

Trace carbonyl sulfide and phosphine in ethylene or propylene

Application Note

Energy & Fuels

Authors

Agilent Technologies, Inc.

Introduction

Organic sulfur and phosphorus occur naturally in crude oil. Ethylene and propylene are formed from the crude oil during the refining process. As these products are purified trace amounts of sulfur or phosphorus may be carried through the process. During polymerization of these compounds to form polyethylene or propylene, trace sulfur or phosphorus components must be accounted for and kept to a minimum since they may poison the polymerization catalysts and adversely affect the quality of the product polymer. Contaminants generally monitored by the plastics industry include carbonyl sulfide (COS) and phosphine (PH₃).

These two compounds may be resolved from the two bulk gases using an Agilent PoraPLOT Q column and selectively detected with the pulsed flame photometric detector (PFPD).



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Experimental

The plumbing schematic is shown in Figure 1. A 100 μL loop mounted on a 6-port gas sampling valve served as the injector to the capillary column. Inlet, valve loop, and connection to the column were constructed of 1/16 in Silcosteel tubing to prevent adsorption of analytes. Two primary gas standards (Scott Specialty Gases) were used: 1) 10 ppmv COS in nitrogen and 2) 10 ppmv PH_3 in nitrogen. Matrix standards were prepared by passing ethylene or propylene dilutions of the primary standards through the sample loop.

Figure 1: Schematic of System

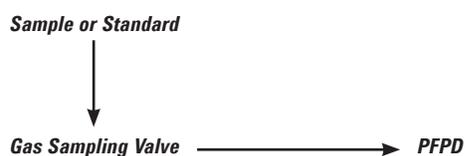


Table 1: Chromatographic Parameters, COS

Sample	100 μL
Column	Agilent PoraPLOT Q, 0.32 mm x 50 m (10 μm) (Part no. CP7552)
Carrier	Helium, 3mL/min
Column Oven	30 $^{\circ}\text{C}/15$ min, 5 $^{\circ}\text{C}/\text{min}$ to 120 $^{\circ}\text{C}/0$ min
PFPD	200 $^{\circ}\text{C}$, S filter (BG-12), R647 PMT 3 mm combustor H_2 : 13 mL/min Air 1: 17 mL/min Air 2: 10 mL/min

Table 2: Chromatographic Parameters, PH_3

Sample	100 μL
Column	Agilent PoraPLOT Q, 0.32 mm x 50 m (10 μm) (Part no. CP7552)
Carrier	Helium, 3mL/min
Column Oven	70 $^{\circ}\text{C}/0$ min, 5 $^{\circ}\text{C}/\text{min}$ to 120 $^{\circ}\text{C}/0$ min
PFPD	300 $^{\circ}\text{C}$, P filter (GG 495), R647 PMT, 3 mm combustor Flows same as above

Results

Chromatographic Considerations

A sample volume of 100 μL was used to prevent overloading of the column with the sample matrix, i.e. ethylene or propylene. The peak shapes and retention times of the COS or PH_3 are therefore less affected by the matrix gas. Figures 2 and 3 show the separation of 1 ppm COS from ethylene and propylene, respectively. The COS elutes after ethylene and gives a similar peak geometry to that obtained in a nitrogen matrix. Its chromatographic behavior is, therefore, unaffected by the ethylene. The COS which elutes shortly before the propylene produces a peak that is taller and narrower. This is due to matrix effects on the PLOT column.

Figure 2: COS in Ethylene, 1 ppm

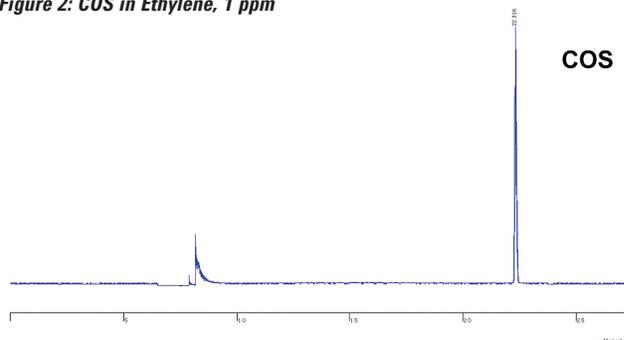
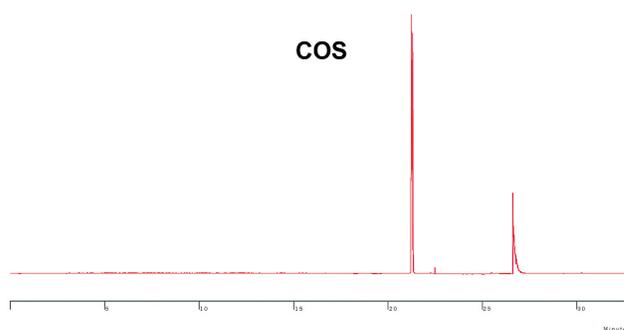


Figure 3: COS in Propylene, 1 ppm



Phosphine also elutes before propylene and after ethylene as shown in Figures 4 and 5. While the peak area of the phosphine is equivalent in both chromatograms, the peak shape is also sharper where the analyte elutes prior to the matrix gas.

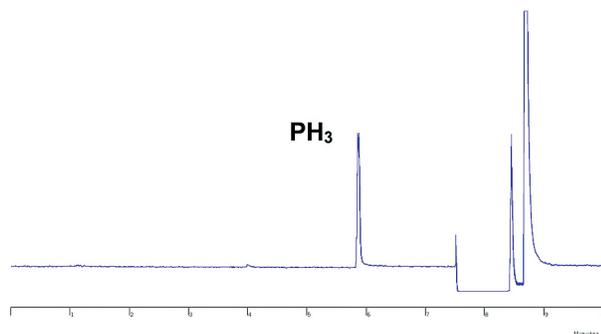


Figure 4: PH_3 in Propylene, 1 ppm

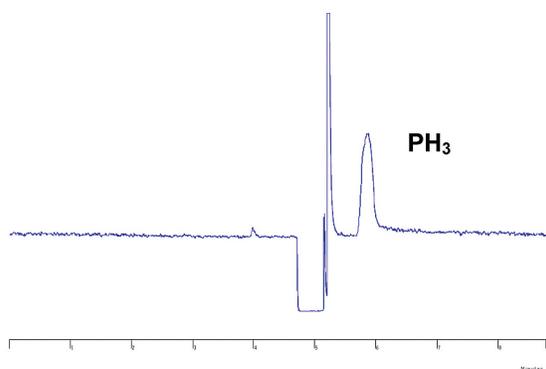


Figure 5: PH_3 in Ethylene, 1 ppm

Statistical Data

The relative standard deviation (RSD) of area and retention time measurements for COS and PH_3 in ethylene and propylene were measured for five runs each and are shown in Table 3.

Table 3: Statistical Data

Compound	t_r %RSD	Area % RSD	RSD (ppm)	MDL (ppm)
COS/C2 =	0.02	2.7	0.003	0.10
COS/C3 =	0.07	5.1	0.005	0.12
PH_3 /C2 =	0.17	2.6	0.026	0.07
PH_3 /C3 =	0.17	3.9	0.039	0.12

Method Detection Levels

With the statistical data from Table 3, it is possible to estimate the method detection levels (MDL) by multiplying the concentration (RSD) by the student (t) value of 3.1 (five runs and 99% confidence level).

Conclusions

Carbonyl sulfide and phosphine may be determined in ethylene and propylene down to concentration levels of about 100 ppb using a PoraPLOT Q capillary column and the PFPD. A small sample loop of 100 μL is used to minimize the matrix effects that affect the geometry of the targeted analytes.

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