BEYOND MEASURE

SCION INSTRUMENTS

Trace Carbonyl Sulphide and Phosphine in Ethylene or Propylene

Application Note AN0011

INTRODUCTION

Organic Sulphur 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 sulphur or phosphorus may be carried through the process. During polymerization of these compounds to form polyethylene or propylene, trace sulphur or phosphorus components must be accounted for and kept to a minimum. Any contamination from these components can poison polymer catalysts and adversely affect the quality of the product polymer. Contaminants routinely monitors by the plastics industry include Carbonyl Sulphide (COS) and Phosphine (PH_3).

Using a custom SCION GC with PLOT Q column and selective pulsed flame photometric detector (PFPD), it is possible to easily resolve these two bulk gases from the matrix.

EXPERIMENTAL

A 100µL sampling loop and six port gas sampling valve both served as the injector to a PLOT Q capillary column. Two primary gas standards; 10ppmv COS in Nitrogen and 1-ppmv PH_3 in Nitrogen were used to prepare matrix standards in which ethylene or propylene dilutions were passed through the sample loop. Analytical parameters used can be found in Table 1.

Table 1. Analytical conditions of the GC-PFPD

Conditions	
Sample	100µL
PLOT-Q column	50m x 0.32mm x 10µm
Carrier	Helium, 3mL/min
Oven	30°C (hold 15 min), 5°C/min to 120°C
PFPD Flow	H_2 13/mL/min Air 1: 17mL/min Air 2: 10mL/min
PFPD COS	200°C, S Filter, 3mm combustor
PFPD PH_3	300°C, P Filter, 3mm combustor

RESULTS

A sample volume of 100µL was used to prevent overloading of the column with the sample matrix, either ethylene or propylene. The matrix effects due to the gas sample were minimised resulting in greater peak shapes and stable retention times of the COS and PH_3. Figures 1 and 2 show the separation of 1ppm COS in ethylene and propylene.

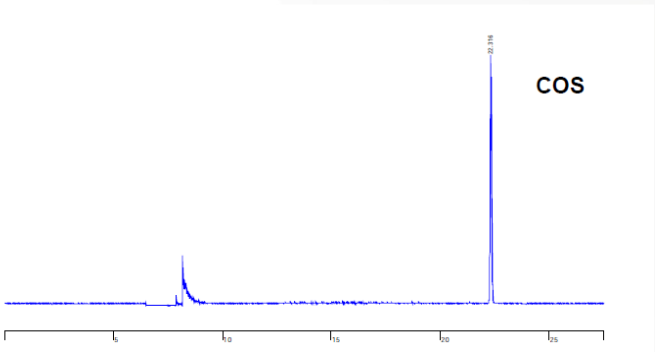

Figure 1. COS in Ethylene at 1ppm

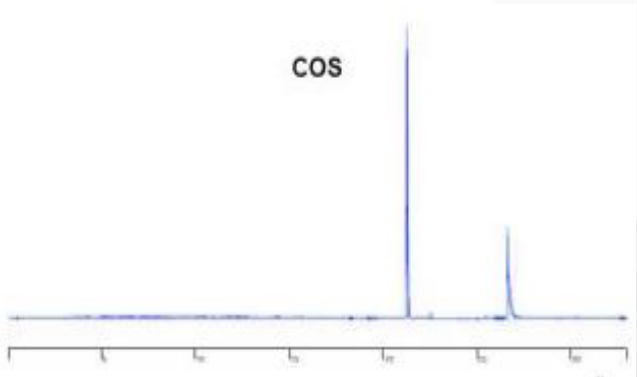

Figure 2. COS in Propylene at 1ppm

COS elutes after ethylene, giving a similar peak geometry to that obtained in a nitrogen matrix. However, in propylene, COS elutes before propylene, as shown by the narrow, tall peak; due to the matrix effects of the PLOT column. Figures 4 and 5 show the elution of phosphine in both ethylene and propylene.

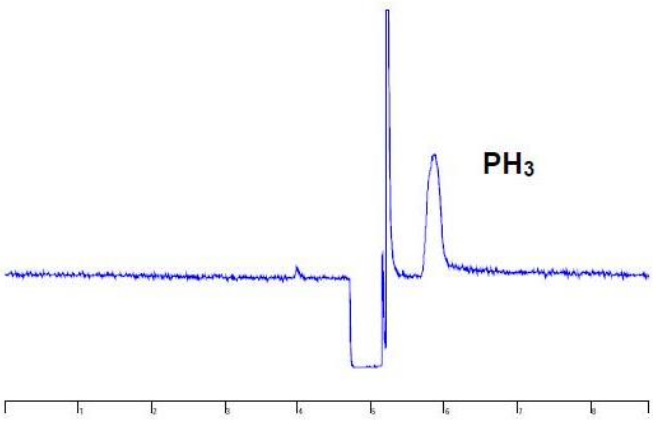

Figure 3. PH3 in Ethylene at 1ppm

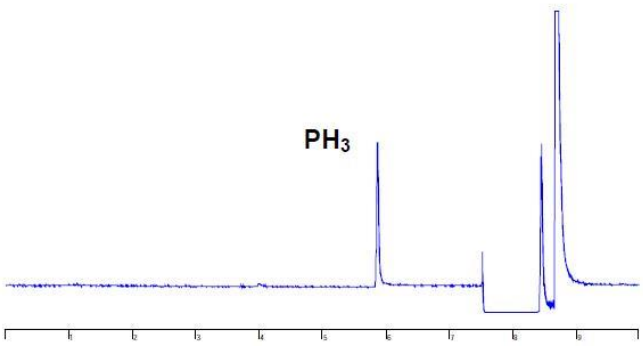

Figure 4. PH3 in Propylene at 1ppm

Phosphine elutes after ethylene but before propylene. Peak shape is sharper when the phosphine elutes prior to the matrix gas. The relative standard deviation (RSD) of the area and retention time measurements for COS and PH_3, in both matrix gases, were measured for five runs. Additionally, the method detection limits (MDL) were also measured. The results of which can be found in Table 2.

Table 2. RSD values of retention time, peak area and concentration with MDL.

Compound	T_r	Area	RSD (ppm)	MDL (ppm)
COS/C_2	0.02	2.7	0.003	0.10
COS/C_3	0.07	5.1	0.005	0.12
PH_3/C_2	0.17	2.6	0.026	0.07
PH_3/C_3	0.17	3.9	0.039	0.12

The MDL were estimated by multiplying the concentration RSD by the student t value of 3.1 (5 runs with 99% confidence).

CONCLUSION

Carbonyl sulphide and phosphine can be determined in ethylene and propylene down to a concentration level of 100ppb, when a PLOT Q column is used with the PFPD. Small sample amounts are implemented to minimise matrix effects. Excellent reproducibility is shown through low RSD values for retention time and peak areas. The SCION analyser is the perfect solution for monitoring contaminants in crude oil.

SCION Instruments
1 Bain Square, Livingston
EH54 7DQ, UK
Tel: +44 1506 300 200
sales-eu@scioninstruments.com
www.scioninstruments.com

SCION Instruments NL BV
Stanleyweg 4
4462GN, Goes, Netherlands
Tel: +31 113 348926
sales-eu@scioninstruments.com
www.scioninstruments.com