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Poster E.06

RECENT DEVELOPMENT IN WALL COATED OPEN TUBULAR COLUMN FOR ANALYSIS OF SULFUR COMPOUNDS USING SCD

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Introduction

Analyzing volatile sulfur containing compounds is important in a wide variety of industrial and petrochemical applications. Sulfur contaminant analyses in process streams using gas chromatography with sulfur selective, chemiluminescence detector (SCD) has become the tool of choice. Monitoring these reactive compounds is critical for quality control of feedstocks, precursors and final products. This is not limited to light sulfur gases but also extends to sulfur containing hydrocarbons out to C20+.

Columns commonly used for GC-SCD in these analyses are plagued with the paradox of needing a high retention stationary phase (i.e. thick stationary phase) to provide good resolution of the low molecular weight sulfur analytes, but also needing low bleed performance at the upper temperature range when eluting the high molecular weight sulfur analytes. Generally speaking, columns with higher bleed profile installed on the SCD, can contribute to detector overloading in which hydrocarbons and aromatics as well as components of stationary phase bleed exiting the column are reduced in the hydrogen rich atmosphere which "coke" SCD reaction tubes in the burner.

This inadvertent passivation of the reaction tubes in turn causes a rapid decline in the SCD sensitivity. The only solution is to replace the reaction tube, which not only incurs the cost of the reaction tube, but also the down time for performing preventive maintenance on the analyzer. A novel wall coated open tubular column with low bleed and exceptional inertness to sulfur compounds enables separation a broad range of the active solutes at low concentrations. Performance for sulfur selective detectors, and in particular the SCD, demonstrates minimal column contribution to reaction tube coking which results in improved system ruggedness and greatly reduced downtime and for costly detector maintenance.

Issues & Causes of SCD Sulfur Signal Instability

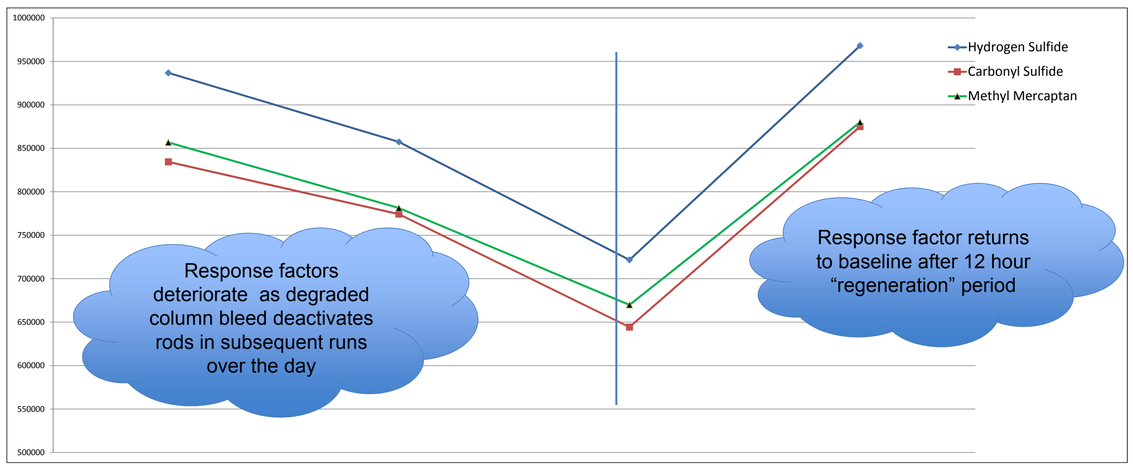


Figure 1. The coking of reactor tubes under reduced state (hydrogen rich environment). Column phase decomposition, with the SCD reactor operating in excess of 800°C, is especially problematic for the thick film columns that are popularly employed for analysis of volatile sulfur compounds.

Column: 50 m x 0.32 mm I.D., 5 um film, PDMS

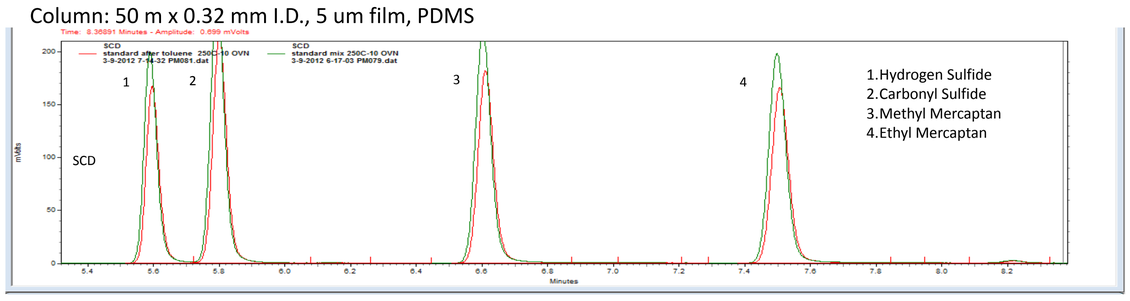
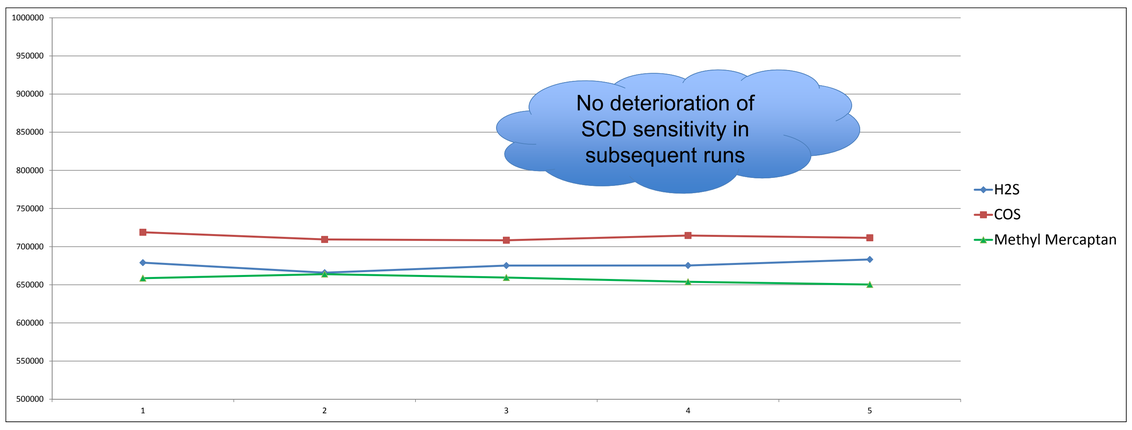
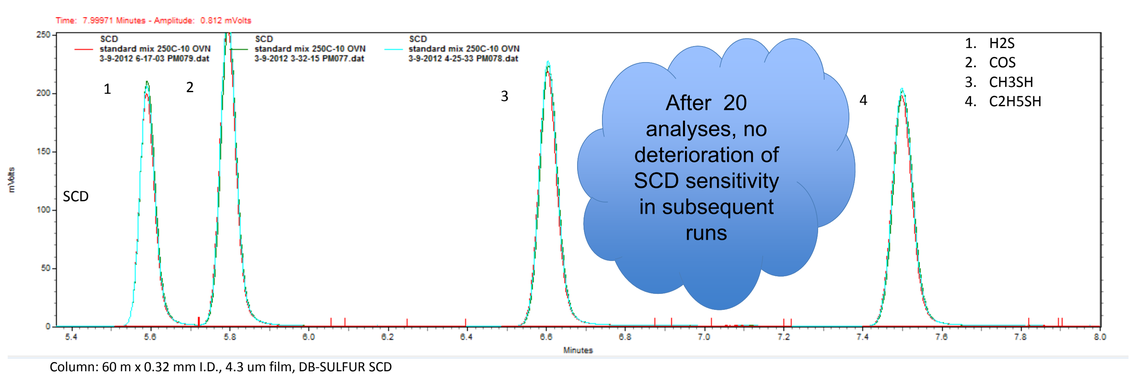


Figure 2. This chromatogram demonstrates injections of hydrocarbon rich samples can cause decline of sulfur response in as few as 3 injections. Column phase decomposition can exacerbate sulfur signal decline due to build up of silicon dioxide in the sample flow path.

SCD Signal Stabilized With New DB-Sulfur SCD Column

The Agilent DB-Sulfur SCD GC column is specifically developed for sulfur compound analyses and optimized for GC/SCD.





Column: 60 m x 0.32 mm I.D., 4.3 um film, DB-SULFUR SCD

Figure 3. Improved thermal stability in thick film column for lower phase degradation in high temp SCD reactor. Increased inertness towards reactive sulfur compounds.

Applications

Sulfur compounds in Cracked Gasoline

Inlet: 275 °C, Split ratio 10:1 (Inert Flow Path split/splitless inlet)
Carrier: Helium, constant flow mode, 2.8 mL/min
Oven: 35 °C for 3 min, 35 °C to 250 °C at 10 °C/min, 250 °C for10 min
Detector: SCD

According to ASTM D5623

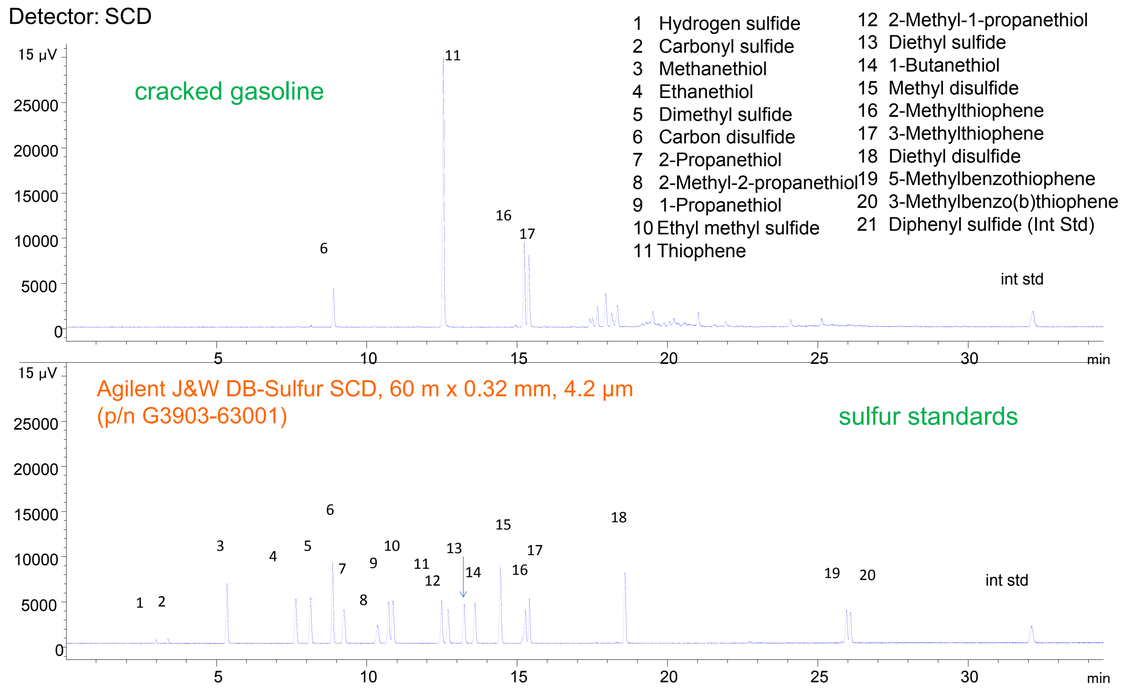


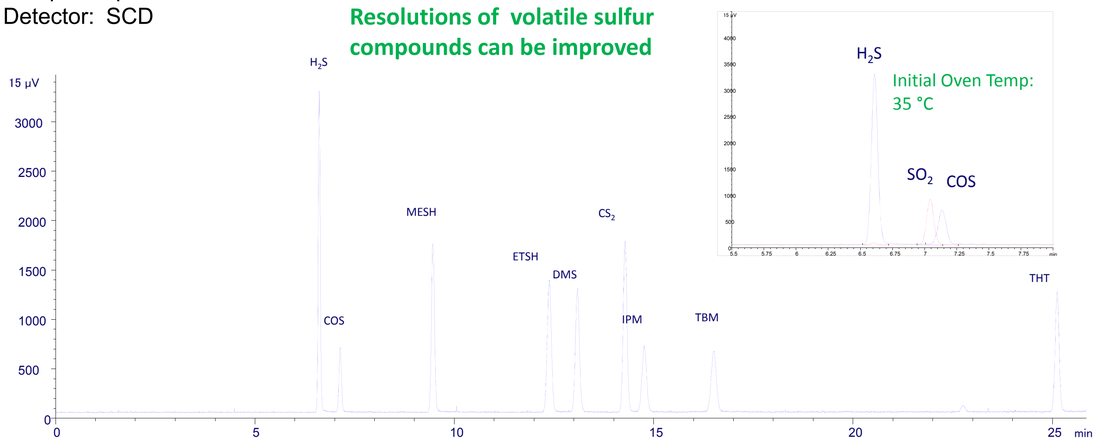
Figure 4. Hydrogen sulfide and carbonyl sulfide can be separated very well at ambient temperature, which avoids cryogenic cooling. The DB-Sulfur SCD column can provide excellent resolution, peak shape, and response for about 20 polar and reactive sulfur compounds due to its low bleed and improved inertness performance.

Sulfur compounds in Natural Gas

Column: Agilent J&W DB-Sulfur SCD, 70 m x 0.53 mm, 4.3 µm
Deactivated Fused Silica Tubing, 1 m x 0.18 mm,
Inlet: Split/Splitless, 240 °C , Split ratio 10 :1
Oven: 35 °C (2 min), 10 °C/min to 80 °C (6 min), 15 °C /min to 220 °C (10 min)
Sample loop: 1mL
Detector: SCD

According to ASTM D5504

Resolutions of volatile sulfur compounds can be improved



Column: Agilent J&W DB-Sulfur SCD, 70 m x 0.53 mm, 4.3 µm
Inlet: VI, 200 °C, 4 :1
Oven: 35 °C (2 min), 10 °C/min to 80 °C (6 min), 15 °C /min to 220 °C (10 min)
Sample loop: 1mL
Detector: SCD

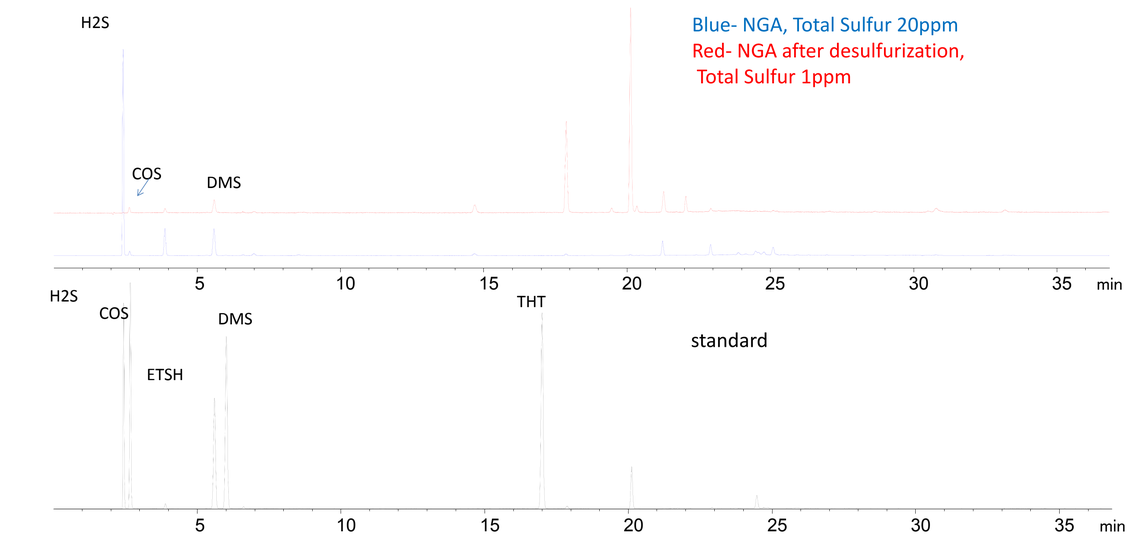


Figure 6. The analysis of sulfur compounds in natural gas

Conclusion

Agilent New DB-Sulfur SCD column successfully deployed in multiple hydrocarbon production laboratories with

- Column in service for 7 months with no signs of degradation
- Increased SCD detector stability
- Reduction in instrument recalibration
- Reduction in column replacement
- Low bleed and exceptional inertness, which provides good resolution and peak shape to the reactive sulfur compounds.