Determination of sulfur compounds in various light hydrocarbon matrices by Sulfur Chemiluminescence Detector

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Introduction

C1 to C5 hydrocarbon streams can contain significant to trace amounts of volatile sulfur impurities. It is very important to analyze these impurities since these compounds can be critical to final product purity as well as poisoning of costly catalysts in the processing stream. The analysis of sulfur compounds is important not only in the petrochemical industry but also in environmental, industrial hygiene and food products applications (sulfur compounds in beer or wine, beverage grade CO_2 analysis, etc.). Lowering of detection limits is of great importance for these applications. Quantification limits for sulfur compounds as hydrogen sulfide or methyl mercaptan can be down to low ppb levels.

Accurate detection of sulfur compounds in light hydrocarbon streams is very challenging. The GC analysis of the more reactive volatile sulfurs, such as H_2S, COS and mercaptans, is complicated because of absorption in the GC system and capillary column, which results in low responses and poor peak shapes. In order to analyze these compounds at ppb concentration level with sulfur specific detectors like the Sulfur Chemiluminescence Detector (SCD) or Pulsed Flame Photometric Detector (PFPD) it is necessary to use large volume injections in order to reach the detection limits. When injecting these large volumes GC columns will show matrix overload phenomena and the detector will show quenching effects which will cause inaccurate quantification.

This poster shows examples of sulfur compounds analysis within various hydrocarbon streams using a special PLOT column designed for low level sulfur analysis using SCD detection. This column has very low to non-existent adsorption of low molecular weight sulfur species which results in near 100% sulfur responses at concentration levels under 100 ppb. The unique highly retentive stationary phase with excellent inertness for sulfur compounds enables consistent and reliable detection of H_2S, COS and mercaptans from 10 to 100 ppb in light hydrocarbon streams with excellent separation characteristics between the hydrocarbon matrix and sulfur compounds to avoid detector quenching.

Experimental

Sulfur compounds is LPG

GC Settings

Column: Agilent J&W Select Low Sulfur, 60 m 0.32 mm (p/n CP8575)
Oven: 65 C (18 min), 50 C/min, 185 C (6 min)
Carrier gas: Helium, constant flow
2.0 mL/min for SCD mounted on FID
1.2 mL/min for SCD only
Injector: 200 C
Injection volume: 1 mL, split 100:1 for SCD mounted on FID
20 µL, split 75:1 for 30 ppbv and 100:1 for 20 ppbv using SCD only
Injection: Gas sampling valve

Sulfur compounds in propylene

GC Settings

Column: Agilent J&W Select Low Sulfur, 60 m 0.32 mm (p/n CP8575)
Oven: 65 C (5.5 min), 10 C/min, 170 C
Carrier gas: Helium, constant flow, 2.0 mL/min
Injector: 200 C
Injection volume: 1 mL, split 10:1
Injection: Gas sampling valve

Results and Discussion

Commonly applied PLOT columns for light sulfur analyses are often based on porous silica adsorbents which exhibit low response of H_2S at these ppb concentration levels. In contrast, the new column exhibits near 100% sulfur responses at low concentration levels. The stationary phase shows a good permeability and sample capacity resulting in an excellent matrix loadability performance needed for these trace analyses.

The column exhibits an excellent mechanical stability which is evident from the zero particle loss under demanding flow and backflush conditions. The stationary phase shows good selectivity between H_2S, COS, mercaptanes and hydrocarbon matrices thus avoiding detector quenching phenomena for sulfur compounds.

Figure 1. Agilent 355 Sulfur Chemiluminescence Detector.

Results and Discussion

Table 1. SCD settings when SCD is mounted on FID

SCD settings	
Burner temperature	800°C
Vacuum of burner	450 torr
Reactor hydrogen flow	40 mL/min
Reactor air flow	5 ml/min
Ozone air pressure	5 psig

Table 2. FID settings when SCD is mounted on FID

FID settings	
Temperature	300°C
Hydrogen flow	30 ml/min
Air flow	400 mL/min
Make-up (N_2) flow	30 ml/min

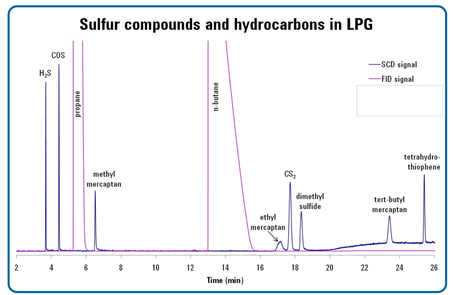

Figure 2. Sulfur compounds (1 ppmv, about 150 pg S on column) in LPG matrix analyzed with SCD detector mounted on FID detector.

Figure 2 shows a chromatograms of sulfur compounds in LPG matrix. Ethyl mercaptan shows peak broadening from column overloading caused by the large amount of the n-butane matrix.

When the SCD detector is mounted on top of the FID detector approximately 10% of the FID exhaust gases are drawn into the SCD burner through the restrictor. Therefore the sensitivity of the SCD drops to around 10% of the signal that one would obtain if all of the column effluent went to the detector. For analyzing very low concentrations in LPG bulk it's not recommended to use this detection technique.

The SCD detector by itself can't measure hydrocarbons but quenching can be observed when a hydrocarbon and sulfur compound elute at the same time. This GC column can provide separation between the hydrocarbons and the sulfur compounds as can be seen in Figure 2.

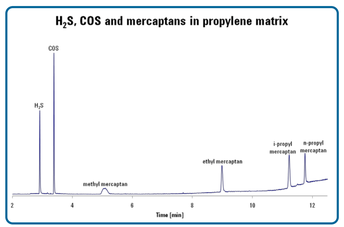

Figure 3. Elution of 400 ppbv H_2S, COS and mercaptans.

Table 3. SCD Detector Settings

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

Figure 3 shows a chromatograms of sulfur compounds in propylene matrix. The peak broadening of methyl mercaptan is due to the large amount of propylene matrix. The propylene matrix elutes between COS and methyl mercaptan.

In Figure 4 the linearity of H_2S, COS and methyl mercaptan is shown using the column in combination with an SCD detector.

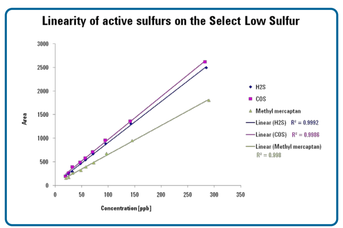

Figure 4. Linearity of active sulfurs, 20 ppbv to 300 ppbv.

Table 4. SCD Detector Settings

SCD settings	
Burner temperature	800°C
Vacuum of burner	400 torr
Reactor hydrogen flow	40 mL/min
Reactor air flow	65 ml/min
Ozone air pressure	5 psig

Figure 5 shows a chromatograms of sulfur compounds at 30 ppbv concentration level. The combination of the SCD detector and the Agilent J&W Select Low Sulfur column provides the right solution for analyzing low level sulfur compounds. For H_2S, COS and methyl mercaptan even analyzing 20 ppbv is no problem as can be seen in figure 6.

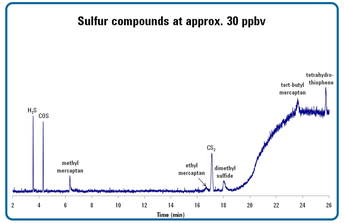

Figure 5. Sulfur compounds at 30 ppbv concentration level analyzed with SCD detector.

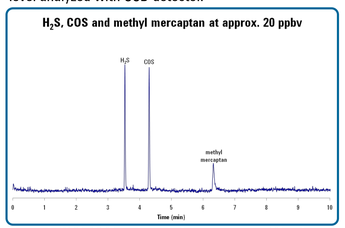

Figure 6. H2S, COS and methyl mercaptan at 20 ppbv concentration level.

Conclusions

The detection of low ppb levels H_2S and COS in hydrocarbon streams is an important analysis with many challenging aspects. The combination of high compound reactivity and low detection levels require careful optimization of many analytical parameters. The GC column has always played a key role and sometimes limiting factor.

The Agilent J&W Select Low Sulfur used in a GC with a sulfur specific detector, such as an SCD, can detect sulfur compounds at a trace level in hydrocarbon matrices as a result of excellent separation of the sulfur compounds and the matrix. Separation of the matrix from the sulfur compounds 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 ppbv 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 combined with switching valves.

References

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