An Alternative Application for a Highly Oxygen-Selective Capillary GC Plot Column

Application Note

Hydrocarbons

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Abstract

This application note successfully shows selective retention and resolution of low molecular weight sulfur containing species on an Agilent J&W GS-OxyPLOT column. The selective retention for sulfur species enables enough of a retention shift away from hydrocarbon matrices such as base gasoline and n-butane to demonstrate the feasibility of effective quantification of sulfur species in process streams. Using an Agilent J&W GS-OxyPLOT column it is possible to shift the retention of sulfur containing analytes away from a hydrocarbon matrix to achieve effective quantification in the low ppm range.

Agilent Technologies

Introduction

The Agilent J&W GS-OxyPLOT column is highly selective for oxygen-containing species. Most of the initial applications for this column focus on the determination of trace level oxygenates in hydrocarbon matrices [1,2]. Example applications include testing and quantification of species containing oxygen in complex matrixes such as reformulated gasoline and C1-C4 hydrocarbon process streams. ASTM method 7059 is in effect for the analysis of methanol in crude oil by GC [3]. A recently approved method (June 2009, subcommittee D02.D04) D7423 for the analysis of trace oxygenates in light hydrocarbon matrices is also an application of the Agilent J&W GS-OxyPLOT column. Sub 10 ppm quantifications of alcohols, aldehydes and ethers in these feed stocks are important analyses to avoid poisoning of the catalysts used in processing these materials.

Oxygen and Sulfur Chemical Similarity

Chemical species that contain oxygen and sulfur share similar chemical behaviors often undergoing similar reactions to form similar products [4]. Affinity and retention on a highly oxygen selective PLOT column by sulfur-containing species is no exception. This application note demonstrates that the chromatographic behaviors of species containing sulfur on an Agilent J&W GS-OxyPLOT are quite similar to the behaviors demonstrated by oxygen-containing species on the same phase.

Selective retention and resolution of species containing sulfur from complex hydrocarbon matrices can help facilitate trace level analysis of low boiling mercaptans, thiols and sulfides. Monitoring levels of these compounds at low ppm levels has become increasingly important as stack emission and fuel content regulations have stiffened. In hydrocarbon processing, analyses of the sulfur content in feedstocks are used to make processing decisions that hopefully avoid sulfur poisoning of expensive catalysts and enhance refinery throughput.

Experimental

Three different sulfur standards, from liquid to gas, were tested using the Agilent J&W GS-OxyPLOT column.

For the test of a liquid sample, a standard mix of 14 sulfur containing compounds in base gasoline was purchased from Spectrum Quality Standards, Houston TX. Class A volumetric flasks and pipettes were used for dilutions. The liquid sample was analyzed at Agilent Technologies Little Falls Site in Wilmington DE.

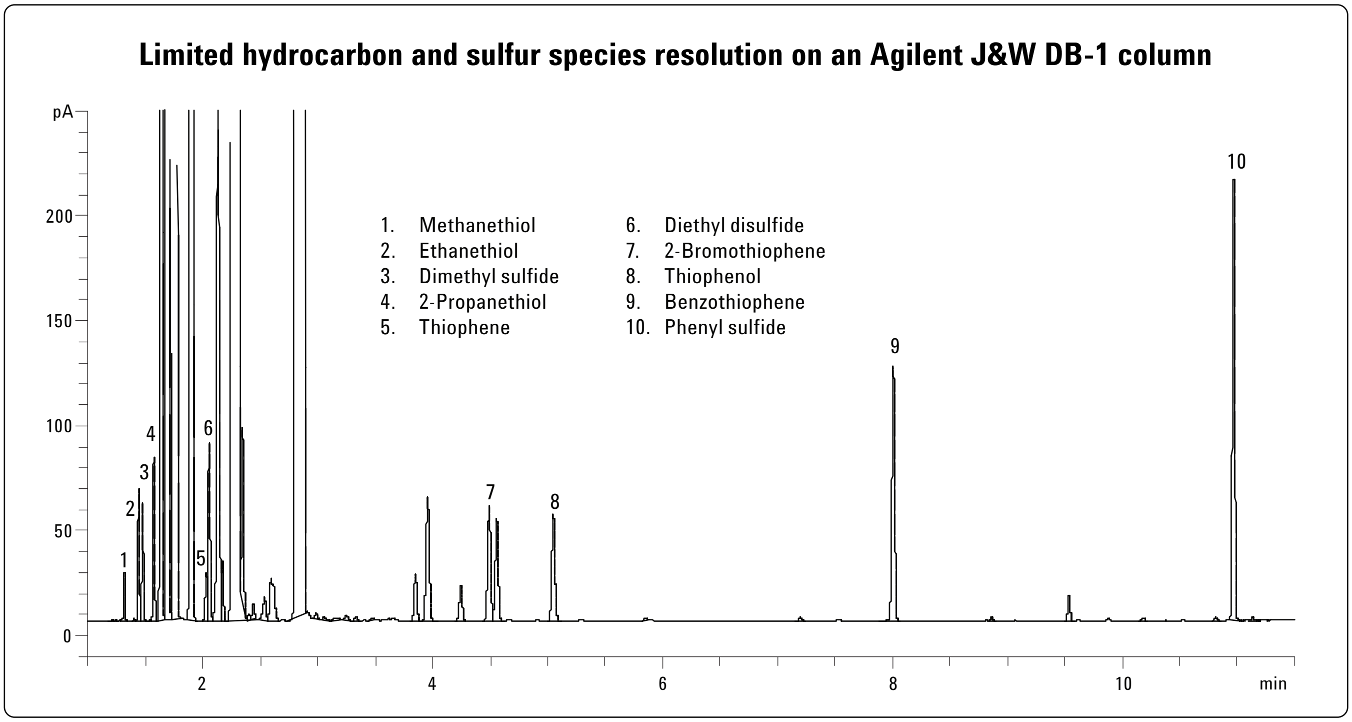
For the test of a gaseous sample, a sulfur mix of 11 sulfur compounds in N_2 was prepared and analyzed in DCG Partnership, Pearland TX.

For the test of a liquefied gas-liquid sample, a sulfur standard mix of 5 sulfur compounds in n-butane was prepared and analyzed in DCG Partnership, Pearland TX.

Chromatographic conditions appear beneath each figure.

Results and Discussion

Figure 1 shows the injection of a liquid sulfur standard in a base gasoline matrix on an Agilent J&W DB-1 column. Most of the sulfur species of interest elute early in the chromatogram along with the hydrocarbon species in the gasoline matrix. This figure illustrates the difficulty in separating sulfur species commonly found in gasoline from hydrocarbons in the gasoline matrix with a primarily boiling point separation mechanism. Higher selectivity and retention for the lighter sulfur species is necessary to resolve the peaks containing sulfur from the hydrocarbon matrix. This type of application is where the selective retention of sulfur species on the Agilent J&W GS-OxyPLOT is most useful.



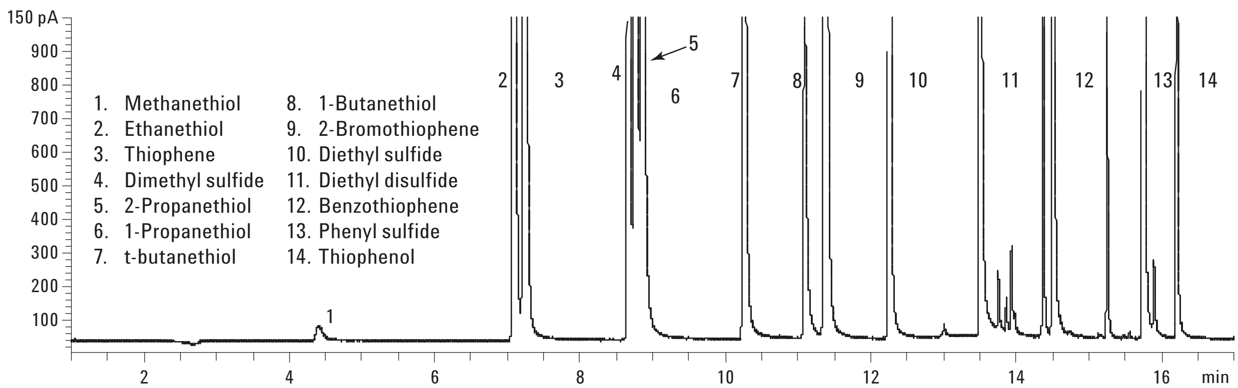
GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 25 m, 1.0 µm (Agilent part number 125-102J)
Oven:	60 °C (0.5 min), 10 °C/min to 120 °C, then 20 °C/min to 300 °C (3 min)
Injection:	250 °C, 1 µL, 25:1 split
Carrier:	He, constant flow, 30 cm/s at 60 °C (3.9 mL/min)
Detection:	FID 350 °C, H_2 40 mL/min, Air 450 mL/min, N_2 makeup 30 mL/min

Figure 1. Chromatogram of a liquid sulfur standard mix in base gasoline on an Agilent J&W DB-1 column.

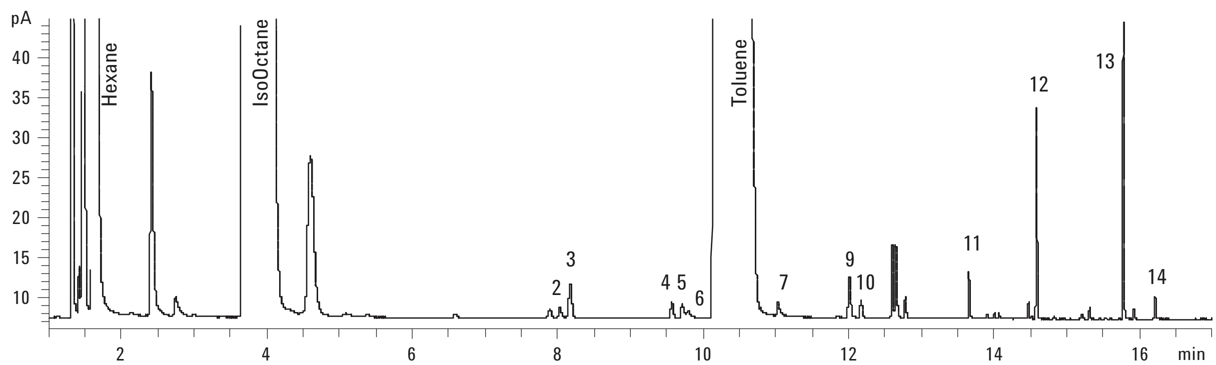
Figure 2 illustrates the selective retention of the sulfur-containing species versus the components in a base gasoline standard. The FPD signal in Figure 2A shows the elution of the sulfur-containing species and helps with peak identification. The FID signal in Figure 2B shows the elution of both the hydrocarbons and the sulfur species as they elute from the Agilent J&W GS-OxyPLOT. Most of the hydrocarbon components of the gasoline matrix, with the exception of toluene, elute early in the chromatogram and are resolved from the sulfur species of interest.

Selective sulfur species resolution from hydrocarbons on an Agilent J&W GS-OxyPLOT

A) 25 ppm Liquid Std OxyPLOT/FPD



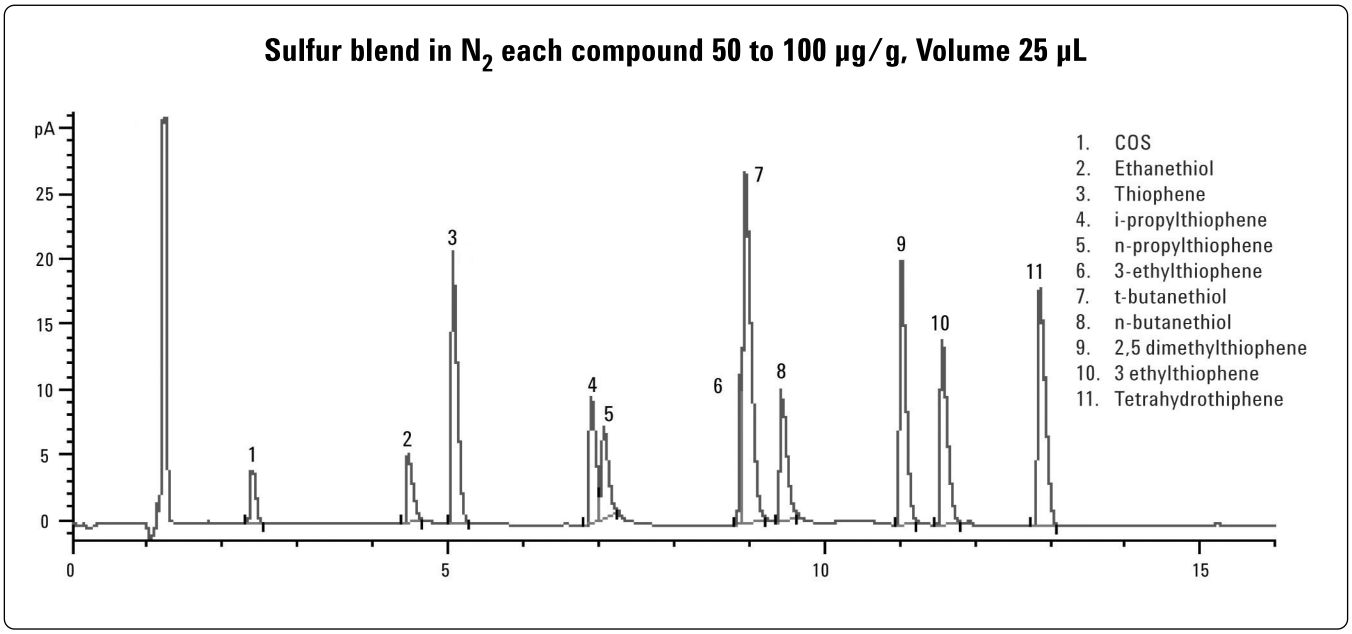
B) 25 ppm Liquid Std OxyPLOT/FID



GC:	Agilent 6890N network GC system, Dual Injection
Columns:	Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm (Agilent part number 115-4912)
Oven:	40 °C (3 min), 8 °C/min to 110 °C, then 35 °C/min to 300 °C (3 min)
Injection:	250 °C, 1 µL, 25:1 split, gas saver 20 mL/min at 2min
Carrier :	He (Col 1 to FID), 4.7 mL/min constant flow
	He (Col 2 to FPD), 3.15 mL/min constant flow
Detection:	FID 350 °C, H_2 40 mL/min, Air 450 mL/min, N_2 makeup 30 mL/min
	FPD 250°C, H_2 50 mL/min, Air 60 mL/min, N_2 makeup 60 mL/min

Figure 2. Chromatogram of a liquid sulfur standard mix in base gasoline on an Agilent J&W GS-OxyPLOT columns with simultaneous injection. Figure 2a (top) is the FPD signal and Figure 2b (bottom) is the FID signal.

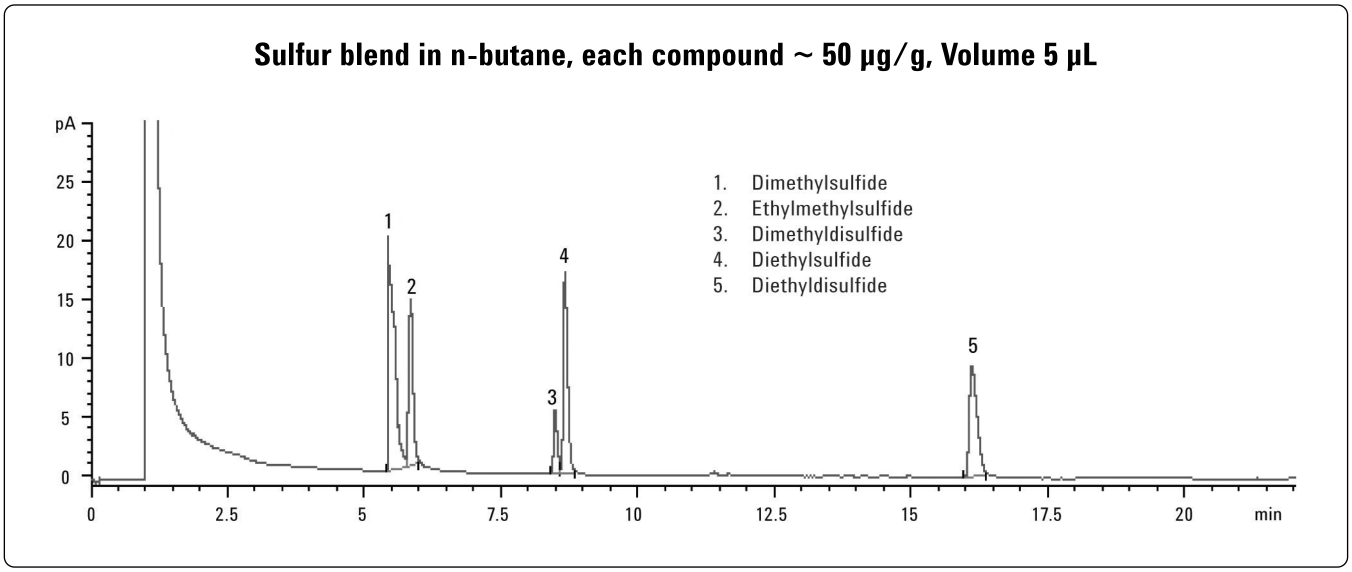
Figure 3 shows the injection of a gaseous sulfur species blend in N_2 on a combination of an Agilent J&W DB-1 connected by a glass insert with an Agilent J&W GS-OxyPLOT. The sulfur species in this sample are well retained. The selective retention of the Agilent J&W GS-OxyPLOT was again useful in separating the sulfur species of interest and achieving retention for these low boiling sulfur compounds.



GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 10 m, 0.5 µm (Agilent part number 125-1017)
	+ Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm (Agilent part number 115-4912)
Oven:	40 °C (0.1 min), 10 °C/min to 300 °C (5 min)
Injection:	250 °C, 25 µL, 10:1 split
Carrier:	H_2, 0.9 mL/min constant flow
Detection:	FID 250 °C, H_2 30 mL/min, Air 300 mL/min, N_2 makeup 15 mL/min

Figure 3. Chromatogram of a gaseous sulfur standard blend in N_2 on an Agilent J&W GS-OxyPLOT column.

Figure 4 shows an injection of a low molecular weight sulfur standard blend in a liquid n-butane matrix on a combination of an Agilent J&W DB-1 column connected by a glass insert with an Agilent J&W GS-OxyPLOT column. Excellent retention and resolution for the sulfur species from the n-butane were observed. An FID detector was used for this test. Figure 4 shows evidence of overloading of the trace level components in this detector, due to the large sample size. The large volume of injection caused no baseline problem, because of the effective separation away from the non-polar matrix of the analytes.



GC:	Agilent 6890N network GC system
Column:	Agilent J&W DB-1 0.53 mm × 10 m, 0.5 µm (Agilent part number 125-1017) + Agilent J&W GS-OxyPLOT 0.53 mm × 10 m, 10 µm (Agilent part number 115-4912)
Oven:	40 °C (0.1 min), 10 °C/min to 300 °C (5 min)
Injection:	250 °C, 5 µL, 10:1 split
Carrier:	H_2, 0.9 mL/min constant flow
Detection:	FID 250 °C, H_2 30 mL/min, Air 300 mL/min, N_2 makeup 15 mL/min

Figure 4. Chromatogram of a liquefied gas-liquid sulfur standard blend in n-butane on an Agilent J&W GS-OxyPLOT.

Conclusions

This application note successfully demonstrates selective retention and resolution of low molecular weight sulfur containing species on an Agilent J&W GS-OxyPLOT column. The selective retention for sulfur species enables enough of a retention shift away from hydrocarbon matrices such as base gasoline and n-butane to suggest that effective quantification of sulfur species in process streams is quite feasible.

The Agilent J&W GS-OxyPLOT column also retained toluene in the base gasoline sample where co-elution was observed between toluene and tert-butanethiol in the liquid standard mix. Potential interferences between analytes of interest and aromatic species are a possibility with the Agilent J&W GS-OxyPLOT column that should be manageable with careful planning and method design.

References

1. A. K. Vickers, "GS-OxyPLOT: A PLOT Column for the GC Analysis of Oxygenated Hydrocarbons," Technical Overview, Agilent Technologies publication 5989-6447EN, March 2007
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4. Jerry March, "Advanced Organic Chemistry; Mechanisms and Structure," 4th Edition, John Wiley and Sons, 1992

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