O·I·Analytical

Application Note 16570301

Description of a New GC System with a Pulsed Flame Photometric Detector for Analysis of Volatile Sulfur Compounds in Process Gas Streams

Keywords
GC System
Permeation Tube Oven
PFPD
Process Gas Stream
S-PRO 3200
Sulfur

Introduction

Recently, demand for a fast, reliable, and accurate "turnkey" GC system that will analyze sulfur-containing compounds in process gas streams has been on the rise. Analysis of hydrogen sulfide, carbon disulfide, and carbonyl sulfide plus other volatile sulfur-containing compounds in process gas streams is a critical quality control step in a variety of industries ranging from petrochemical to carbonated beverage. Failure to quickly detect and accurately quantify an "event" can lead to disastrous results and could easily cost millions of dollars in contaminated product and production downtime. A new turnkey GC system using the pulsed flame photometric detector (PFPD) is described. Data demonstrating instrument reproducibility, reliability, linearity, and speed of analysis are also presented.

S-PRO 3200 System Description

The OI Analytical S-PRO 3200 Series GC System incorporates integrated calibration capability, automated sample introduction, and compound quantitation (to ppb levels) on an integrated Agilent 6890 platform. The system consists of an Agilent 6890 gas chromatograph (GC) and a built-in permeation tube oven with Aux EPC control. Sample introduction is through an OI Volatiles Interface with a split/splitless injector and an EPC module coupled to an air-actuated dual valve system in a heated valve box. The entire sample pathway is Sulfinert™ coated and can accommodate 25 to 500-µL gas-sampling loops or liquid sample loops. An Agilent GS-GasPro® column is used to chromatographically separate the individual volatile sulfur compounds for detection and quantitation on the OI Analytical Model 5380 PFPD. The low-maintenance PFPD employs an OIM EPC flow module to control all gases to the detector and has the capacity to output signals to two analog input boards simultaneously. The S-PRO 3200 System features include the following:

- Completely automated sample injection, calibration, and QA/QC check samples
  - No need for unstable, expensive sulfur gas standards
- OI Volatiles Interface provides low-volume split or splitless injection
  - Split injection provides wide dynamic range capabilities
- Entire sample pathway is Sulfinert treated
  - Minimal absorption surfaces

Presented at the 2001 Pittsburgh
Conference on Analytical Chemistry
and Applied Spectroscopy
New Orleans, LA
March 4–9, 2001

- Integrated Permeation Tube Oven with EPC Flow Control
    - Single or multiple calibration compounds
    - Automated multiconcentration capabilities
    - No benchspace required

- PFPD stability, sensitivity, selectivity, and equimolar sulfur response
    - Long-term stable performance with minimal maintenance
    - Ease-of-calibration

- Linear or quadratic calibrations

- Multi-element capability
    - PFPD can detect 28 different elements

- Single digit ppb sensitivity for sulfur analysis

- Full EPC control of all injector, permeation oven, and detector gases

- Alternative detector options available for other applications

Permeation Tube Oven

The OI Analytical Permeation Tube Oven can accommodate four or more permeation devices and allows for automated calibration and sequenced introduction of QA/QC check standards. Temperature stability of the oven is ±0.05°C, and gas flow through the oven is controlled by the Agilent 6890 Aux EPC flow control module. Figure 1 shows a photograph of the Permeation Tube Oven mounted on an Agilent 6890 GC.

Figure 2 illustrates the operation of a permeation tube and the Permeation Tube Oven. The neat sulfur compound (e.g., COS, MeSH) is packaged in a permeable Teflon® tube and diffuses across the Teflon barrier at a constant rate and temperature. A controlled gas flow is passed through the oven and across the permeation tube, and a known, constant concentration of compound in the gas is generated. Figure 3 is a chart illustrating the stability of the OI Analytical Permeation Tube Oven over approximately a two-month period.

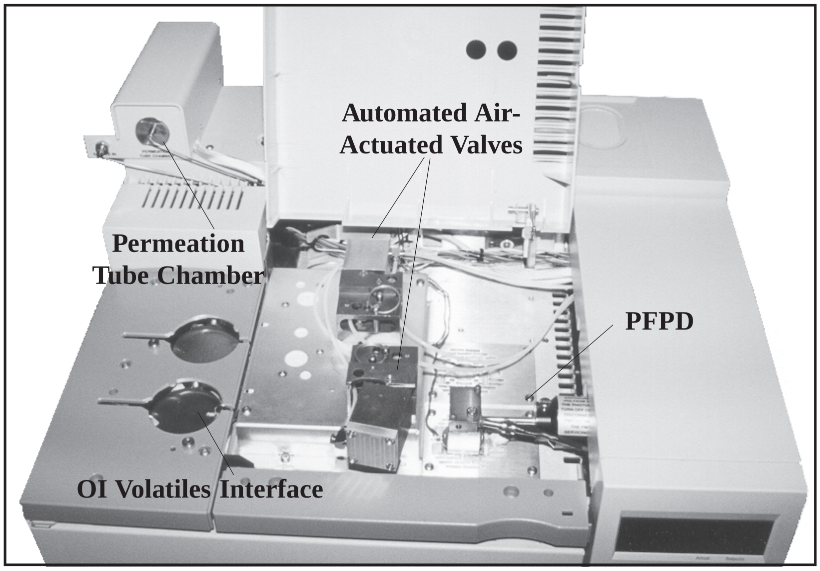

Figure 1. Key Components of the OI Analytical S-PRO 3200 GC System

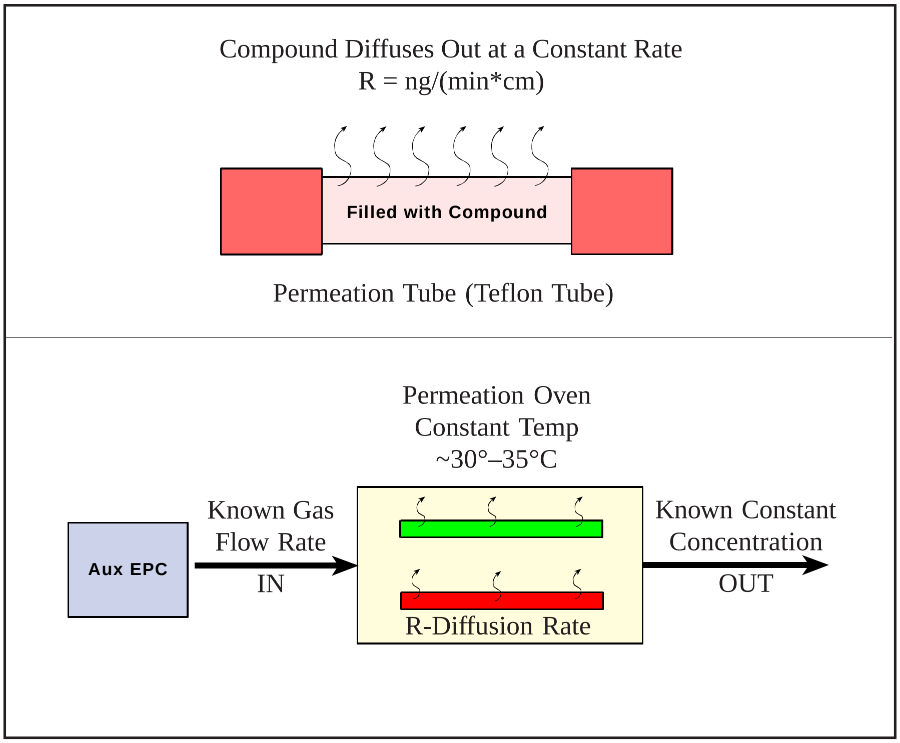

Figure 2. Operation of a Permeation Tube and the Permeation Tube Oven

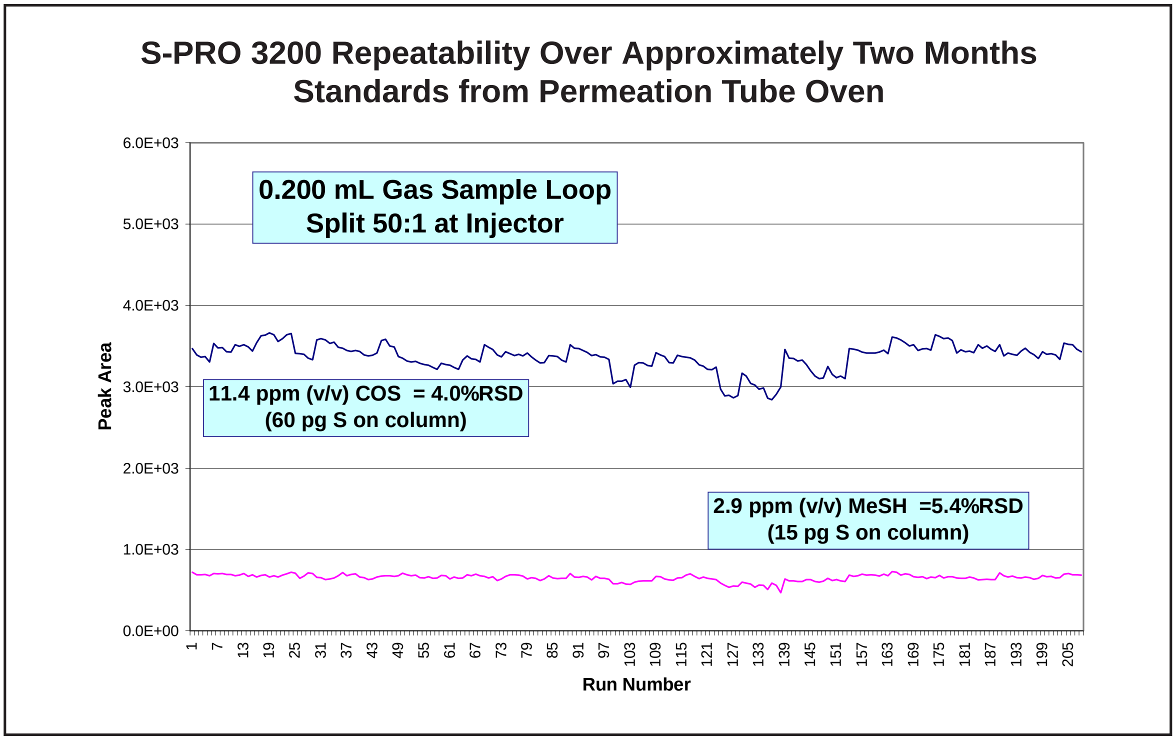

Figure 3. Repeatability of COS and MeSH as Introduced by the S-PRO 3200 Permeation Tube Oven Over a Two-Month Period

OI Volatiles Interface

The OI Volatiles Interface is designed specifically for introducing low-concentration gas samples at either splitless or reduced split flows from gas sampling valves. All surfaces in the sample pathway and the low-volume interface block are Sulfinert treated, and column installation is done easily and quickly from inside the GC oven. Figure 4 is a cut-away diagram of the OI Volatiles Interface.

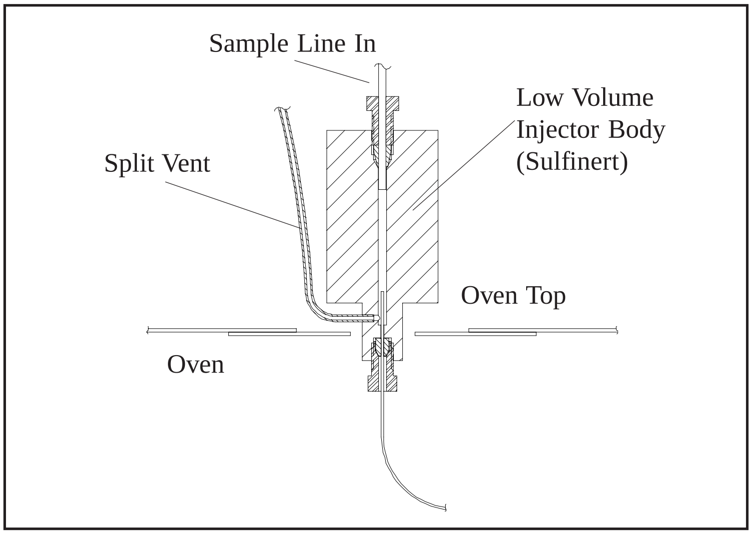

Figure 4. Diagram of the OI Volatiles Interface Illustrating Quick and Easy Column Installation From the GC Oven

Automated Dual Valve System

The automated dual valve system consists of a pair of air-actuated selection valves, the associated Sulfinert-treated sample lines, and a gas or liquid sampling loop. The first valve is a four-port switching valve that allows the user to select between two sample sources, either the permeation tube oven for calibration and check standards or a user specified sample stream. The second valve is a six-port switching valve with a gas or liquid sample loop and a transfer line to the OI Volatiles Interface. With this valve in the “Load” position, the gas sample stream is allowed to flow continuously through the sample loop, assuring a constant supply of fresh sample until the time of injection. When switched to the “Inject” position the sample loop is placed in line with the GC carrier gas flow, and the sample is quickly transferred from the loop to the OI Volatiles Interface. Figure 5 is a photograph of the dual valve system with the air actuators removed. Figure 6 shows flow diagrams illustrating the GC carrier gas, the permeation tube oven, and sample flow paths during the “Load” and “Inject” stages (from the permeation oven).

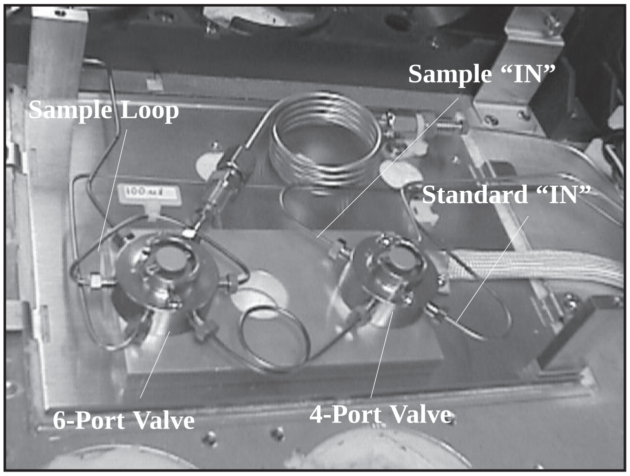

Figure 5. Photograph of the S-PRO 3200 Automated Dual Valve Systems with Covers and Actuators Removed to Show Detail. Sample Loops are Available in 25-µL, 50-µL, 100-µL, 200-µL, and 500-µL Sizes.

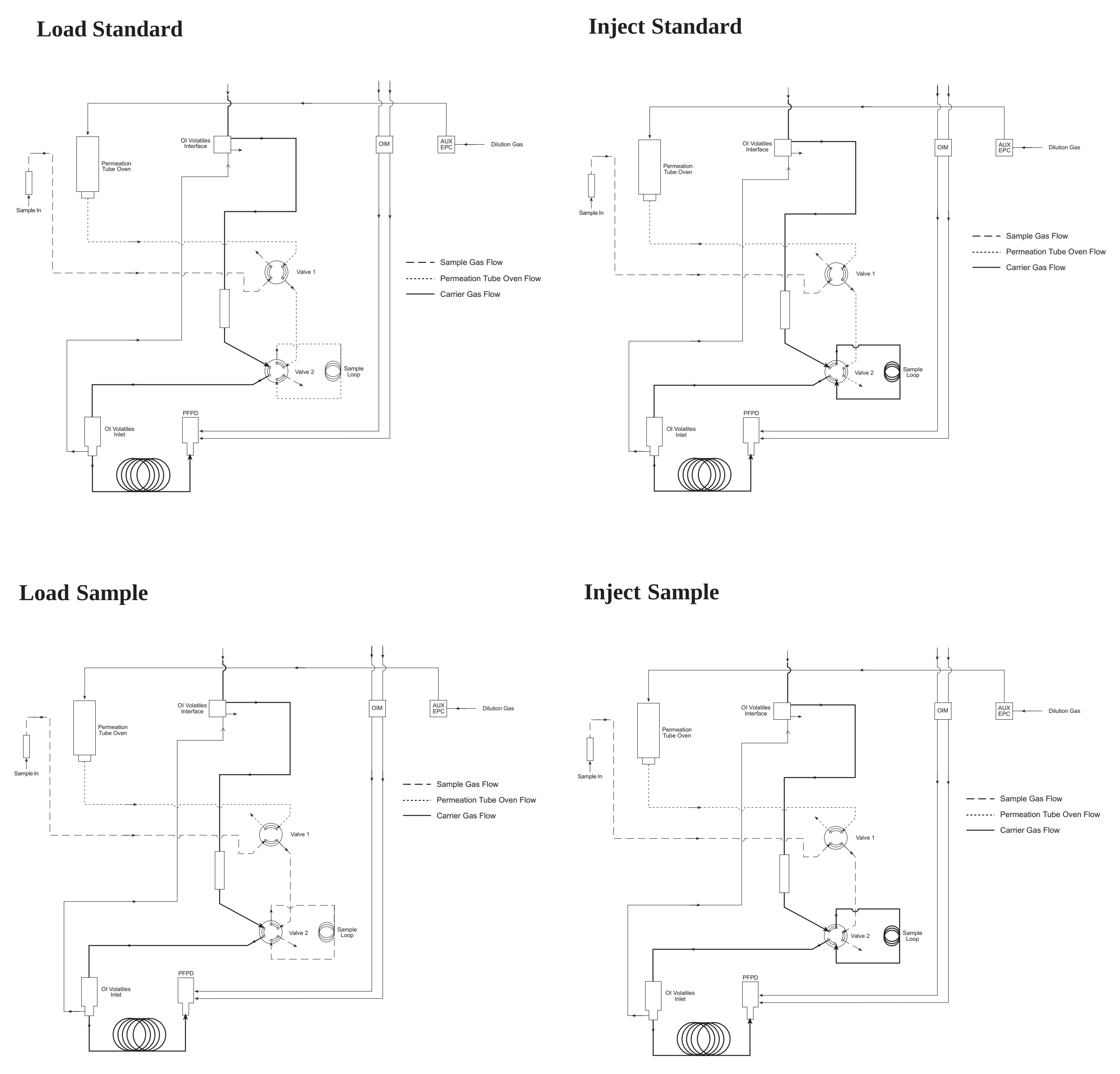

Figure 6. Flow Diagrams of the GC Carrier Gas, the Permeation Tube Oven Gas, and the Sample Gas Pathway During “Load” and “Inject”

Pulsed Flame Photometric Detector (PFPD)

The sulfur specific PFPD is an ideal choice for lab or at-line analytical systems because it can operate almost indefinitely with little or no maintenance or repair. The PFPD reduces the problems associated with other detectors used to determine speciated sulfur in process streams. The PFPD uses a hydrogen and air mixture at a flow rate that does not support continuous combustion. The combustor is filled with an ignitable gas mixture, the flame is ignited, the flame propagates through the combustor, and it burns out when all the fuel is consumed. (See Figure 7.) The cycle is repeated continuously at a rate of 3–4 hertz. As a result of this pulsing of the flame, the PFPD adds a time dimension to the emission analysis in addition to the wavelength selectivity in a conventional FPD. By analyzing a specific time slice of the emitted light, the selectivity of the detector is significantly enhanced. Furthermore, since the time separation of the emissions adds selectivity, wider band-pass filters can be used, permitting more light to be detected and resulting in an increased sensitivity for the PFPD vs. the FPD.

Other selective or nonselective detectors can be easily incorporated into the S-PRO 3200 design to detect and quantify other target compound groups. A halogen specific detector (XSD™) or electrolytic conductivity detector (ELCD) can be substituted for the analysis of halogenated species, or a PID/FID tandem detector can be added to detect aromatic and hydrocarbon compounds.

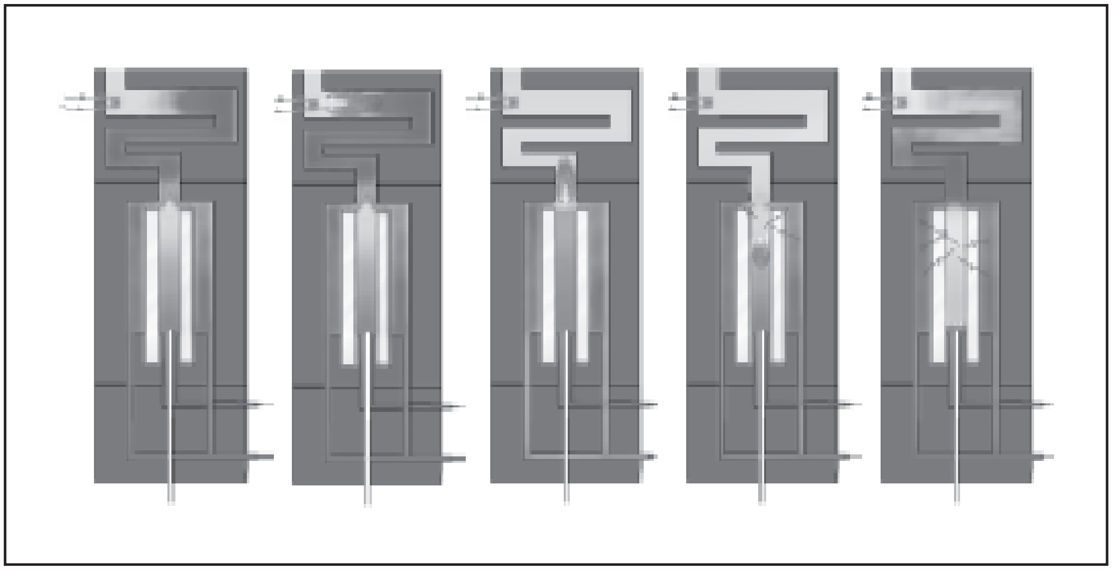

Figure 7. PFPD Phase Cycle of the Propagating Flame

Application: Sulfur in CO_2 Process Streams

The presence of sulfur compounds in CO_2 used in the production of carbonated beverages can have a considerable detrimental effect on the flavor and fragrance of the final product. Even very low concentrations of sulfur compounds can greatly affect the quality of the soft drinks, and because their presence is noticeable even at very low, sub-ppm levels, accurate detection and quantitation is an important manufacturing quality control step. For this study, the S-PRO 3200 System was used to determine the concentration of sulfur compounds in beverage grade CO_2. A description of the experiment conditions and a brief discussion of the analytical results are shown in Tables 1 and 2, and Figures 8 and 9.

Table 1. Description of Sample Used to Test Repeatablility and Calibration of the S-PRO 3200 System

Sample Description
• Two sulfur compounds in CO_2:SO_2 and MeSH • 500-µL gas sample loop, split 20:1 at injector • Permeation chamber at 30°C • Concentrations were varied by changing the permeation flow rate • All concentrations reported as ppb sulfur (ppbS) to the detector • Sulfur concentrations in CO_2 prior to split; SO_2 – 2.3 ppm, MeSH – 260 ppb • Column: GS-GasPro® 30 m x 0.32 mm I.D., Isothermal at 150°C

Table 2. S-PRO 3200 Repeatablity of SO_2 and MeSH in a CO_2 Matrix Using a 500-µL Gas Sample Loop and a 20:1 Split Ratio. Concentrations of the Two Compounds were Varied by Changing the Gas Flow Rate Through the Permeation Tube Chamber.

SO_2 in CO_2		**MeSH in CO_2**	
Concentration (ppbS)	**%RSD (n=10)**	**Concentration (ppbS)**	**%RSD (n=10)**
112.0	0.99	12.4	2.71
216.8	1.54	24.1	2.35
432.8	1.88	48.2	2.59
775.4	1.02	86.4	0.88

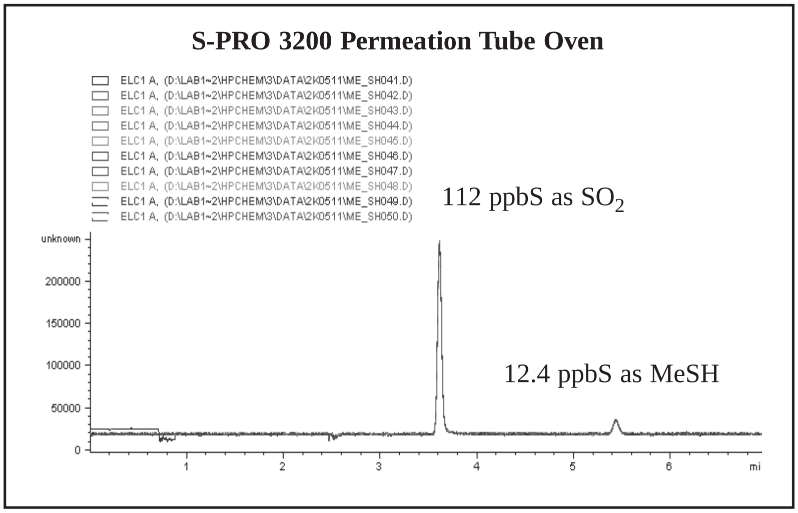

Figure 8. Repeatability of Sulfur Compounds in CO_2. Overlaid Chromatograms of 10 Replicate Analyses of SO_2 and MeSH in a CO_2 Matrix Using a 500-µL Gas Sample Loop and a 20:1 Split Ratio. (Concentrations Reported as ppbS On-Column)

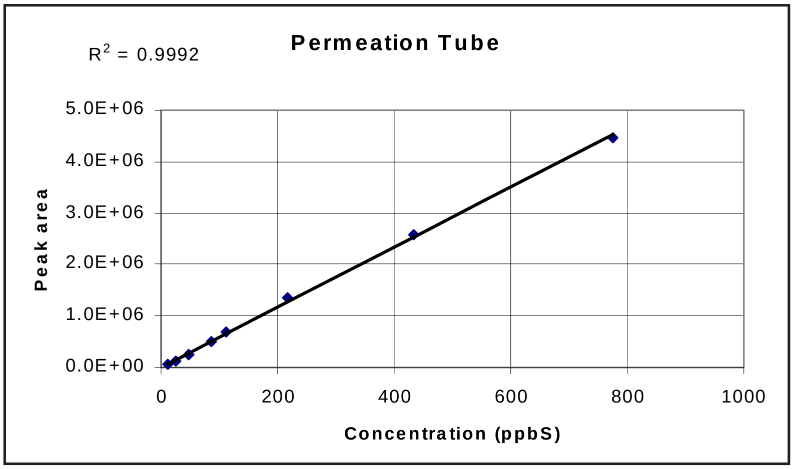

Figure 9. S-PRO 3200 Calibration Curve for Sulfur Compounds in CO_2 Generated Using a 500-µL Gas Sample Loop and a 20:1 Split Ratio. Concentration of Sulfur Ranged From 12.4 to 775.4 ppbS. Data were Acquired in the Linear Mode of the PFPD with an R^2 value of 0.9992.

Application: Sulfur in Propylene/Ethylene Feedstocks

Excessive sulfur in petrochemical process streams can corrode equipment, inhibit or destroy catalyst beds, and produce undesirable odors. Purity of ethylene and propylene feedstock is especially critical in the polymer industry because sulfur contaminants can destroy catalyst beds and alter the properties of the final polymer products. Figure 10 is a PFPD chromatogram from the analysis of a feedstock gas sample before separating the propylene and ethylene components and before any sulfur scrubbing. The large peak in the sulfur chromatogram at approximately 10 minutes is the COS contaminant. Note that the presence of high concentration hydrocarbons does not interfere with the sulfur selectivity. Figure 11 is a chromatogram of a propylene standard containing 13 light sulfur compounds at 1 ppm (w/v). The sample was supplied in a pressurized gas tank (DCB Partnership 1, Ltd., Pearland, TX) and introduced to the S-PRO 3200 via a regulator and Sulfinert-treated sample transfer line. The liquid propylene was converted to a gas prior to reaching the GC Sysem. Figure 12 is an expanded view of the sulfur and carbon channels illustrating chromatographic resolution of the H_2S, propane, and propylene. The chromatogram was acquired with a 200-µL gas sample loop and a 5:1 split ratio at the OI Volatiles Interface. Figure 13 illustrates repeatability of analysis of this sample stream over a two-month period.

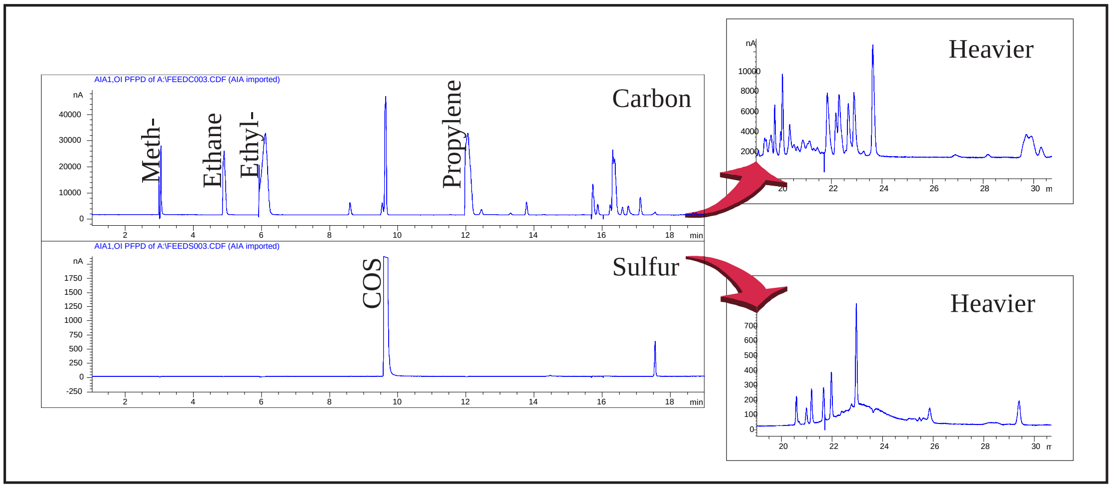

Figure 10. Chromatograms of a Feedstock Gas Before Separation of the Propylene and Ethylene Components and Before any Sulfur Scrubbing

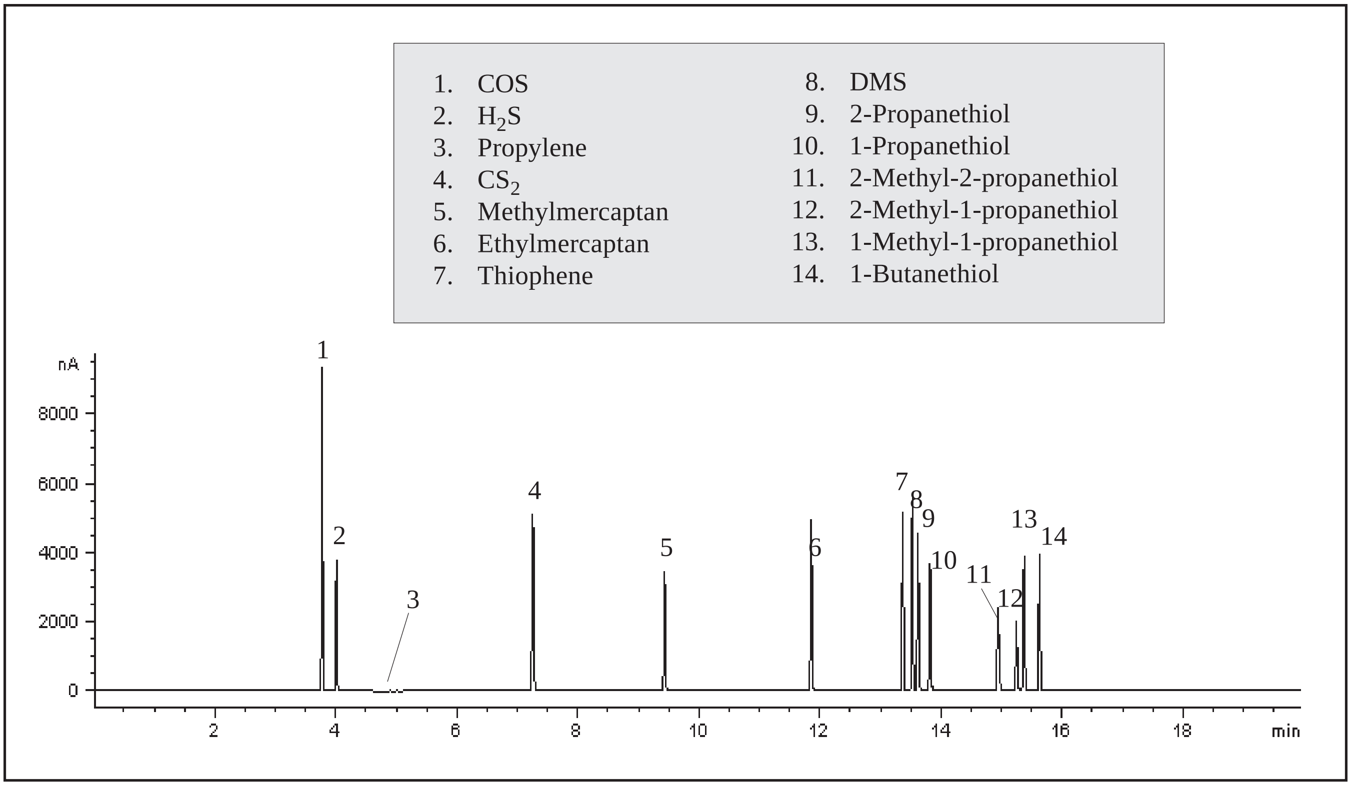

Figure 11 Thirteen Light Sulfur Compounds in a Propylene Standard on the S-PRO 3200 (1 ppm, 200-µL Gas Sample Loop, 5:1 Split Ratio) Using a GS-GasPro Column (30 m x 0.32 mm I.D.) and a Ramped GC Oven Program

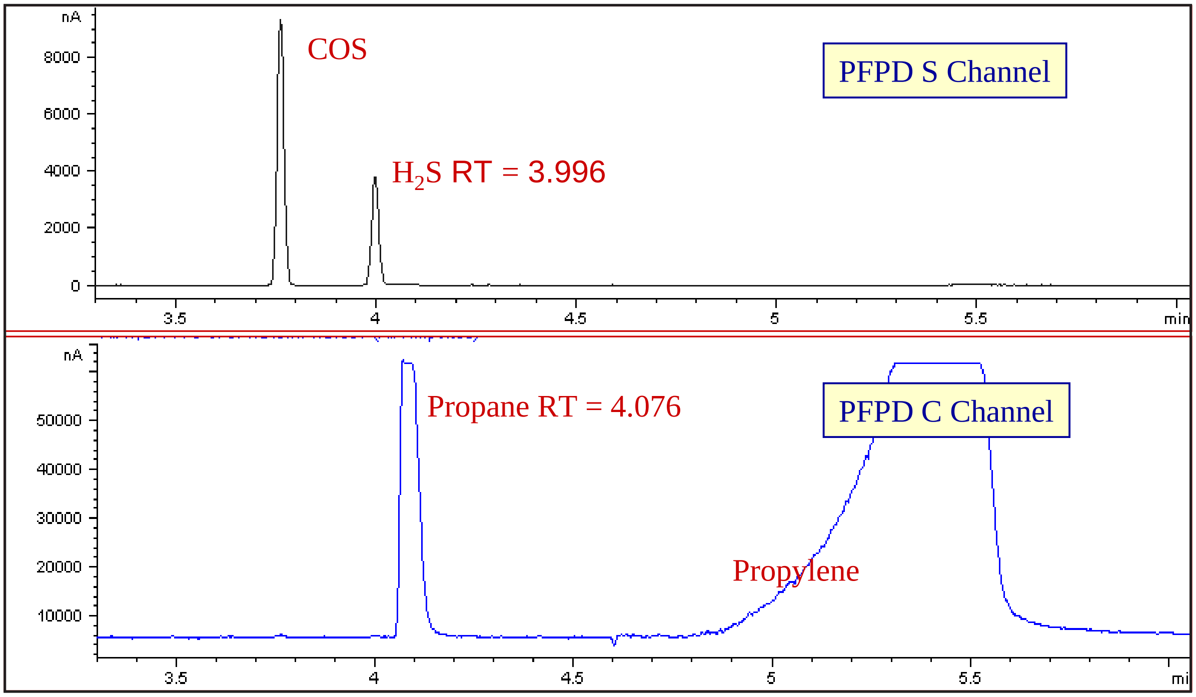

Figure 12. Separation of H_2S and Propane

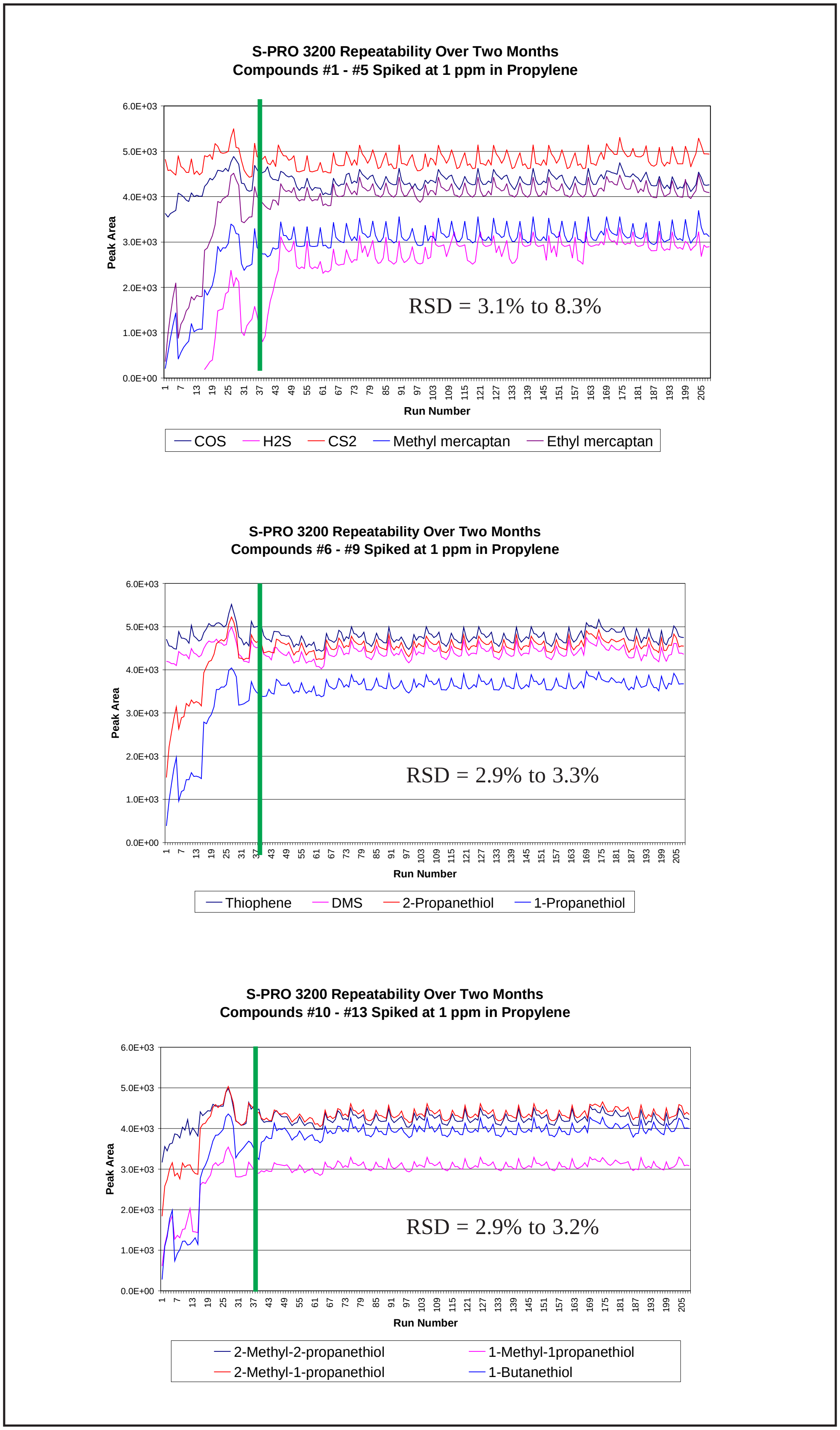

Figure 13 S-PRO 3200 Repeatability of 13 Light Sulfur Compounds in a Propylene Standard Over a Two-Month Period (1 ppm (w/v), 200-µL Gas Sample Loop, 5:1 Split Ratio). The Vertical Line Represents the Point in Time When the Gas Flow from the Sample Tank was Allowed to Stabilize at ~10 mL/min.

Five replicate aliquots of the gas sample were analyzed twice a day over approximately a two-month period. The first gas sample from each series of five had a slightly higher response than the four subsequent analyses by about 1–3%. Introduction of an identical sequence of standards from the permeation oven over the same time period did not follow the same “spike” pattern, as illustrated in Figure 3. It was not obvious what caused the spike pattern when run from the sample tank. However, since it was not observed with the permeation oven series, it was likely introduced by the tank sampling apparatus prior to the S-PRO 3200. The initial instability in the system, especially for highly reactive compounds like H_2S, was caused by opening and closing of the LPG sample tank valve for sampling twice each day. Once the valve was left open and the sample gas flow was allowed to stabilize and remain constant at ~10 mL/min, %RSD for detector response was improved significantly and 3.6% or better for most compounds (see Table 3).

Table 3. Long-term Stability of the S-PRO 3200 Measuring Sulfur Compounds in Propylene

Compound	**pgS on Column**	**Response %RSD (n=173)**
COS	33.6	3.1
H_2S	30.9	8.3
CS_2	69.1	3.6
Methylmercaptan	33.6	5.8
Ethylmercaptan	34.5	3.6
Thiophene	34.6	3.0
DMS	34.5	3.2
2-Propanethiol	34.6	2.9
1-Propanthiol	33.9	3.3
2-Methyl-2-propanethiol	34.6	3.0
2-Methyl-1-propanethiol	32.0	3.1
1-Methyl-1-propanethiol	33.6	2.9
1-Butanethiol	33.6	3.2

Conclusion

The OI Analytical S-PRO 3200 Series GC System is a single-vendor turnkey solution for the analysis of volatile sulfur compounds in process gas streams. It is an exceptionally stable and dependable system that improves accuracy and repeatability, and requires little or no maintenance. The PFPD’s high sensitivity permits reliable analysis of sulfur down to the single digit ppb level. The integrated Permeation Tube Oven eliminates the need to purchase expensive and unstable low-level sulfur standards. The PFPD is known for its selective, equimolar sulfur response allowing calibration and quantitation using as few as one or two compounds. The extreme sulfur selectivity allows the PFPD to be used where hydrocarbon background may cause interference. By configuring the detector for other elements (e.g., P, As, N, Ge) or for dual element capabilities, additional applications can be performed using the system

GC-GasPro is a registered trademark of J&W Scientific.
Sulfinert is a trademark of Restek Corporation.
Teflon is a registered trademark of E.I. du Pont de Nemours.

O·I·Analytical

P.O. Box 9010
College Station, Texas 77842-9010
Tel: (979) 690-1711 • FAX: (979) 690-0440 • www.oico.com