

Initial Experiences from the Field with the OI Analytical S-PRO 3200 Series GC System

Application Note 17620302

Keywords

COS
Gas Chromatography
GC System
H₂S
PFPD
Propane
Pulsed Flame Photometric
Detector
S-PRO 3200
Sulfur

Introduction

The OI Analytical S-PRO 3200 Series GC System is a complete solution for the analysis of speciated volatile sulfur compounds in gas phase matrices. It is an exceptionally stable and dependable system that requires little or no maintenance. Initial experiences from field installations of the S-PRO 3200 are promising and demonstrate that the extreme sulfur selectivity of the Pulsed Flame Photometric Detector (PFPD) allows it to be used where hydrocarbon background or other factors may otherwise be expected to cause interference. The detector's high sensitivity permits ppbv analysis of most sulfur-containing compounds.

This application note illustrates how the S-PRO 3200 can be applied to a variety of different industry uses, discusses proper column selection for a specific petrochemical application, and describes two different calibration techniques. Data from field installations, including linearity, accuracy, and repeatability, show that this new system provides fast, reliable, and accurate results.

Industry Applications

The OI Analytical S-PRO 3200 shown in Figure 1 can be used in any application that requires analysis of speciated volatile sulfur compounds in gas phase matrices and minimum system maintenance. Figures 2 through 6 illustrate the wide range of industry uses for the S-PRO 3200.

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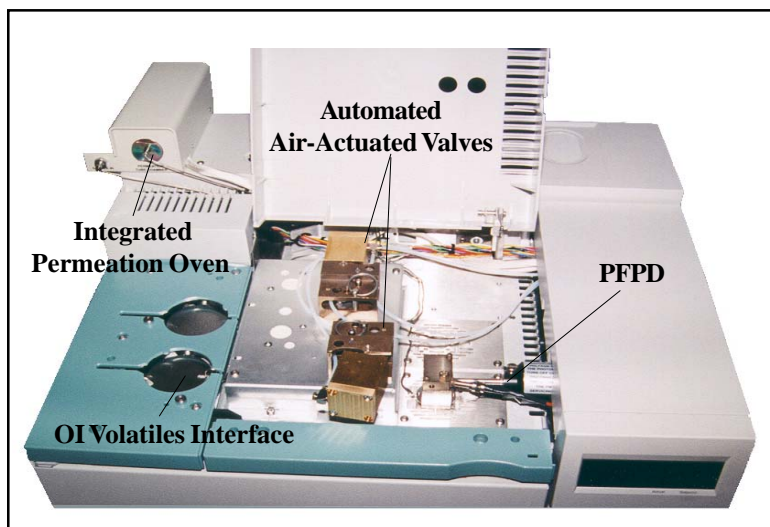


Figure 1. The OI Analytical S-PRO 3200 Series GC System

Figure 2 is a chromatogram of 3.4 ppmv H₂S in natural gas on the S-PRO 3200. The additional unknowns are easily quantified using the equimolar response feature of the PFPD. The bottom chromatogram is the hydrocarbon profile for this natural gas sample. Data were acquired using a 0.5-mL gas sample loop, a 9:1 split ratio, a GS-GasPro[®] column, and a ramped oven program. Calibration of H₂S was simplified with the S-PRO 3200's built-in permeation system. Use of an H₂S permeation device and the system's electronic flow control allow automated calibration and ongoing QA/QC runs to be programmed at user-specified intervals.

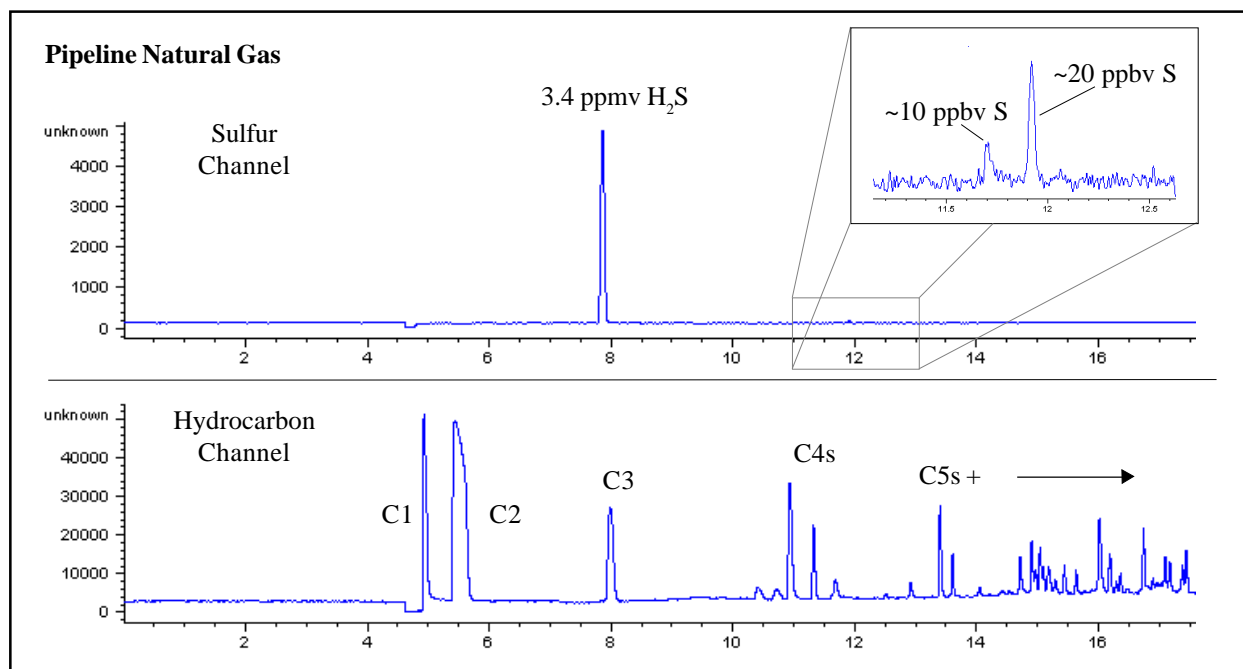


Figure 2. PFPD Chromatogram of 3.4 ppmv H₂S in Natural Gas on the S-PRO 3200

Figure 3 shows the overlaid chromatograms of SO₂ and MeSH standards in beverage grade CO₂. The overlaid chromatograms of 10 replicate analyses in this CO₂ matrix had relative standard deviations (RSDs) of 0.99% for the SO₂ and 2.71% for the MeSH. The S-PRO 3200 routinely provides analytical repeatability of 5% or better. Data were acquired using a 0.5-mL gas sample loop, a 20:1 split ratio, a GS-GasPro column, and an isothermal oven program.

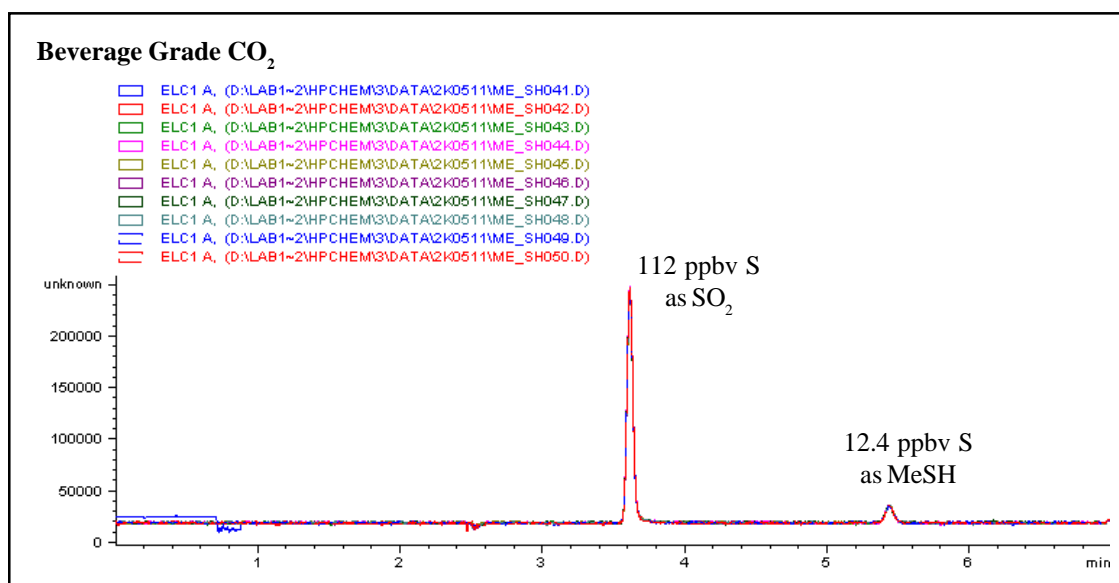


Figure 3. Overlaid PFPD Chromatograms of SO₂ and MeSH Standards in Beverage Grade CO₂

Figure 4 illustrates the detection of ppbv and ppmv levels of sulfur compounds in a fuel cell feedstock. The large peak at approximately 15 minutes is tetrahydrothiophene (THT), an odorant commonly added to natural gas. Detection of trace level sulfur compounds in this complex hydrocarbon matrix was possible because of the PFPD's exceptional selectivity for sulfur in the presence of potential hydrocarbon interferences. Because the PFPD has equimolar response, all of the unknown sulfur compounds can be easily quantified using the response factor from a single calibration compound. Data were acquired using a 1-mL gas sample loop, a 9:1 split ratio, a Supelco HAP-1 column, and a ramped oven program.

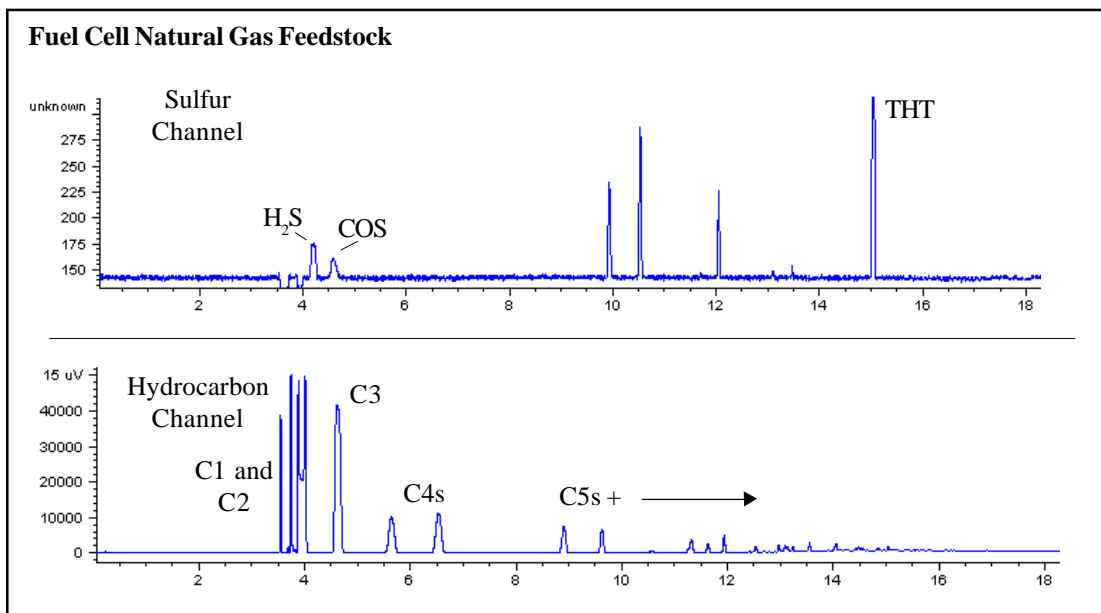


Figure 4. PFPD Chromatogram of ppbv and ppmv Level Sulfur Contaminants in a Fuel Cell Natural Gas Feedstock. THT is the Odorant Commonly Added to Natural Gas at ppmv Levels.

Figure 5 illustrates detection of ~0.2 ppmv COS in a mixture consisting primarily of propane and propylene, with smaller concentrations of methane and ethane. Chromatographic separation of the COS from the propane in the matrix is necessary for proper identification and quantitation. The GS-GasPro column does this well. Several other sulfur compounds were also detected in the mix. Data were acquired with a 0.2-mL gas sample loop, a 5:1 split ratio, a GS-GasPro column, and a ramped oven program.

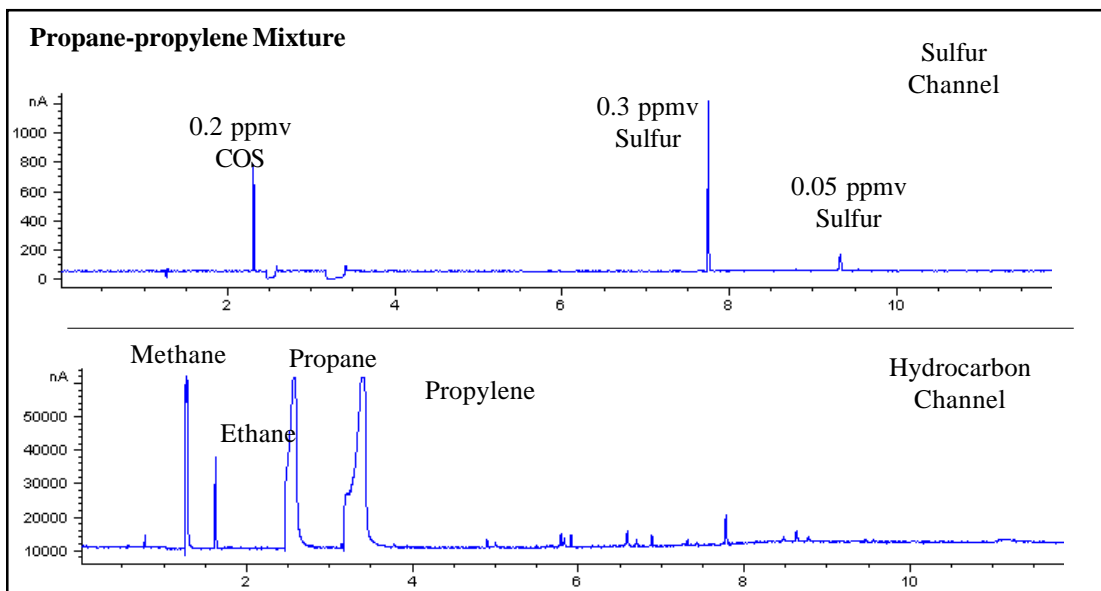


Figure 5. PFPD Chromatogram of COS in a Propane-propylene Mixture

Figure 6 illustrates the detection of low-level sulfur compounds (ppbv) in a stack vent gas at a petrochemical plant. Speciation of the volatile sulfur compounds is possible using the S-PRO 3200. Individual sulfur compounds can be identified by their retention time, and unknowns are quantified by taking advantage of the PFPD's equimolar response feature. Total sulfur concentrations are easily calculated by summing all of the peak areas.

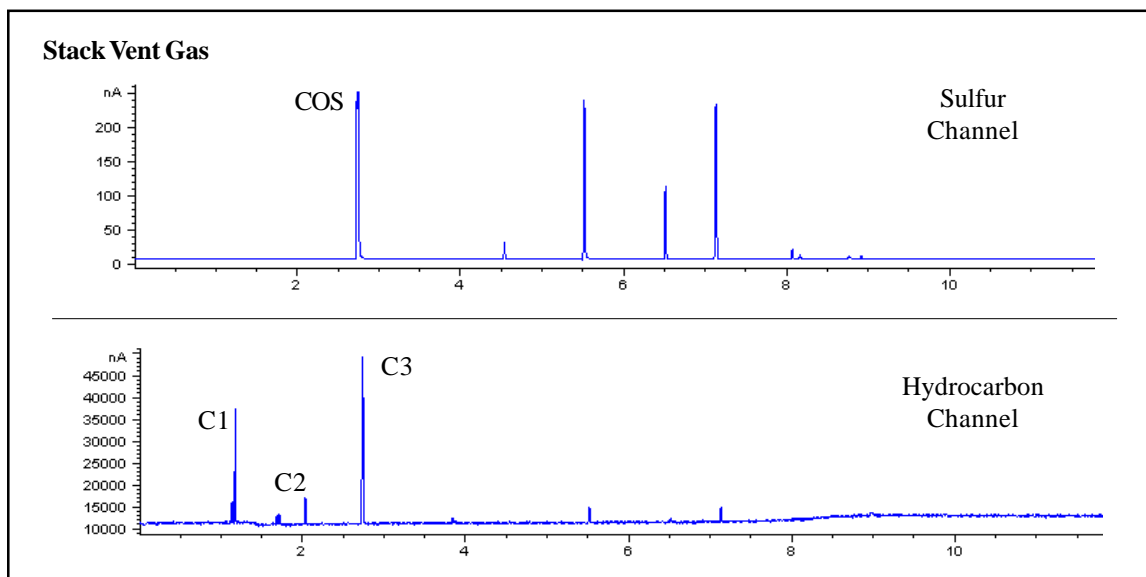


Figure 6. PFPD Chromatogram of Trace Level Sulfur Compounds in a Stack Vent Gas at a Petrochemical Plant

Column Selection for Propane/Propylene Applications

One of the most challenging dilemmas of the S-PRO 3200 fieldwork was finding the right GC column for complete chromatographic separation of COS, H₂S, and propane in propane-propylene mixtures. The propylene portion of the matrix is easily separated from the COS and the H₂S on many types of GC columns. However, it is quite common for either the COS, the H₂S, or both to co-elute with the propane when propane is a majority percentage of the sample matrix. Also, COS and SO₂ typically co-elute on most silicone-based columns.

A variety of different column phases, column combinations, column lengths, and operating conditions were tested to determine if they could provide adequate chromatographic separation of the COS, H₂S, and propane. Only the 60-meter Agilent GS-GasPro column was able to give adequate separation of all three components without the need for a more complex column-switching GC configuration. One drawback to the GS-GasPro column is that it will adsorb H₂S, and even though this may reduce H₂S sensitivity, it has been shown to be extremely reproducible. Peak shape and elution profile for the propane matrix peak is a key consideration for this important application. Figures 7 through 11 demonstrate the effects of several different variables on this critical separation. (In the following chromatograms, note that levels of H₂S varied considerably; it was used to demonstrate retention time (RT) only and not overall quantitation.)

When using the 60-meter GS-GasPro column, complete chromatographic separation of the COS, H₂S, and propane was possible even for C3 mixes that contained up to 97% propane (Figure 7). The H₂S co-elutes with propane on the shorter 30-meter column, making the additional length necessary. The COS RT shifted with increasing concentrations of propane due to a solvent effect on this PLOT column and will be observed on any type of system or detector using this column. Because COS is the only sulfur compound in that portion of the chromatogram, the RT shift does not pose any significant difficulty.

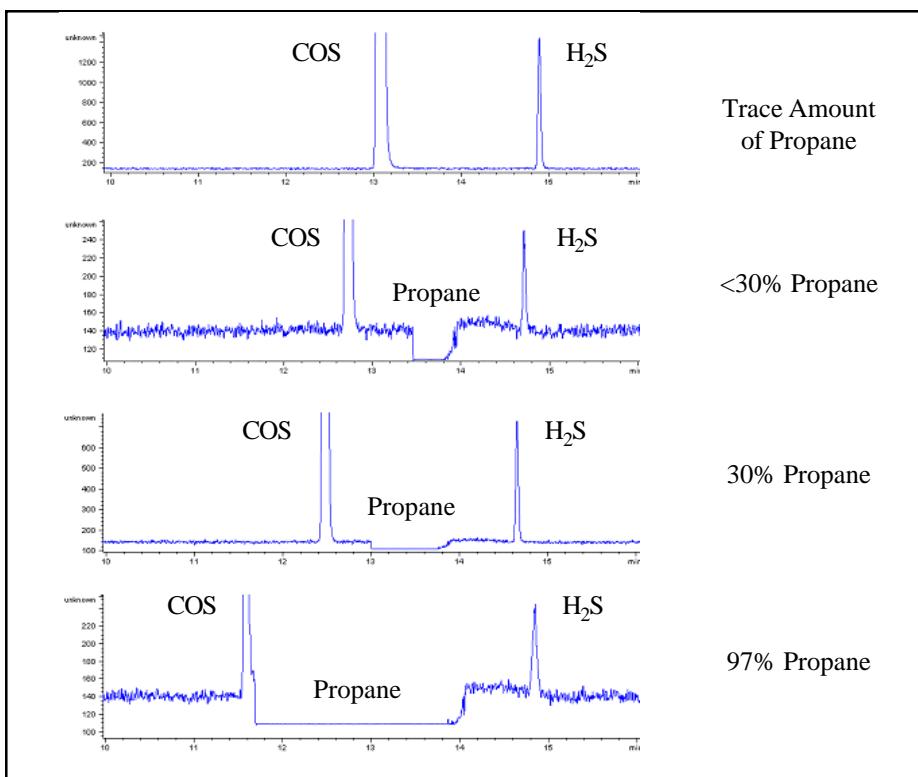


Figure 7. Effects of Propane Concentration on the Separation of COS, H₂S, and Propane (Note: Concentrations of COS and H₂S varied considerably, depending on propane flow rate through the permeation oven and are not intended to be quantitative.)

An increase in initial oven temperature produced shorter overall GC analyses, but the earlier RT for H₂S resulted in co-elution at higher concentrations of propane (Figure 8). Isothermal runs at the cooler oven temperatures were necessary for complete chromatographic separation of H₂S and high concentrations of propane.

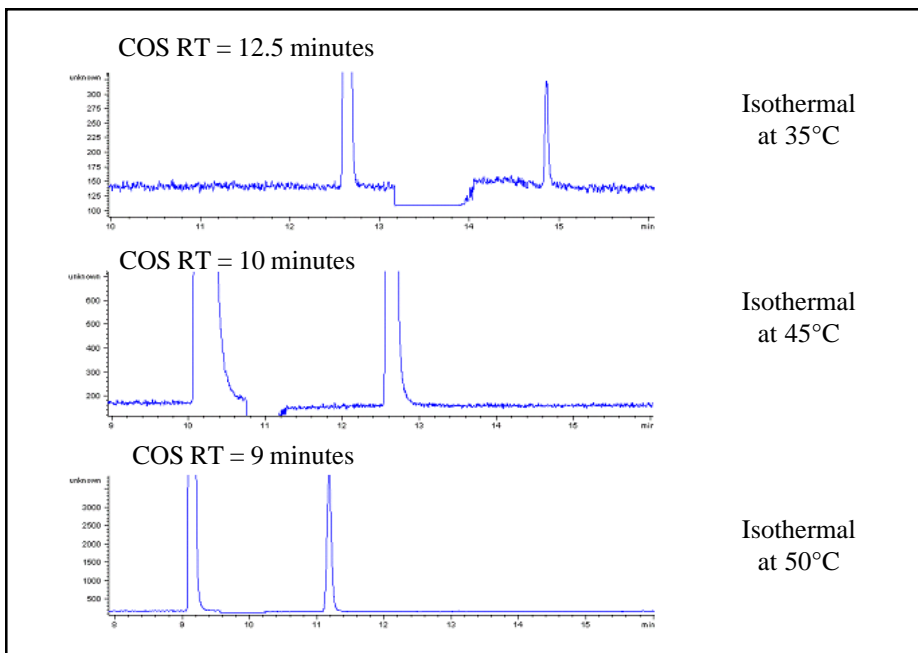


Figure 8. Effects of Oven Temperature on the Separation of COS, H₂S, and Propane (Note: Concentrations of COS and H₂S varied considerably, depending on propane flow rate through the permeation oven and are not intended to be quantitative.)

Split ratios are another key GC parameter to consider for these applications, with reduced sensitivity being the trade-off for higher split ratios. As expected, higher split ratios transferred less propane onto the GC column and resulted in better resolution between the three compounds of interest, as well as a narrower propane peak profile (Figure 9). As seen above, the COS RT is a function of the amount of propane on column.

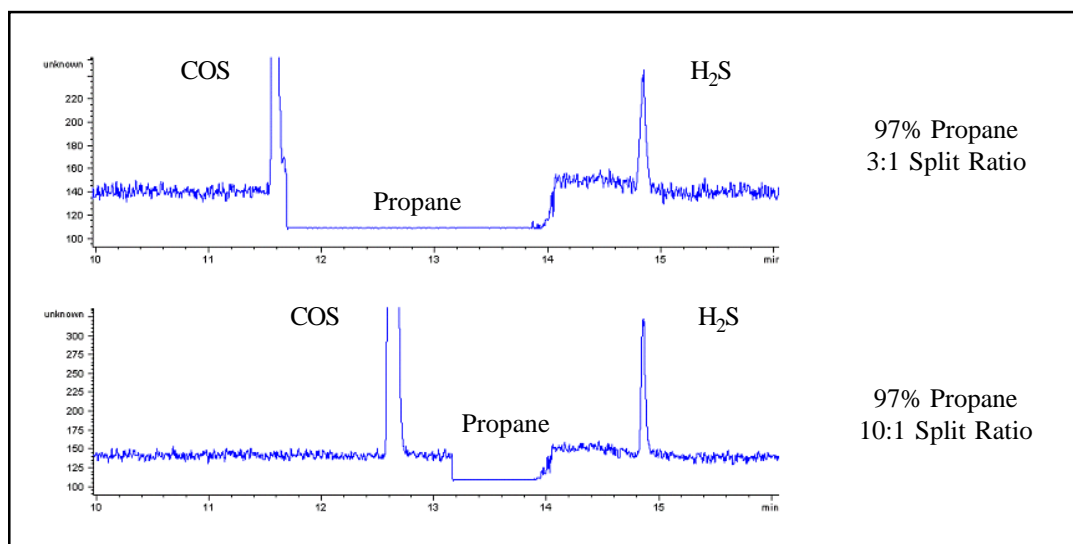


Figure 9. Effects of Split Ratio on the Separation of COS, H₂S, and Propane (Note: Concentrations of COS and H₂S varied considerably, depending on propane flow rate through the permeation oven and are not intended to be quantitative.)

Using the lowest split ratio (3:1) to maximize sulfur detection limits and an LPG mixture that had the highest concentration of propane (97%), a maximum amount of propane was transferred onto the column, and a “worst case scenario” was generated in terms of separating the COS and H₂S from the propane. Complete separation of all three compounds was easily achieved, and there was no “quenching” of the H₂S in spite of the large propane background (Figure 10). Broadening of the propane matrix peak resulted in a reduction of the amount of hydrocarbon eluting with the H₂S. Even though the propane peak tail is eluting with the H₂S, it is at a level that is significantly below what would result in quenching of the sulfur signal.

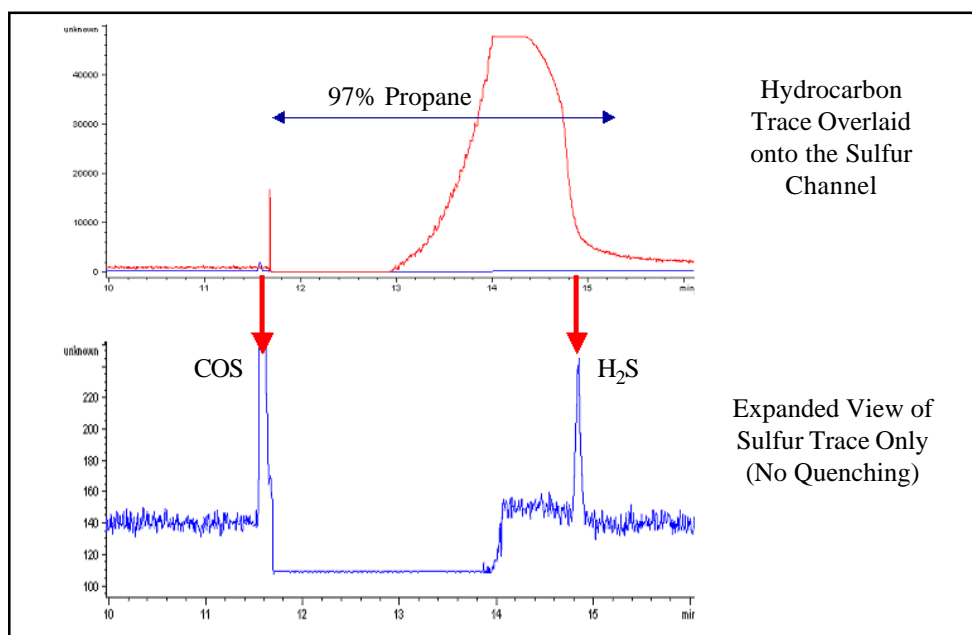


Figure 10. “Worst Case Scenario” for Separation of COS, H₂S, and Propane

Figure 11 is a PFPD sulfur chromatogram of a 1 ppmv gas standard containing 13 sulfur compounds in a propylene standard with a small amount of propane. Note that none of the expected sulfur compounds co-elutes with the propylene. This set of GC conditions achieved excellent chromatographic performance across the entire range of compounds tested with no interference from either the propane or propylene. This chromatogram was acquired using a 0.2-mL gas sample loop, a 9:1 split ratio, a 30-meter GS-GasPro column, and a ramped oven program.

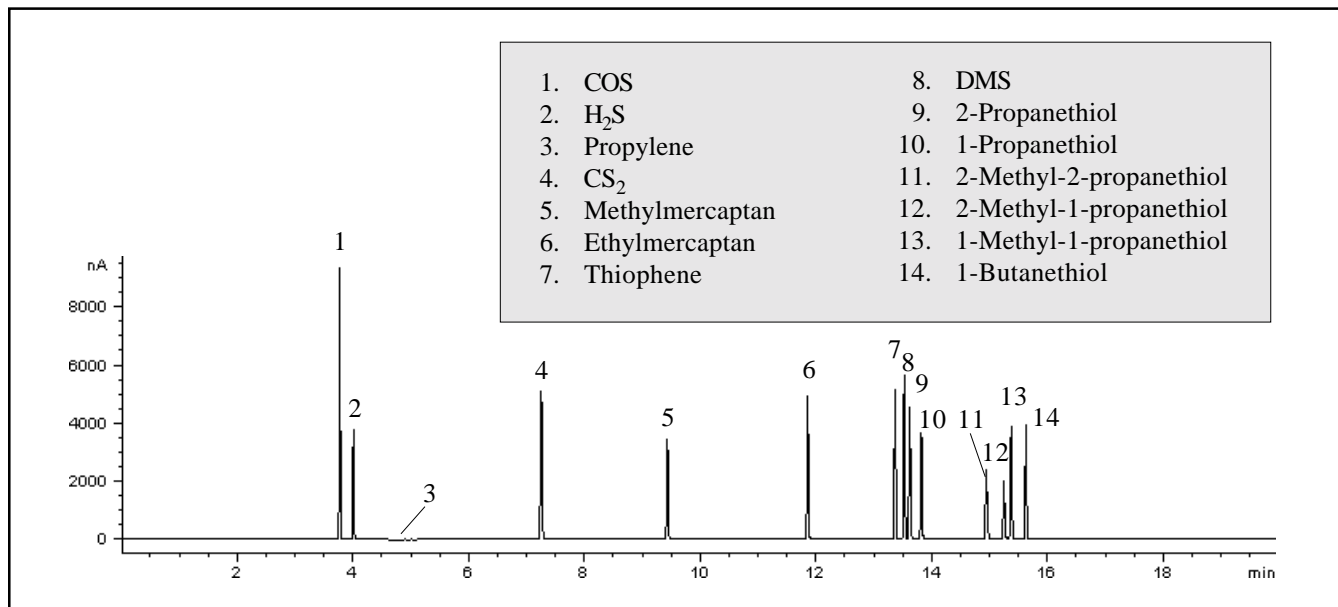


Figure 11. Standard of Thirteen Sulfur Compounds in a Propylene Standard with a Small Amount of Propane

Calibration Techniques

The S-PRO 3200 features a fully integrated permeation oven that automatically generates its own calibration gas standards and permits sequenced calibration. The calibration gas standard can also be analyzed at regular intervals to monitor system performance (QA/QC).

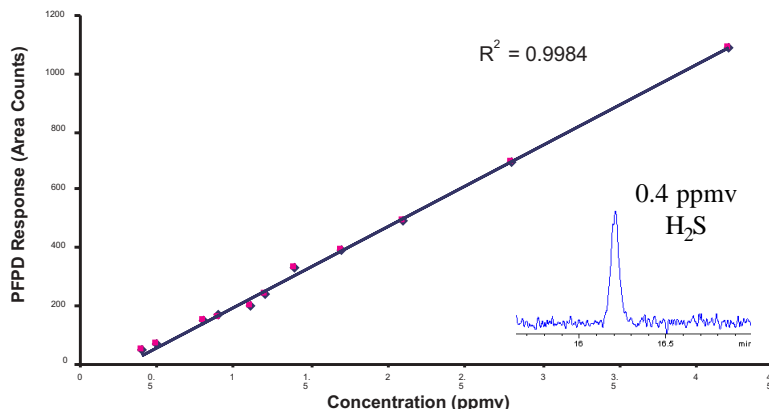
A neat sulfur compound (e.g., COS or H₂S) is packaged in a small device with a permeable Teflon[®] membrane and diffuses across the Teflon barrier at a constant rate. The permeation device is held at a constant temperature inside the permeation oven, and when a dilution gas is passed through the oven at a constant rate, a calibration gas of known concentration is generated. Simply changing the flow of the dilution gas through the oven can change the concentration of the sulfur compounds in the calibrant. Control of the permeation oven temperature and EPC dilution gas flow is integrated through the GC control of the S-PRO 3200, thus allowing fully automated multi-point calibration curves. This technique is illustrated in Figure 12. Figure 13 illustrates a similar technique, generation of a calibration curve by varying the injection port split ratio.

Permeation devices containing COS and H₂S were placed in the permeation oven at 35°C. The dilution gas (He) flow rate was varied over a wide range to generate calibration gas mixtures with different concentrations. The calibration gas was analyzed in triplicate at each concentration level, and the average peak areas were plotted as a function of concentration to generate the linear calibration curves seen in Figure 12. Flow rates across the entire concentration range were tested for this experiment; in practice only three to five concentration levels are necessary to generate a linear calibration curve. Dilution gas flow rates, especially low flow rates, should be allowed time to equilibrate before acquiring data. All data were acquired with a 0.5-mL gas sample loop, a 9:1 split ratio, a GS-GasPro column, and a ramped oven program.

H₂S Permeation
Rate = 7.6 ng/min

Dilution Gas Flow Rate (mL/min)	H ₂ S Concentration (ppmv)
20.0	0.4
10.0	0.8
7.0	1.2
4.0	2.1
2.0	4.2

H₂S Calibration by Varying Dilution Gas Flow Rate
0.4 to 4.2 ppm H₂S (0.5-mL loop, split 9:1)
60-meter GS-GasPro column, ramped oven program



COS Permeation
Rate = 71.7ng/min

Dilution Gas Flow Rate (mL/min)	COS Concentration (ppmv)
75.0	0.6
20.0	2.2
8.0	5.4
6.0	7.2
4.0	10.8

COS Calibration by Varying Dilution Gas Flow Rate
0.6 to 10.8 ppm COS (0.5-mL loop, split 9:1)
60-meter GS-GasPro column, ramped oven program

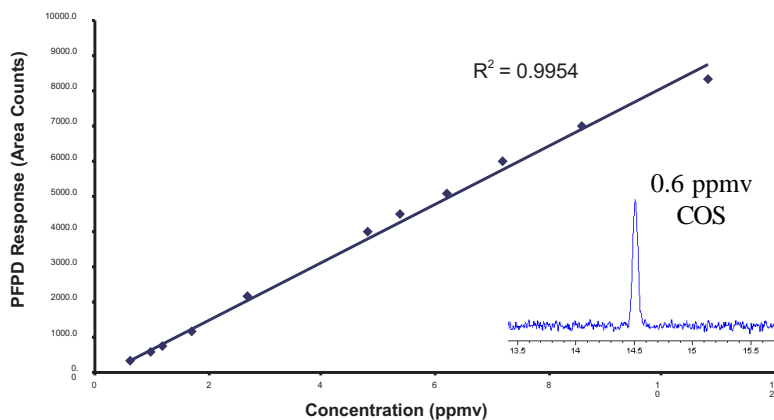


Figure 12. Calibration of COS and H₂S on the S-PRO 3200 by Varying the Dilution Gas Flow Rate

An alternate calibration technique is to vary the amount of compound to the detector by changing the injection port split ratios. The PFPD is an inherently equimolar response detector and the sulfur's chemiluminescence response is independent of a compound's molecular structure. A fixed concentration of sulfur will give the same PFPD response regardless of the parent compound, and this feature allows quantitation of the sulfur content in complex samples. When the peak area counts are plotted as a function of the amount of sulfur on column (in pg) the resulting calibration curve response ratio (slope of the line) can be used to quantify pg of sulfur in any unknown sulfur peak. This technique is illustrated in Figure 13.

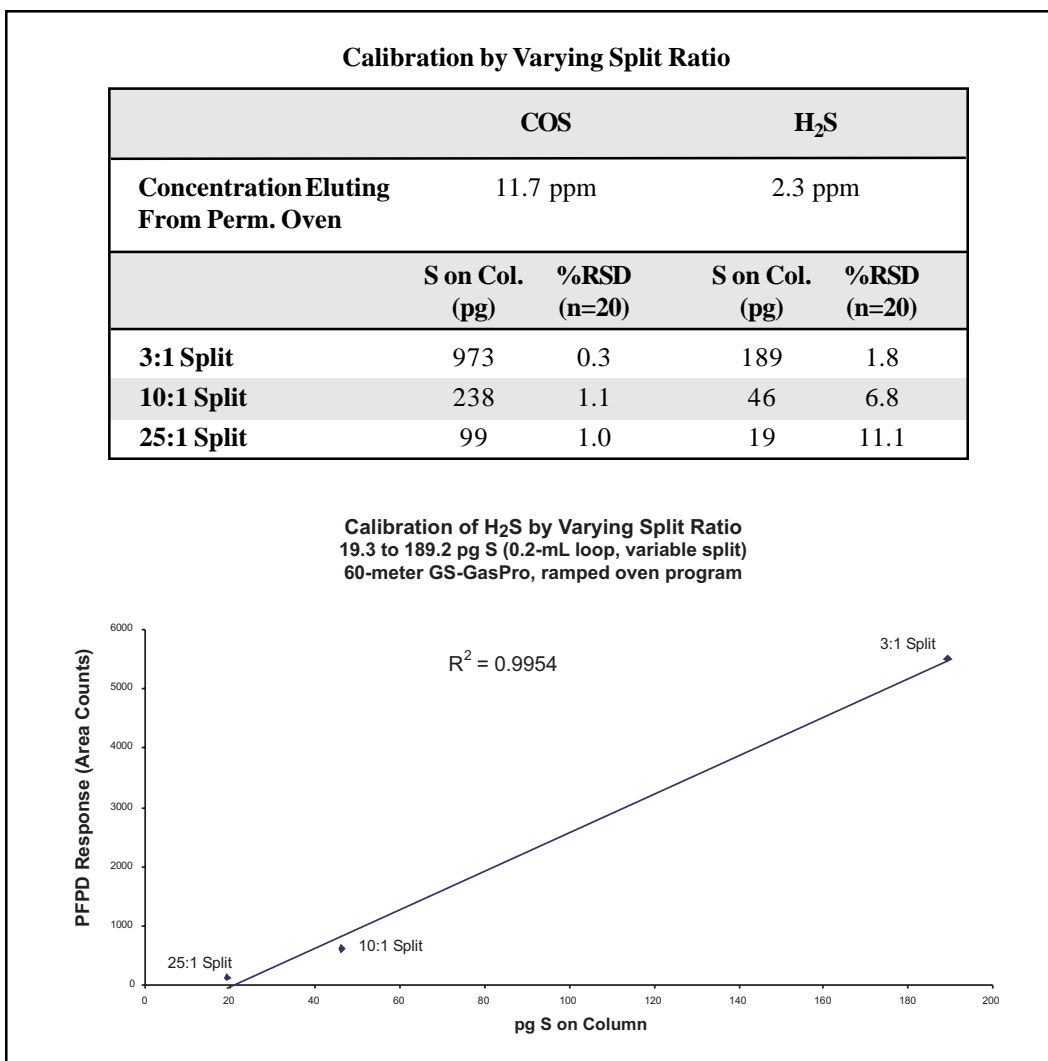


Figure 13. Calibration by Varying the Injection Port Split Ratio

Size of the Gas Sample Loop and Repeatability

Gas sample loops ranging in size from 25 μ L to 1 mL are available with the S-PRO 3200. The loop chosen for a particular application will depend on the expected levels of the individual sulfur compounds of interest. During injection, the GC carrier gas is placed in line with the gas sample loop, and the contents of the loop are flushed into the OI Volatiles Interface and onto the GC column. The total carrier gas flow rate will determine the length of time necessary to completely sweep the loop. Since the total carrier gas flow is made up of the column flow (usually about 1 mL/minute) plus the split flow, the injection port split ratio will be an important factor in determining the injection time (i.e., time necessary to sweep the loop) and will ultimately affect peak shape and chromatographic resolution. This is particularly important for the more volatile, early eluting sulfur compounds, as they are generally not refocused on the column unless subambient oven conditions are used.

For small loop volumes, a minimum injection time will adequately sweep the loop onto the column even at very low total carrier gas flows (i.e., low split ratios). With the 25- μ L loop, even splitless injections can be used and still maintain good peak shape. Larger loop sizes, such as 0.5 and 1.0 mL, require a higher total carrier gas flow, a longer injection time, and at least a minimum split ratio. Figure 14 illustrates the analysis of COS and H₂S with a 30 second splitless injection and a 0.5-mL loop. Note the broad, ill-defined peak shape and the complete lack of chromatographic resolution. Figure 15 demonstrates the need for at least a minimum injection port split ratio to improve transfer of the COS and H₂S onto the column with acceptable chromatographic performance. Optimization of column flow, split ratio, and sample loop size is critical for proper performance of the system.

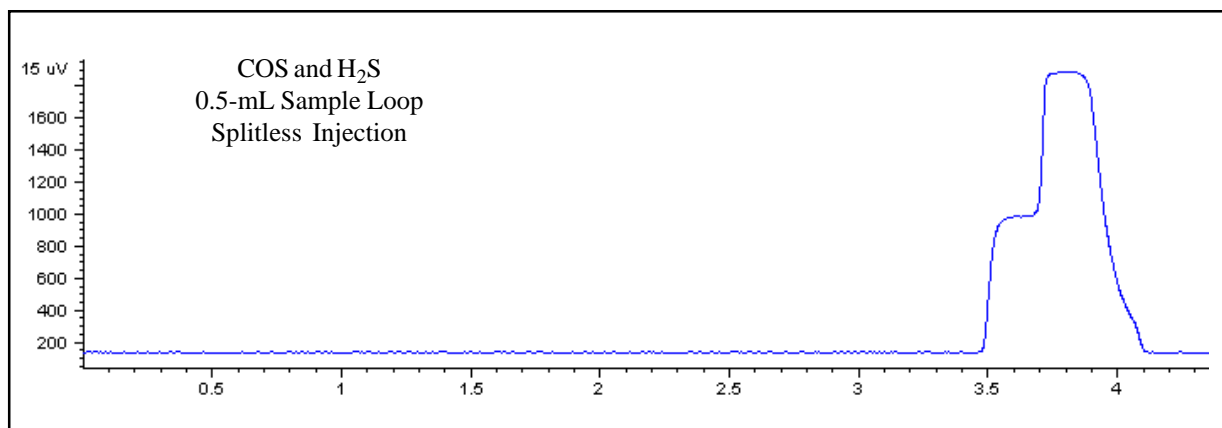


Figure 14. Analysis of COS and H₂S Using a 0.5-mL Gas Sample Loop and a Splitless Injection Technique. The Carrier Gas Flow of Approximately 1.2 mL/minute was Placed In-line with the Loop for 30 Seconds During Injection. The Lack of Adequate Sweep Flow During Injection Resulted in Broad, Ill-defined Peaks.

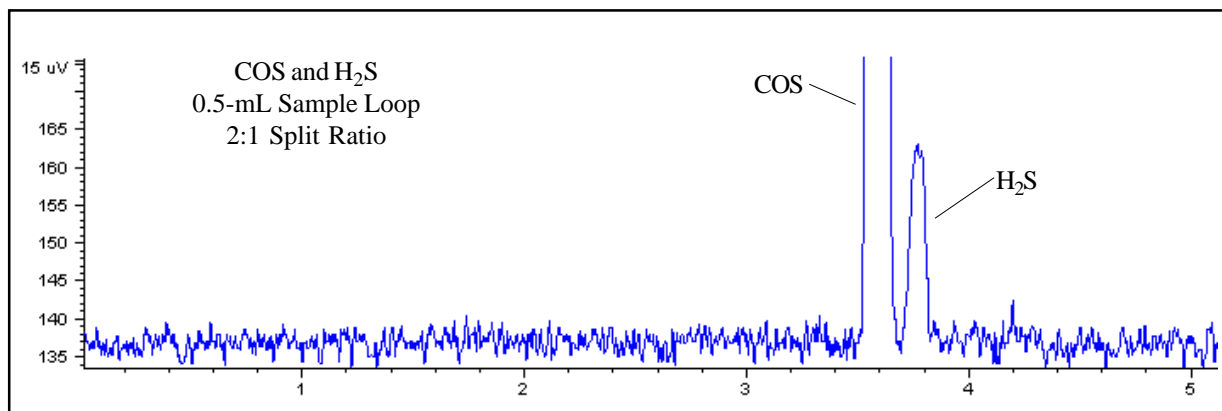


Figure 15. Analysis of COS and H₂S Using a 0.5-mL Gas Sample Loop and a 2:1 Split Ratio. Using Even a Minimum Split Ratio Increased the Total Carrier Gas Flow to Approximately 4.7 mL/minute and Significantly Improved the Chromatographic Peak Shape and Resolution.

System repeatability for the S-PRO 3200 is quite good. For example, the system routinely achieves relative standard deviations (RSDs) of 5% or better under a wide range of operating conditions and loop sizes. Figures 16, 17, and 18 illustrate the type of repeatability that can be expected.

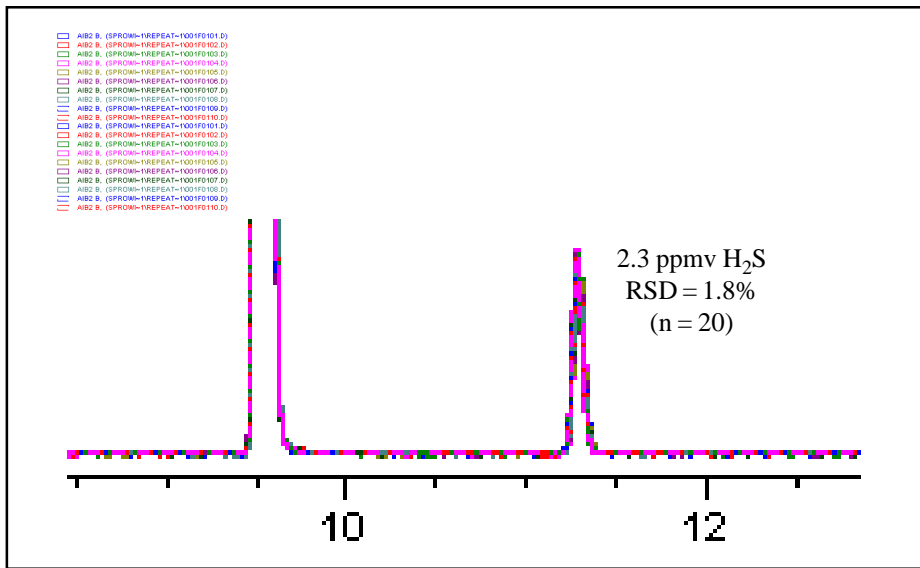


Figure 16. Overlay of 20 Replicate Chromatograms Illustrating the Repeatability of 2.3 ppmv H₂S. RSD = 1.8% for n = 20. Data were Acquired Using a 0.2-mL Gas Sample Loop, a Split Ratio of 3:1, and a 60-meter GS-GasPro Column.

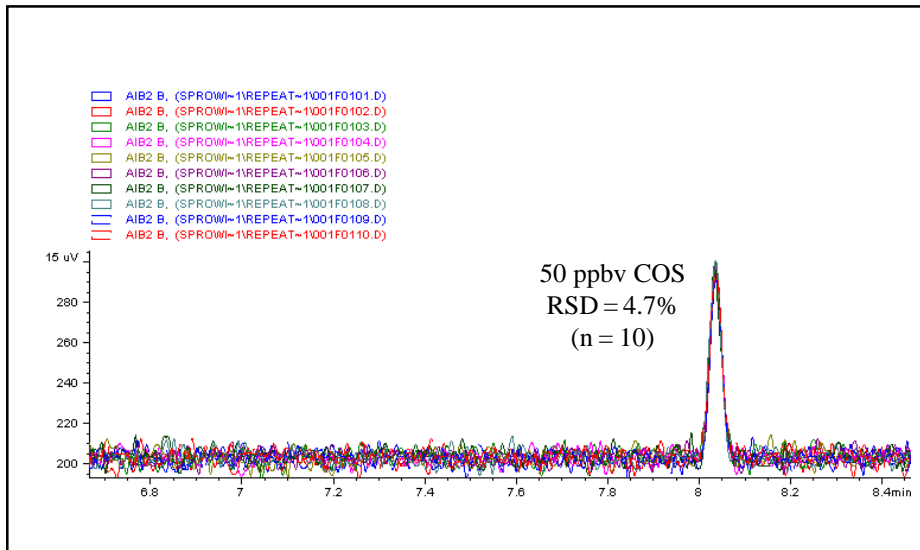


Figure 17. Overlay of 10 Replicate Chromatograms Illustrating the Repeatability of 50 ppbv COS. RSD = 4.7% for n = 10. Data were Acquired Using a 1-mL Gas Sample Loop, a Split Ratio of 9:1, and a 60-meter GS-GasPro Column.

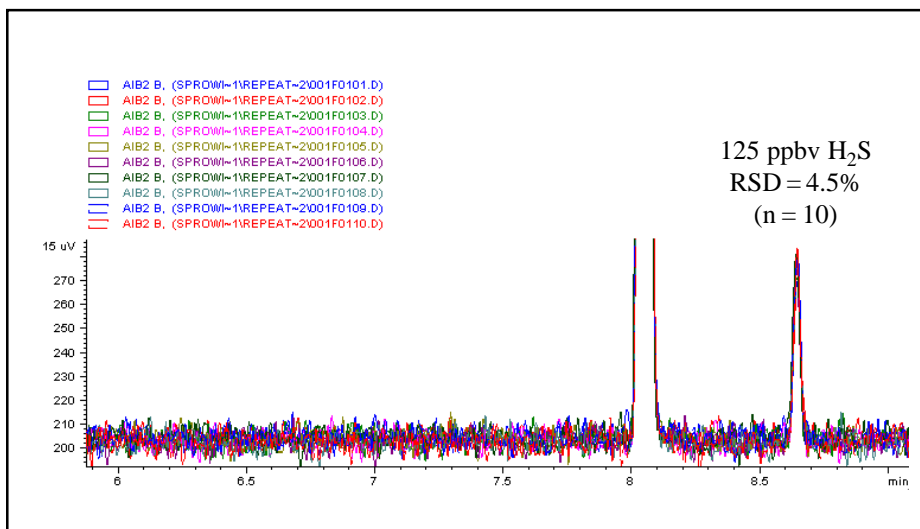


Figure 18. Overlay of 10 Replicate Chromatograms Illustrating the Repeatability of 125 ppbv H₂S. RSD = 4.5% for n = 10. Data were Acquired Using a 1-mL Gas Sample Loop, a Split Ratio of 9:1, and a 60-meter GS-GasPro Column. The GasPro Column has been Found to be Slightly Adsorptive for H₂S, thus Resulting in Higher Detection Limits for that Compound. This Phenomenon has not been Observed with Other Sulfur Compounds on this Column.

Conclusion

The OI Analytical S-PRO 3200 Series GC System is performing analyses of speciated volatile sulfur compounds in a wide range of industry applications, from beverage grade CO₂, petrochemical LPG, and gaseous process streams, to petrochemical stack vent gases. For most sulfur analysis work, the system's standard 30-meter GS-GasPro column is adequate, but for difficult petrochemical C3 analyses, the Agilent 60-meter GS-GasPro column is shown to produce chromatographic separation of COS, H₂S, and propane, even in matrices that are 97% propane in composition. The fully integrated permeation oven generates gas standards that can be used for automated sequenced calibration and monitoring of system performance. Proper matching of gas sample loop size to expected analyte concentrations has been shown to produce excellent chromatographic performance even at extremely low split ratios and with repeatability of less than 5% for most conditions. Addition of a split/splitless injection port to the S-PRO 3200 allows injection of liquid samples, such as gasoline, diesel fuel, and LCOs.

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