O·I·Analytical

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S-PRO 3200 System
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Analysis of Low-Level Sulfur Contaminants in Gas Phase Matrices by Pulsed Flame Photometric Detector (PFPD)

Introduction

Analysis of volatile sulfur-containing compounds at low concentrations in gas phase samples is a critical quality control/quality assurance (QA/QC) step in a variety of industries, including petrochemical sample streams and carbonated beverage bottling. Even parts-per-billion (ppb) levels of some sulfur contaminants cause production problems that range from mere inconvenience to complete plant shutdown. Failure to quickly detect and accurately quantify a sulfur "event" may lead to disastrous results and easily cost millions of dollars in contaminated product and production downtime.

This application note describes a gas chromatography (GC) system that is capable of detecting and accurately quantifying carbonyl sulfide (COS) and other volatile sulfur contaminants in gas phase matrices at low concentrations using the PFPD. This application note includes all analytical conditions used to detect and quantify COS at concentrations near 10 ppbv (parts-per-billion by volume), plus the signal-to-noise ratios and repeatability statistics at different concentration ranges. The linear, equimolar sulfur response of the PFPD can be used to quantify the sulfur content in known and unknown sulfur peaks using a single calibrant from a permeation device.

Experimental

All data were acquired using the OI Analytical S-PRO 3200 System shown in Figure 1. The S-PRO 3200 is a fully integrated GC system that incorporates calibration, QA/QC capability, automated sample introduction, and compound detection and quantitation on an Agilent 6890 GC.

Figure 1. The OI Analytical S-PRO 3200 is designed to detect and quantify 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 1-mL gas sample loop. The sample is then introduced onto the GC column (30-meter GS GasPro) through the OI split/splitless volatiles interface which is optimized for low-volume injections. The entire sample pathway is treated with Sulfinert® surface treatment 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 6890 keypad or via ChemStation. The column installs quickly and easily from inside the GC oven. Figure 2 shows a cross-section of the low-dead volume OI volatiles interface.
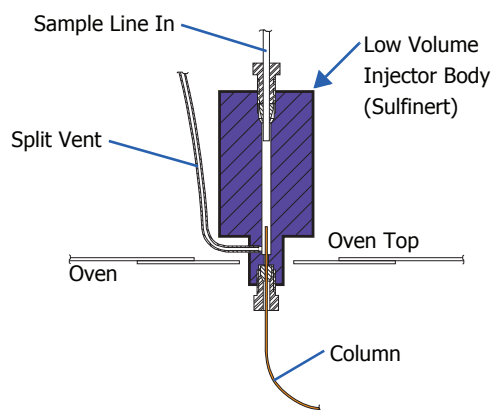

Figure 2. Cross-section schematic of the low-dead volume OI volatiles interface used to make accurate split injections of gas phase samples.

Permeation Oven

The permeation oven is fully integrated into the system with temperature and dilution gas flow controlled through the 6890 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 and diffuses across the permeable membrane at a defined rate for a given 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 without the need for expensive standards in cylinders. Figure 3 illustrates the principle of operation of the permeation device and the permeation oven.

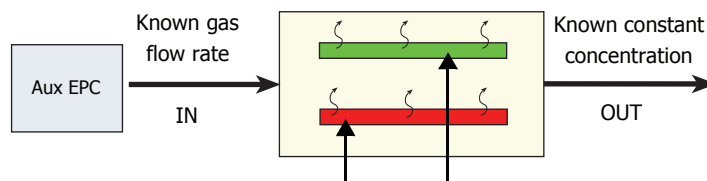**Compound diffuses out at a constant rate for a given temperature**
$R = ng/(min \cdot cm)$

Filled with Compound
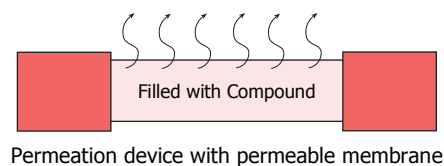
Permeation device with permeable membrane

Permeation oven held at constant temperature
$\sim 30–50\ °C$

Known gas flow rate

Aux EPC

IN

Known constant concentration

OUT

Permeation devices with a known diffusion rate at a given temperature

Figure 3. Principle of operation of the permeation device and permeation oven.

Detection

The S-PRO system 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. The pulse cycle for the PFPD is illustrated in Figure 4.
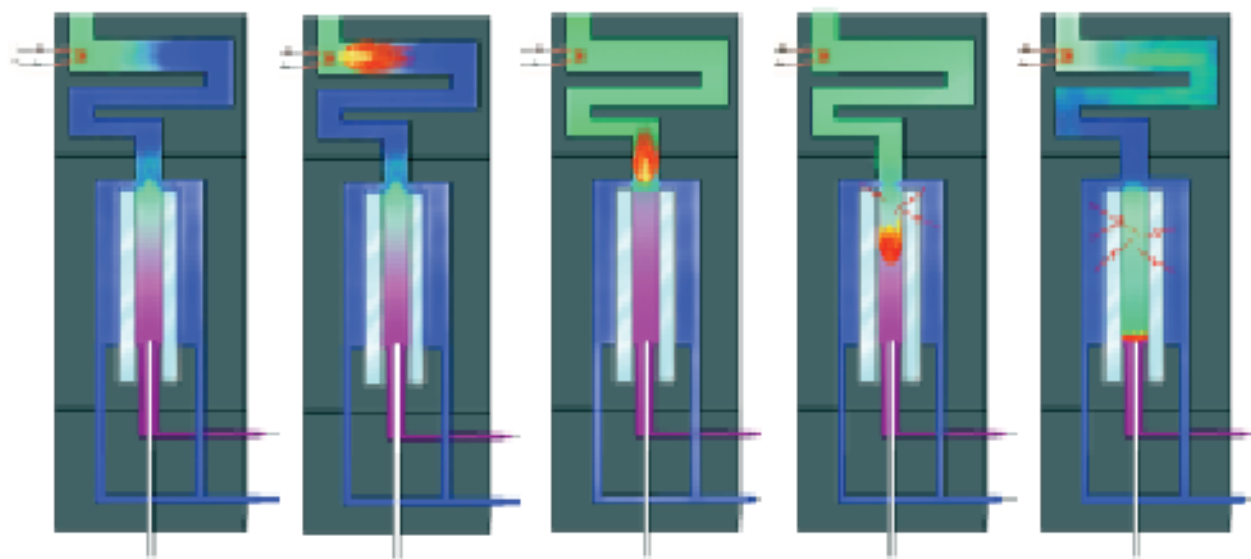
Figure 4. The five-stage cycle of the propagating, pulsing flame of the PFPD.

Results

This application was developed to demonstrate the lowest detectable concentration of sulfur using the S-PRO system. Initial baseline conditions were established to reliably detect and quantify sulfur as COS at approximately 50–100 ppbv. Instrument operating parameters were then modified to determine the lowest measurable level of COS. The instrument operating conditions are shown in Table 1.

Table 1. S-PRO 3200 System operating conditions.

GC Conditions	
Valve Oven and Gas Sample Loop Temperature	110 °C
Column	Agilent GS-GasPro, 30 m x 0.32-mm I.D.
Carrier Gas	He at 1.0 mL/min
Oven Program	Isothermal at 150 °C
Split Ratio	Set-point at 15:1 (18.5 mL/min measured split flow rate)
NOTE: The split ratio was varied from 15:1 to 150:1 to adjust the amount of COS going to the detector.	
PFPD Conditions	
Combustor	2 mm
Filter and PMT	BG-12 and R1924
Gases	H_2 and air, tuned for sulfur-selectivity vs. HC
Frequency	3.7 Hz
PMT Voltage	590 V or 700 V
Range	10 or 1
Sulfur Gate	6–24 ms with square root ON
Permeation Oven Conditions	
Permeation Device and Rate	COS, 91.5 ng/min at 30 °C
Permeation Oven Temperature	30 °C
Dilution Gas Flow Rate	500 mL/min He
Gas Sample Loop	1 mL
Concentration of COS (and Sulfur) Eluting from the Permeation Oven	75 ppbv

Using the baseline conditions outlined in Table 1, the initial concentration of COS and sulfur eluting from the permeation oven was 75 ppbv; with the split ratio set to 15:1, a mass of sulfur on-column of 3.9 pg for each COS peak resulted.

Since the permeation rate of the COS device (91.5 ng/min) was too high to generate the low-level standards required for subsequent testing, and increasing the dilution gas flow rate above 500 mL/min was impractical, the equivalent low-level standard was generated by increasing the split ratio. With a split ratio of 100:1, the equivalent concentration was 11.2 ppbv, with 0.7 pg sulfur on-column; a 150:1 split ratio produced an equivalent concentration of 7.5 ppb and 0.5 pg sulfur on column. Ten replicate injections were made at each concentration level using the programmed, air-actuated 6-port valve and 1-mL gas sample loop. Results are shown in Table 2 and Figures 5, 6, and 7.

Table 2. System variables and analytical results from 10 replicate analyses of COS at three different concentrations.

System Variable	Baseline Concentration	Concentration #1	Concentration #2
Split Ratio	15:1	100:1	150:1
Concentration (or equivalent concentration)	75 ppbv	11.2 ppbv	7.5 ppbv
Mass of Sulfur on Column (per peak)	3.9 pg	0.7 pg	0.5 pg
PFPD PMT Voltage	590 V	590 V	700 V
PFPD Range	10	10	1
Signal-to-Noise (S/N)	25	4	~3
RSD (n=10)	1.6%	6.9%	5.4%

S/N=25
RSD=1.6%
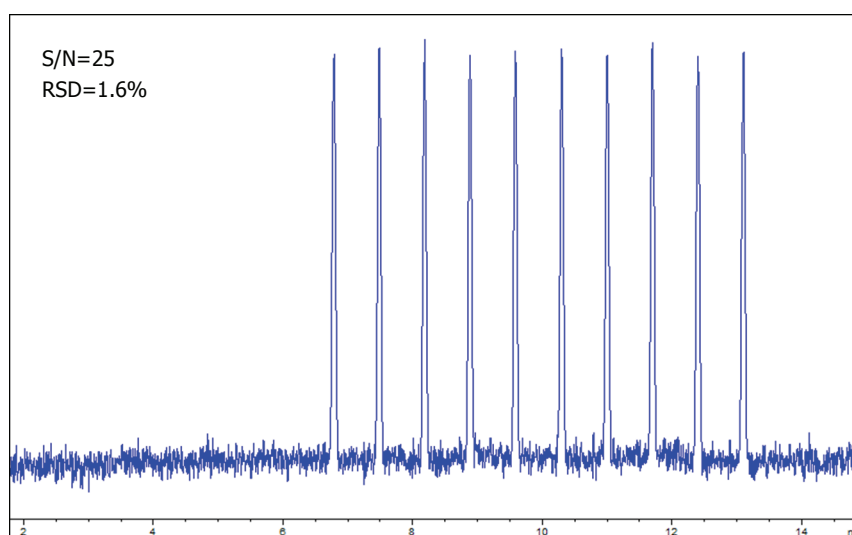
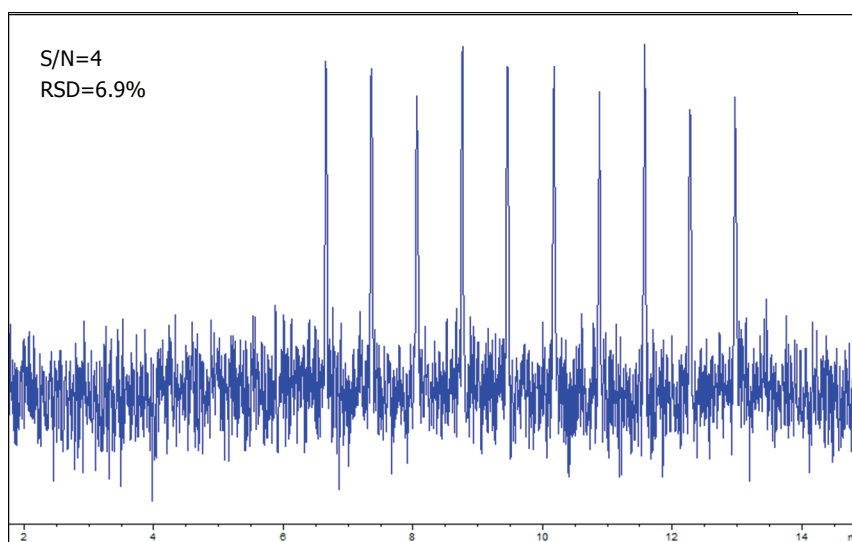Figure 5. Ten replicate analyses of COS at 75 ppbv

S/N=4
RSD=6.9%

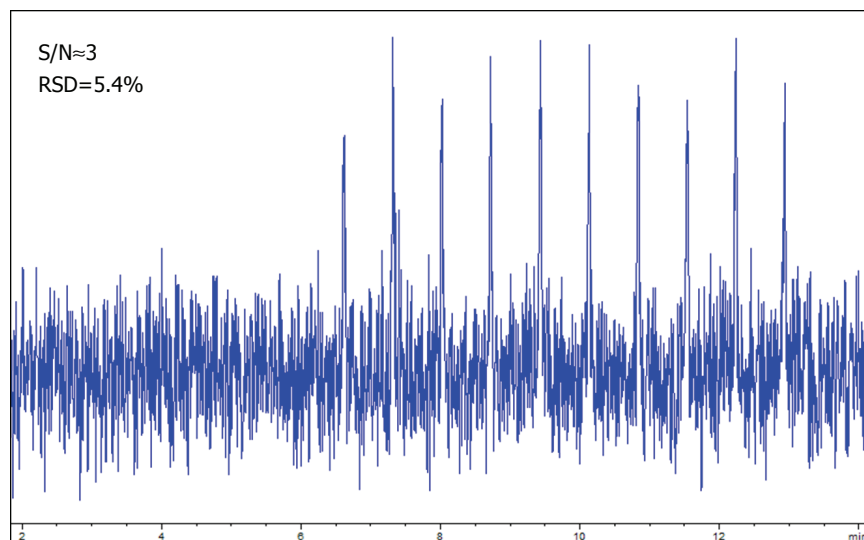Figure 6. Ten replicate analyses of COS at 11.2 ppbv

Figure 7. Ten replicate analyses of COS at 7.5 ppbv

Analysis of sulfur species in real-world samples using the S-PRO System is illustrated in Figures 8 and 9. The system was calibrated by generating compound-specific response factors (RFs) for COS and H_2S using individual permeation devices. The RFs were used to calculate the concentration of COS and H_2S in a propylene sample at 156 and 18 ppbv, respectively (see Figure 8).
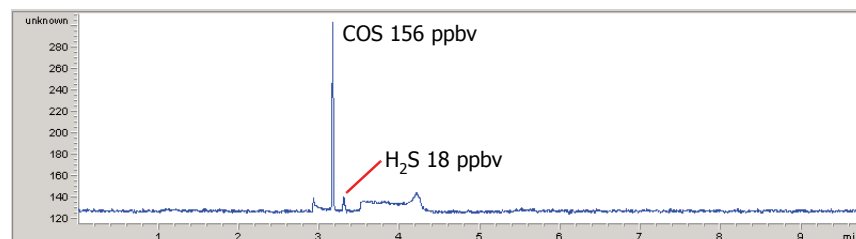

Figure 8. Carbonyl sulfide (156 ppbv) and hydrogen sulfide (18 ppbv) in propylene

Separate analysis of a butane sample using the same conditions did not yield any detectable COS or H_2S, but two unidentified sulfur compounds were revealed later in the chromatogram (see Figure 9). The RF for sulfur in COS was used to calculate the sulfur concentration in the two unknowns at 3.5 ppmv sulfur (10.3 minutes) and 0.5 ppmv (11.9 minutes). The simultaneous sulfur and hydrocarbon chromatograms illustrate the dual-channel capability of the PFPD.
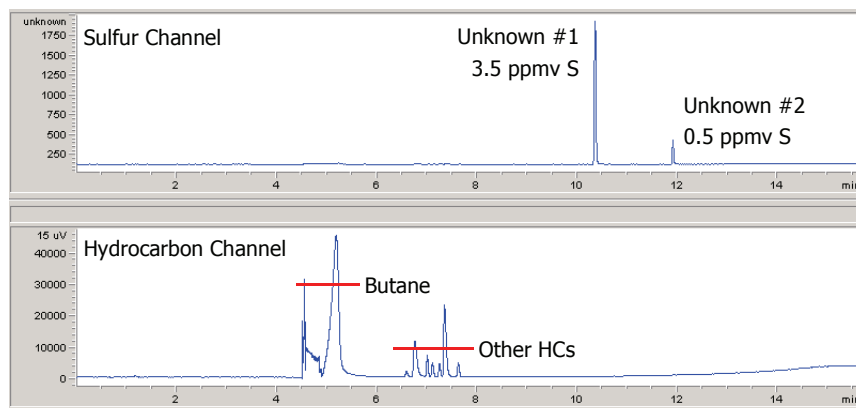

Figure 9. Two unknown sulfur species in a butane sample at 3.5 ppmv and 0.5 ppmv

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Summary and Conclusions

Reliable detection and quantitation of known and unknown sulfur species in gas-phase matrices is possible at concentrations as low as 10–50 ppbv using the OI Analytical S-PRO 3200 System with PFPD. Repeatability of replicate injections is consistently below 10% and is often below 5%. The fully integrated permeation oven generates calibration gas standards at point-of-use, eliminating the need to purchase expensive cylinders for calibration.

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