT.**

Other potential interferences or coelutions between light sulfur compounds and hydrocarbons are avoided with this approach. A coeluting pair on one column will likely be separated on the other. Split ratios were set depending on the application from 0.5:1 to 2:1 in order to achieve the reported detection limits.

The sulfur calibration mix consisted of the following components at 5 ppm each: Hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), dimethyl sulfide, carbonyl sulfide (DMS), t-butyl mercaptan (t-BuSH), and tetrahydrothiophene (THT). The blend in helium was purchased from DCG Partnership, Pearland, TX. These compounds are representative of the most common light sulfur species encountered in gaseous fuels or petrochemical feedstocks.

Some adsorption of H_2S on the GS-GasPro column is possible. Priming the system a few times with a low ppm sulfur stream such as the calibration mix described here can largely eliminate the loss in sensitivity that can result from adsorption. This priming is usually only necessary for low ppb analyses where the active sites in the column could adsorb most of the sulfur present in the sample during an initial run.

Gaseous blends of the sulfur standard in helium or other matrices such as natural gas, propane, liquidfied petroleum gas (LPG), propylene, and refinery gas were prepared using dynamic blending at the point and time of use. Diluent (matrix) gases were mixed with the sulfur calibration standard using an Aux EPC module on the 6890N GC. Accurate concentrations from low ppb to ppm levels can be easily prepared by knowing the flow rates of the two streams as they mix in a Tee fitting prior to the gas sampling valves on the GC. This system and the hardware employed were described previously in detail [3].

Sulfur in Fuel Cell Gases, Natural Gas, and Proypylene

Figure 4 shows the chromatograms from the eight-component sulfur standard diluted with a fuel cell mix to 45 ppb (v/v) each component. The fuel cell

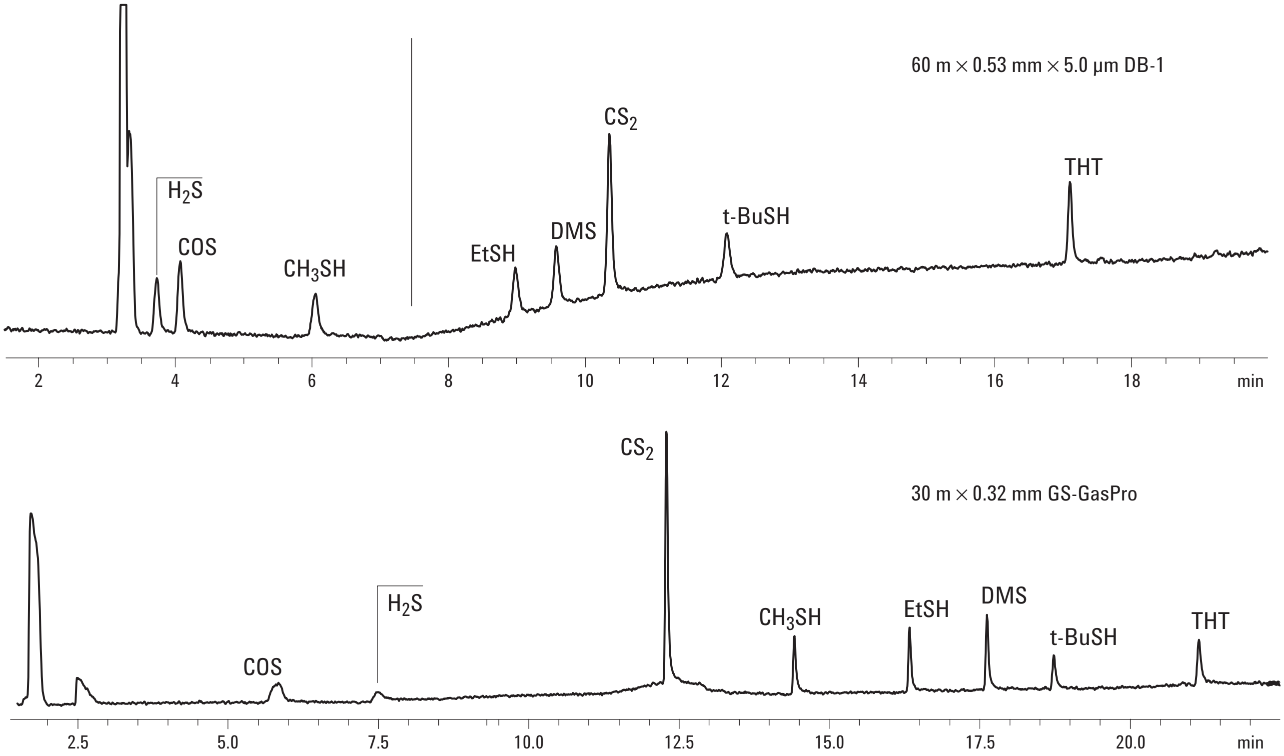

Figure 4. **Simultaneous dual column analysis of fuel cell mix containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.**

mix is 50% hydrogen, 10% carbon dioxide, and 5% methane. This mix is often used to simulate the output stream of a natural gas reformer used as the feed to a fuel cell. This matrix is one of the easier ones because the large hydrocarbon (methane) elutes before all of the sulfurs on both columns. Note that elution order of the sulfurs is significantly different on the GS-GasPro column compared to the DB-1 (see Figure 3). All eight compounds are clearly detectable at 45 ppb.

Natural gas is a much more challenging matrix because of the high concentrations of several hydrocarbons. These interferences extend out into the retention time range of the sulfur compounds.

Figure 5 shows the chromatograms from the eight-component sulfur standard diluted with sulfur free natural gas to 45 ppb (v/v) each component. There are more peaks evident in these chromatograms than just the eight sulfur compounds. The additional peaks are interference responses from the large hydrocarbons in the natural gas.

In the DB-1 chromatogram, H_2S is clear but COS is lost to a severe overlap with a large C_3 peak. Ethyl mercaptan is also overlapped with n-pentane. On the GS-GasPro column, however, only the H_2S is occluded by interference. The COS and EtSH are free from interferences. With the dual-column approach, all eight compounds can be measured down to 45 ppb.

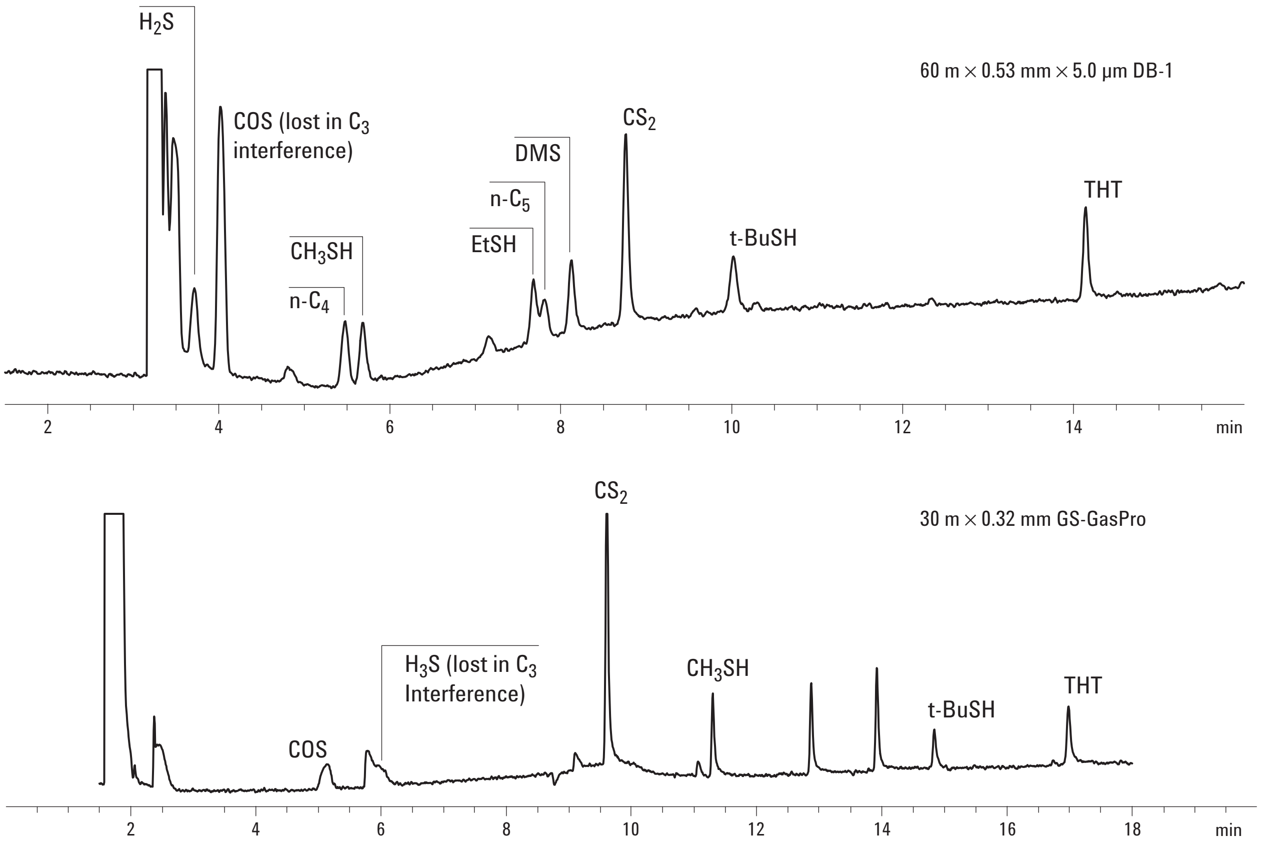

Figure 5. Natural gas blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 0.5:1.

Propylene monomer offers another interesting challenge. The huge C_3 peaks interfere with both the H_2S and COS on both columns used above. To address this, longer versions of the same columns were used (Table 1). The oven temperature and split ratio are also modified (see Experimental on page 2) to improve resolution of the H_2S and COS from the C_3s.

Figure 6 shows the chromatograms from the eight-component sulfur standard diluted with polymer-grade propylene to 45 ppb (v/v) each component. By using longer DB-1 and GS-GasPro columns, lower oven temperature, and a higher split ratio, the H_2S and COS can be measured with somewhat poorer detection limits.

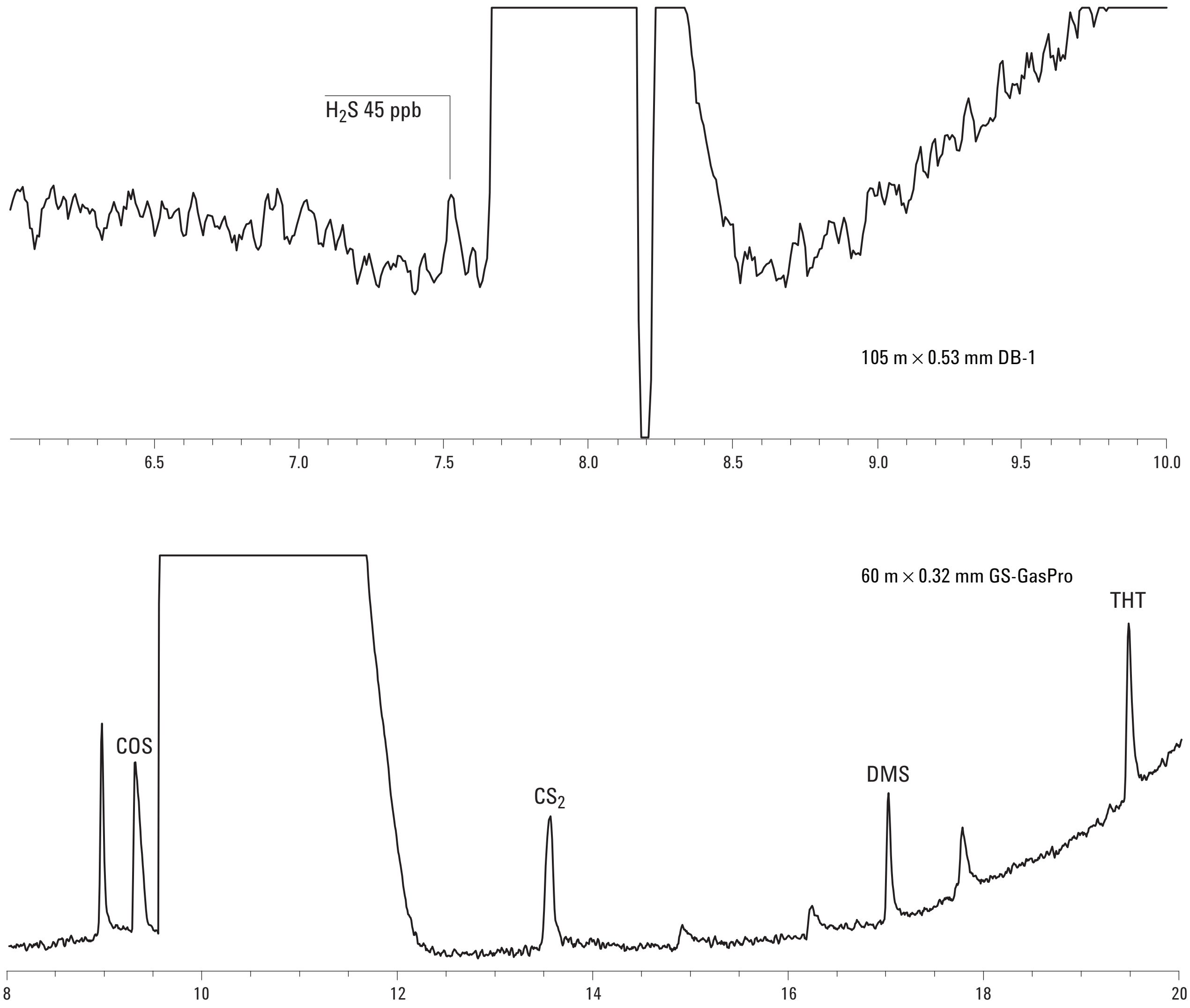

Figure 6. Polymer-grade propylene blend containing 45 ppb (v/v) each of the eight sulfur compounds. Split ratio is 2:1. Top chromatogram: 105 m × 530 µm DB-1 showing only H_2S, bottom: 60 m GS-GasPro.

Cryogenic oven temperatures were evaluated to see if the separation of H_2S and COS could be improved enough to allow use of the more sensitive 0.5:1 split ratio. The oven program tested was: -35 °C for 7 min, 20 °C/min to 300 °C, hold for 5 min. The separation was improved enough to allow the analysis of H_2S on the DB-1 column with the 0.5:1 split ratio, but COS was still occluded by the C_3s on the GS-GasPro. A DB-1 chromatogram illustrating the increased separation between H_2S and propylene is given in Figure 7.

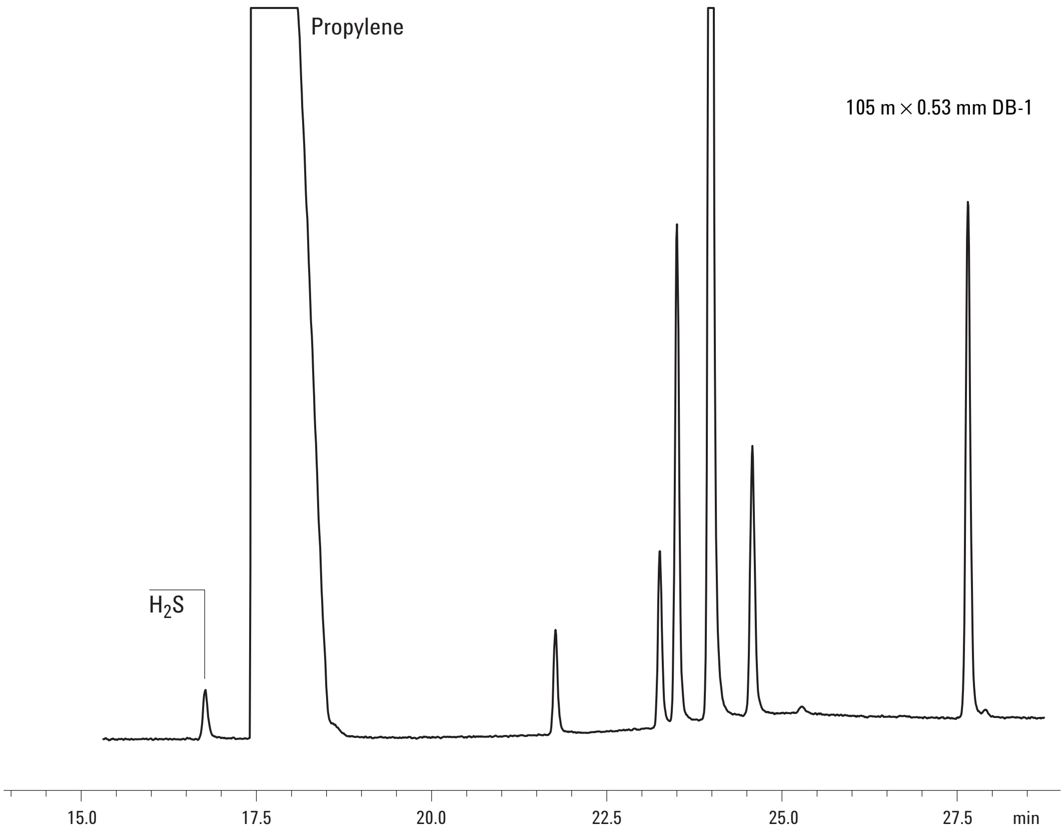

Figure 7. **Use of cryogenic oven temperatures for analysis of H_2S (400 ppb) in propylene at 0.5:1 split.**

Phosphorus and Arsenic on the Same System

One interesting characteristic of the modified FPD is that the filter used also passes the emissions for phosphorus and arsenic. This means that the same detectors can also be used to measure arsine and phosphine in polymer grade ethylene and propylene. A change of detector gas flows to that optimum for each element, followed by a rerun of the sample is all that is required. Since the 6890N detector flows are controlled by EPC, these reruns can be automated.

Figure 8 shows the chromatograms from an arsine and phosphine standard (DCG Partnership) diluted with polymer grade propylene to 36 ppb (v/v) each component. These are run under the same chromatographic conditions as in Figure 6, except that the FPD detector flows are set to those listed for phosphorus detection and the split ratio is back to 0.5:1. The detection limit under these conditions for phosphine in helium is under 5 ppb. If the detector flows are set to those listed for arsenic detection, the detection limit for arsine is about 60 ppb measured in helium. This system is well suited for gas analysis, however it is not really applicable to pesticide analysis due to the lack of selectivity between sulfur, phosphorus, and arsenic.

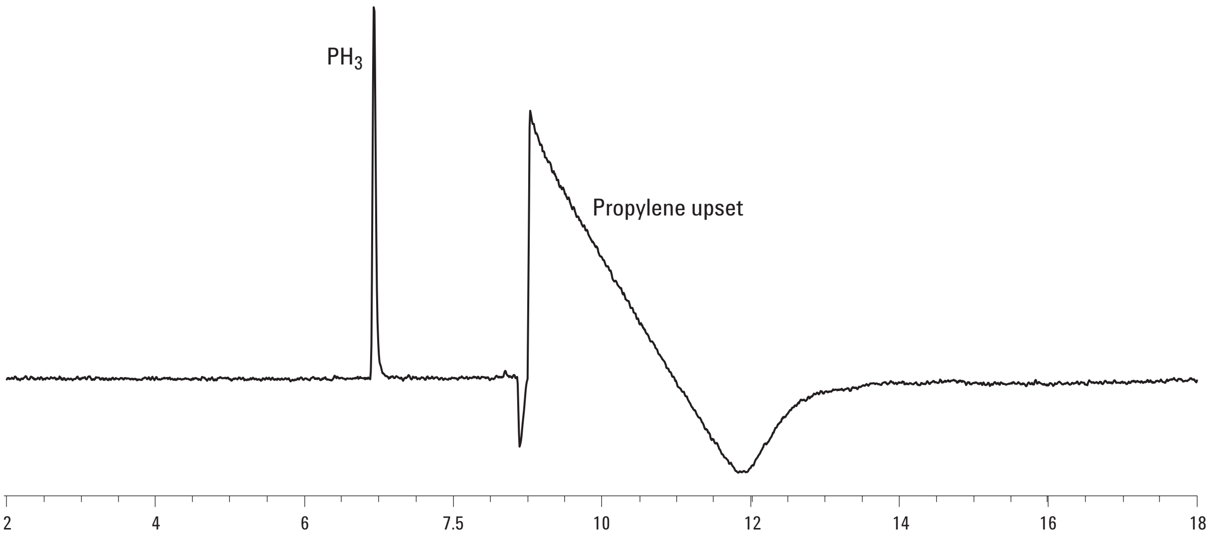

Figure 8. **Polymer-grade propylene blend containing 36 ppb (v/v) each of arsine and phosphine. Split ratio is 0.5:1. Note longer 105 m DB-1 columns are used.**

An example of arsine detection in propylene is shown in Figure 9.

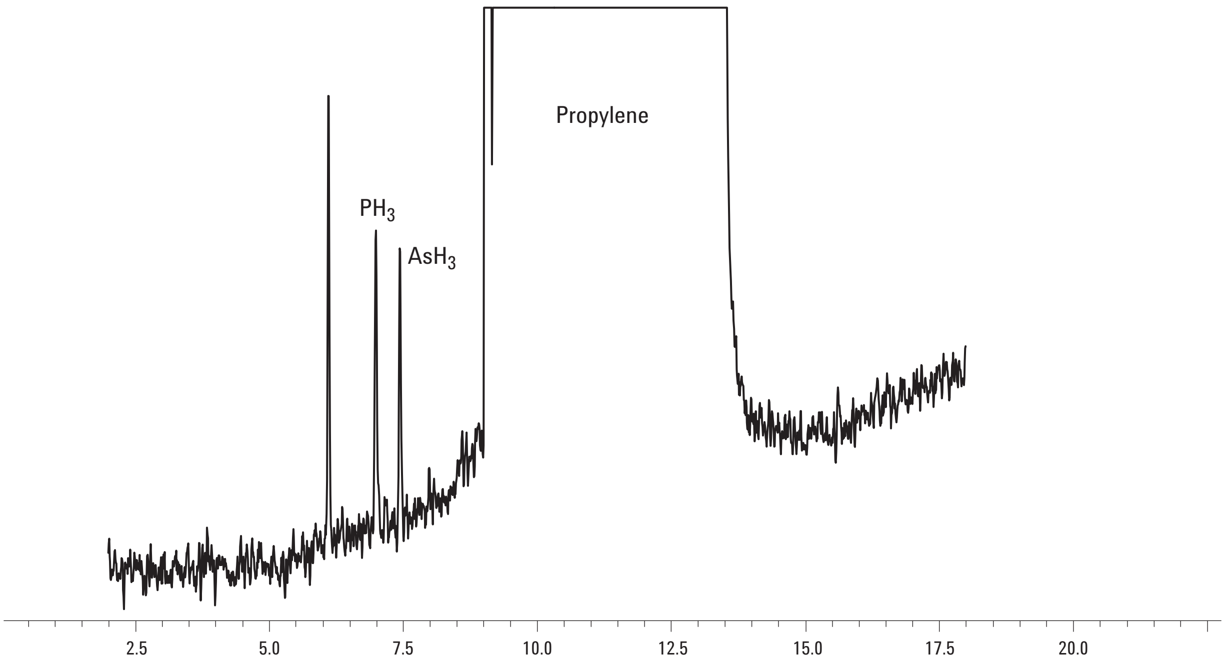

Figure 9. **Arsine optimized FPD flows. H_2: 50 mL/min, air: 150 mL/min. 60 m × 0.32 mm GS-GasPro, 0.5 to 1 split. 90 ppb each of AsH_3 and PH_3.**

How to Order and Configure a Dual-Channel FPD System

The Dual-Channel FPD System, including columns and valves, can be ordered as a special (SP-1) option on any new Agilent 6890N GC. This special also includes the enhanced performance FPD. Contact your local Agilent representative for more information.

Learn more about low-level sulfur detection from these application notes available from any Agilent sales office or Agilent's Web site at www.agilent.com/chem. Just click "Library" in the menu listing, and type "sulfur" in the keyword field.

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