GC Analysis of Sulfur Components in Propylene using a Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

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Abstract

The Agilent J&W Select Low Sulfur column measures trace levels of target components in C3 hydrocarbon streams without any matrix interference.

Introduction

Hydrogen sulfide (H_2S), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH) are common components in light hydrocarbon streams. They have corrosive and toxic properties, causing damage to pipes and equipment. The emission of undesired odors caused by volatile sulfur compounds in intermediates and final products have serious economic and environmental impact. In addition, the presence of sulfur can affect the performance of industrial processes, causing undesired chemical reactions, loss of catalyst activity (catalyst poisoning), and ultimately lower yield.

These sulfur components must be quantified at low ppb levels. They can be measured with sulfur specific detection devices such as the Sulfur Chemiluminescence Detector (SCD) but large sample volumes are needed to reach the desired low parts per billion (ppb) detection limits. This creates matrix overload and quenching effects (decreased signal/sensitivity due to background interferences) on most sulfur specific detectors, limiting the detector's sensitivity and linearity and raising quantification limits. The capillary PLOT column, Agilent J&W Select Low Sulfur column, with a novel stationary phase was developed for the analysis of sulfur species such as H_2S, COS and CH_3SH in light hydrocarbon C3 matrices, with high loadability properties and unique selectivity giving baseline resolution for sulfur components and matrix components.

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Experimental

Technique:	GC-SCD
Column:	Agilent J&W Select Low Sulfur, 60 m × 0.32 mm (p/n CP8575)
Oven:	65 °C for 4 minutes, 30 °C/min to 120 °C for 5 minutes
Carrier gas:	Helium, constant flow, 2.0 mL/min
Injector:	200 °C, split 1:10
Detector:	SCD, 200 °C
Sample:	Propylene matrix containing ~300 ppb H_2S and CH_3SH, ~500 ppb COS
Injection volume:	1 mL
Injection:	Gas sampling valve

Results and Discussion

The stationary phase shows good selectivity between H_2S, COS and low mercaptans in various C3 hydrocarbon matrices. Therefore co-elution of the sulfur components and the matrix, which causes "quenching", is avoided.

The system was equipped with a gas sampling valve. The gas sampling valve event table is shown in Table 1. The detector settings are shown in Table 2.

Table 1. Gas Sampling Valve Event Table

Time (min)	Gas sampling valve
Initial	Fill
0.01	Inject
1.00	Fill

Table 2. Detector SCD Settings

SCD settings	
Burner temperature	800 °C
Vacuum of burner	370 torr
Reactor hydrogen flow	40 mL/min
Reactor air flow	65 mL/min
Attenuation	1
Ozone air pressure	5 psig

Figure 1 shows a chromatogram of sulfur compounds H_2S, COS and CH_3SH in a propylene matrix. Methyl mercaptan shows peak broadening from column overloading by the large amount of propylene matrix. The propylene matrix elutes between COS and methyl mercaptan.

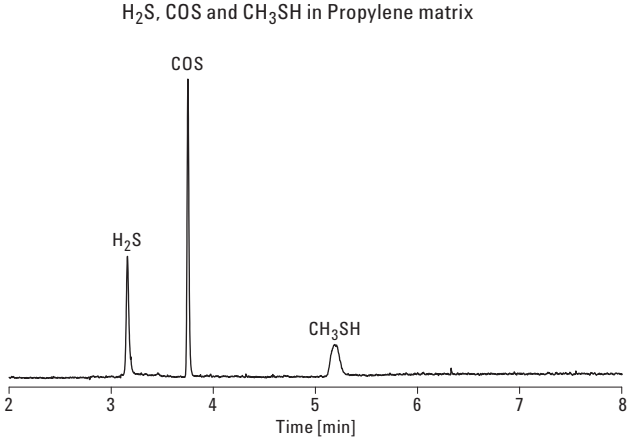

Figure 1. Chromatogram of H_2S, COS and CH_3SH in Propylene matrix, using the Agilent J&W Select Low Sulfur with GC-SCD.

Conclusion

The Agilent J&W Select Low Sulfur used in a GC with a sulfur specific detector, such as an SCD, can detect H_2S, COS and CH_3SH at trace level in a propylene matrix as a result of excellent separation of the sulfur compounds and the matrix. Separating the matrix from the sulfur components eliminates the "quenching" effects caused by the matrix. This provides a better response for the sulfur compounds. The column provides a good response for reactive sulfur compounds, such as H_2S making detections of 20 ppb possible.

Although this is a PLOT column, no spikes will be observed because the column does not shed particles. It can therefore be used safely in combination with switching valves.

References

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2. Roger L. Firor and Bruce D. Quimby, "Comparison of Sulfur Selective Detectors for Low-Level Analysis in Gaseous Streams," Agilent Technologies publication 5988-2426EN.

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