

Column Selection for Speciation of Sulfur Compounds in Natural Gas

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Natural gas is a complex mixture of low molecular weight hydrocarbons, inert gases and other impurities including a variety of sulfur containing compounds. Raw natural gas containing significant amounts of hydrogen sulfide and other organic sulfurs is typically processed to remove these compounds. Odorants are added to the final product to meet safety regulations. Testing of natural gas in its raw and refined states requires the use of chromatography systems that supply sufficient resolution of the hydrocarbons normally found in natural gas from any of the sulfur contaminants or odorants.

Wall coated open tubular (WCOT) columns coated with methyl silicone stationary phases have been successfully used for the separation of low molecular weight hydrocarbons. Analyzing low molecular weight sulfur compounds can also be performed on methyl silicone WCOT columns, but peak shape and sensitivity can be highly influenced by the inertness of the column. A comparison of different column deactivation strategies was evaluated for their impact on sulfur separation and low level analysis.

Porous layer open tubular (PLOT) columns have also been used for light hydrocarbon analysis. The separation mechanism for PLOT columns is significantly different than that observed for WCOT columns. The unique selectivity of different porous polymers can influence relative elution order of sulfur containing compounds versus low molecular weight hydrocarbons. A comparison illustrating elution order patterns and relative inertness of PLOT columns versus WCOT columns for sulfur analysis will be shown.

Instrument Conditions

Oven : 40°C (hold 5.0 min.)
 : 10°C/minute to 220°C (hold 2.0 min.)
Carrier Gas : Helium (10.0psi)
Injector Temp : 250°C
Split Injection : split vent flow rate 10ml/min
 : 2mm ID, single gooseneck Sky™ injection port liner
Sample Introduction: 6-port Sulfinert® treated valve and sample loop (250uL)
Sample Concentrations: Sulfur containing compounds – approximately 1ppmv in
 Natural Gas
Detector Temp. (PFPD):250°C

Columns tested

Rtx-1 – 30m x 0.32mm ID x 5.0um df
Rt-QBOND – 30m x 0.32mm ID x 10um df
Rt-SBOND – 30m x 0.32mm ID x 10um df
Rt-UBOND – 30m x 0.32mm ID x 10um df

Peak Identification

- A. methane
- B. ethane
- C. propane
- D. butane
- E. pentane

- 1. hydrogen sulfide
- 2. carbonyl sulfide
- 3. methyl mercaptan
- 4. ethyl mercaptan
- 5. dimethyl sulfide
- 6. carbon disulfide
- 7. 2-propanethiol
- 8. 2-methyl-2-propanethiol
- 9. 1-propanethiol
- 10. ethyl methyl sulfide
- 11. 1-methyl-1-propanethiol
- 12. thiophene
- 13. 2-methyl-1-propanethiol
- 14. diethyl sulfide
- 15. 1-butanethiol
- 16. 2-methylthiophene
- 17. 3-methylthiophene
- 18. tetrahydrothiophene

PFPD detection

The Pulsed Flame Photometric Detector (PFPD) used in this study is a highly sensitive and selective detector for sulfur. This detector contains a dual mode capability for selective and separate detection of hydrocarbons and sulfur containing compounds. Simultaneous detection of hydrocarbon response and sulfur response was capable with this detector while maintaining selective and specific detection for each group of analytes.

Separations on Rtx-1

Dimethyl polysiloxane stationary phases provide good retention and resolution for hydrocarbons as well as a broad range of sulfur containing compounds. For retaining volatile sulfur compounds, a low β (thick film) stationary phase is required to improve retention and inertness. Although the β value for the column in this study was fairly low, the retention times for the hydrocarbons typically found in natural gas were relatively short. Resolution was achieved for low molecular weight hydrocarbons and sulfur containing compounds, however, the relative retention time of hydrogen sulfide compared to the hydrocarbons was less than desired. When analyzing sour gas samples, large

concentrations of hydrogen sulfide may interfere with the quantitation of ethane and propane. Conversely, quantitating hydrogen sulfide in the presence of large concentrations of co-eluting hydrocarbons may be problematic when using dual mode detectors like the PFPD.

Thick film Rtx-1 type stationary phases are universally used for sulfur measurement due to their exceptional inertness. Their stability at high temperature even for thick stationary phase films allows these columns to separate volatile as well as less volatile sulfur compounds. Figure 1 demonstrates the separation of low as well as high molecular weight sulfur containing compounds.

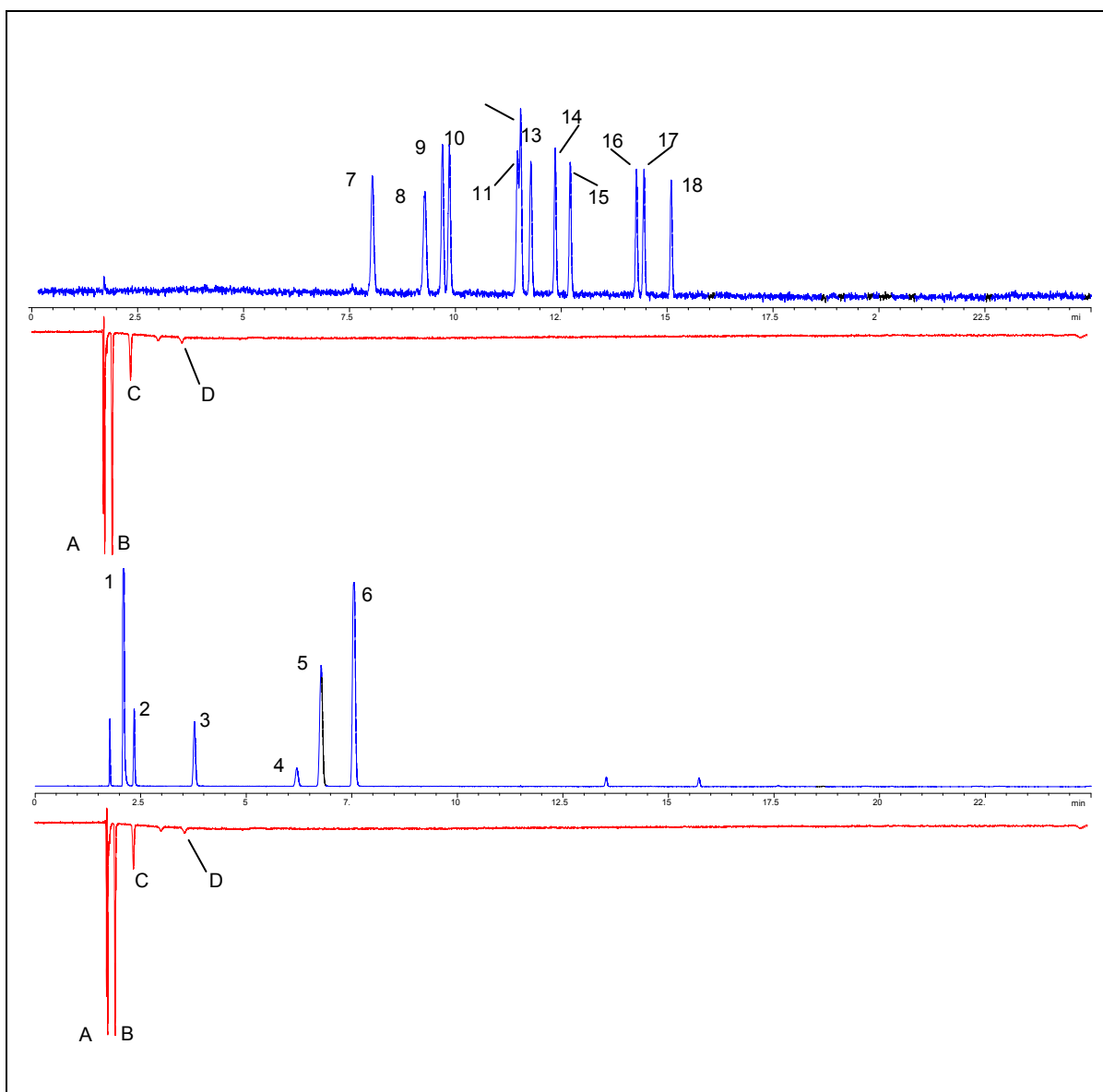


Figure 1 – Low and high molecular weight sulfur compounds on the Rtx-1 column

Figure 2 shows an expanded view of the volatile sulfur separation in Figure 1. H₂S and COS are well resolved from each other in the sulfur trace, but COS elutes with propane in the hydrocarbon trace. When analyzing natural gas, this co-elution is not a problem due to the relatively low concentrations of propane in natural gas. But for applications where the matrix is propylene or propane, the presence of large quantities of co-eluting hydrocarbons can have a quenching effect on the sulfur signal. For samples containing large concentrations of propylene or propane, a different type of column should be used to maximize the separation of hydrocarbons relative to the sulfur compounds.

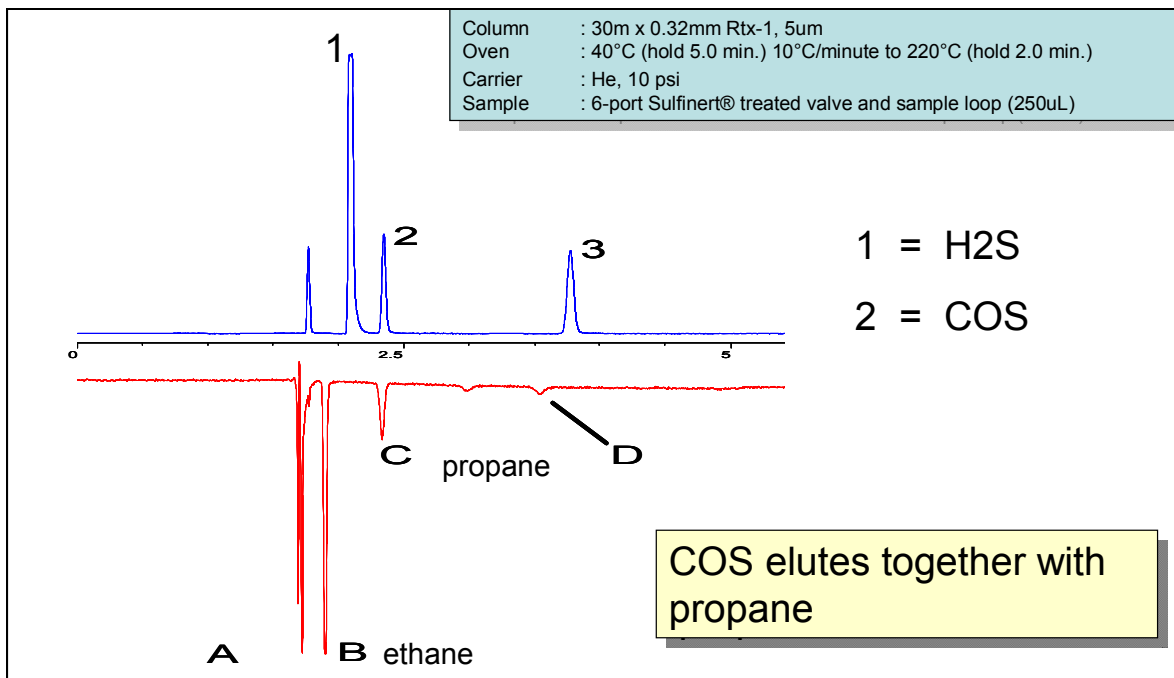


Figure 2 – Volatile sulfur gases on the Rtx-1 column

When testing for trace amounts of sulfur in hydrocarbon samples, large injections may be required to attain adequate sensitivity for ultra-low levels of sulfur. Wide bore columns are more suitable for the higher carrier gas flow rates needed for large sample sizes. When employing a wide bore column instead of a narrower bore column, the β value of the column should be held constant in order to maintain the separation between the most volatile hydrocarbons and as well as the volatile sulfur compounds. A 7um stationary phase film thickness is the preferred column configuration when using a 0.53mm ID column for volatile sulfur analysis.

Sulfur compounds on Rt-Q-BOND

The Rt-Q-BOND column is composed of 100% divinylbenzene. This porous polymer is the least polar of all the porous polymer PLOT columns. It exhibits good retention and separation for C1 through C5 hydrocarbons and also exhibits high retention for low molecular weight sulfur compounds. However, carbon disulfide and dimethyl sulfide are not resolved on this stationary phase. Hydrogen sulfide is well resolved from ethane and propane, but it exhibits a small degree of tailing indicating this column may not be as inert as other columns and hence not suitable for analysis of lower concentrations of sulfur containing compounds. When analyzing volatile sulfurs at concentrations above 1 ppm, the Rt-Q-BOND column provides adequate response and resolution for most compounds and offers good thermal stability at temperatures up to 300°C (See Figure 3 below).

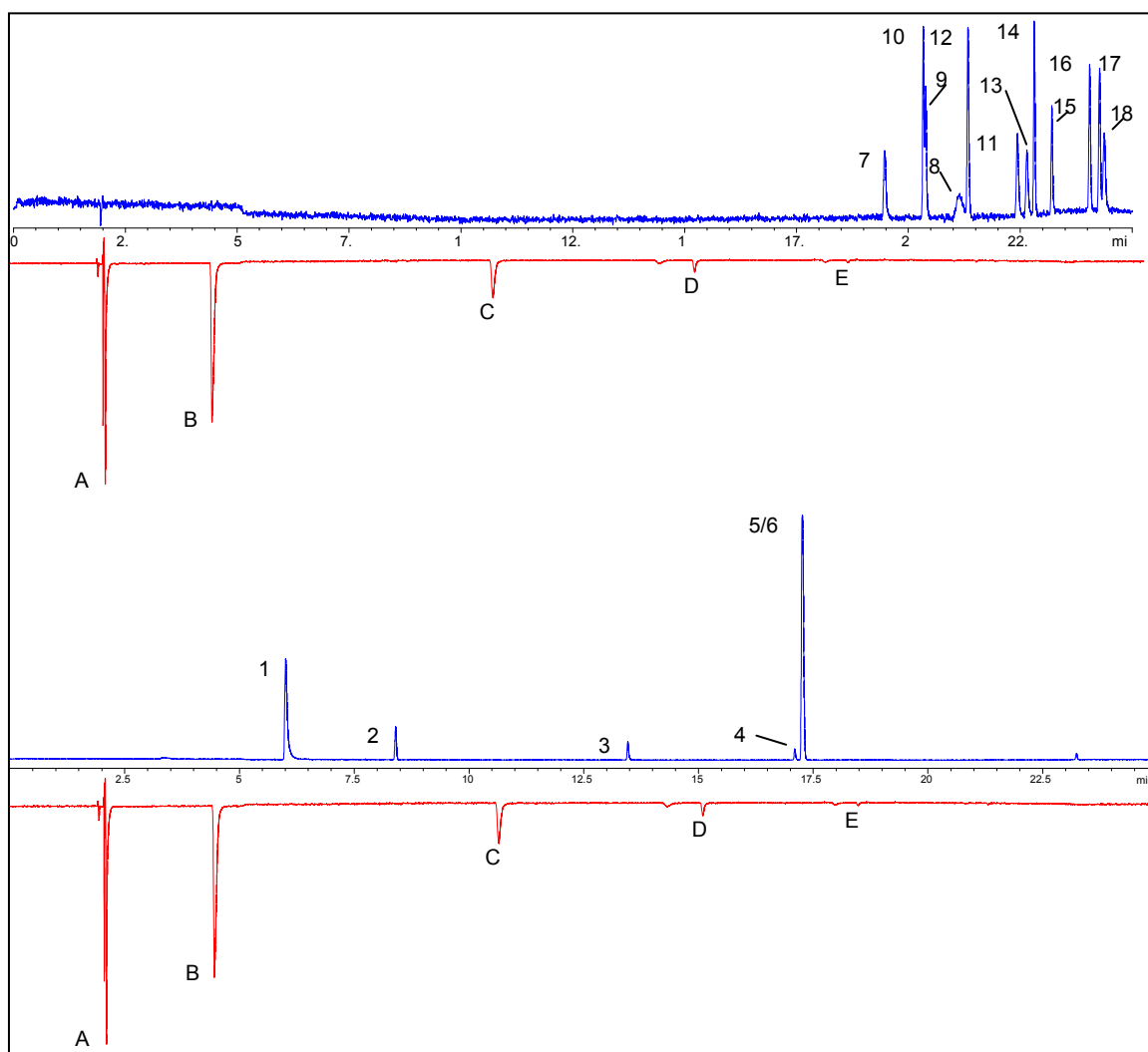


Fig. 3 – Low and high molecular weight sulfur compounds on the Rt-Q-BOND column

Sulfur compounds on Rt-S-BOND

The Rt-S BOND column is manufactured with a porous layer that incorporates 4-vinylpyridine into the divinylbenzene substrate. Although the column exhibits good resolution for the hydrocarbons and adequate resolution for the higher molecular weight sulfur containing compounds, significant problems are apparent in the analysis of low molecular weight sulfur containing compounds. Hydrogen sulfide, methyl mercaptan and ethyl mercaptan were irreversibly adsorbed at the concentrations used in this study. At higher concentrations, a peak response could be achieved for these analytes, but all three peaks exhibited severe tailing indicating inertness problems for sulfur containing compounds when using this stationary phase (See Figure 4 below).

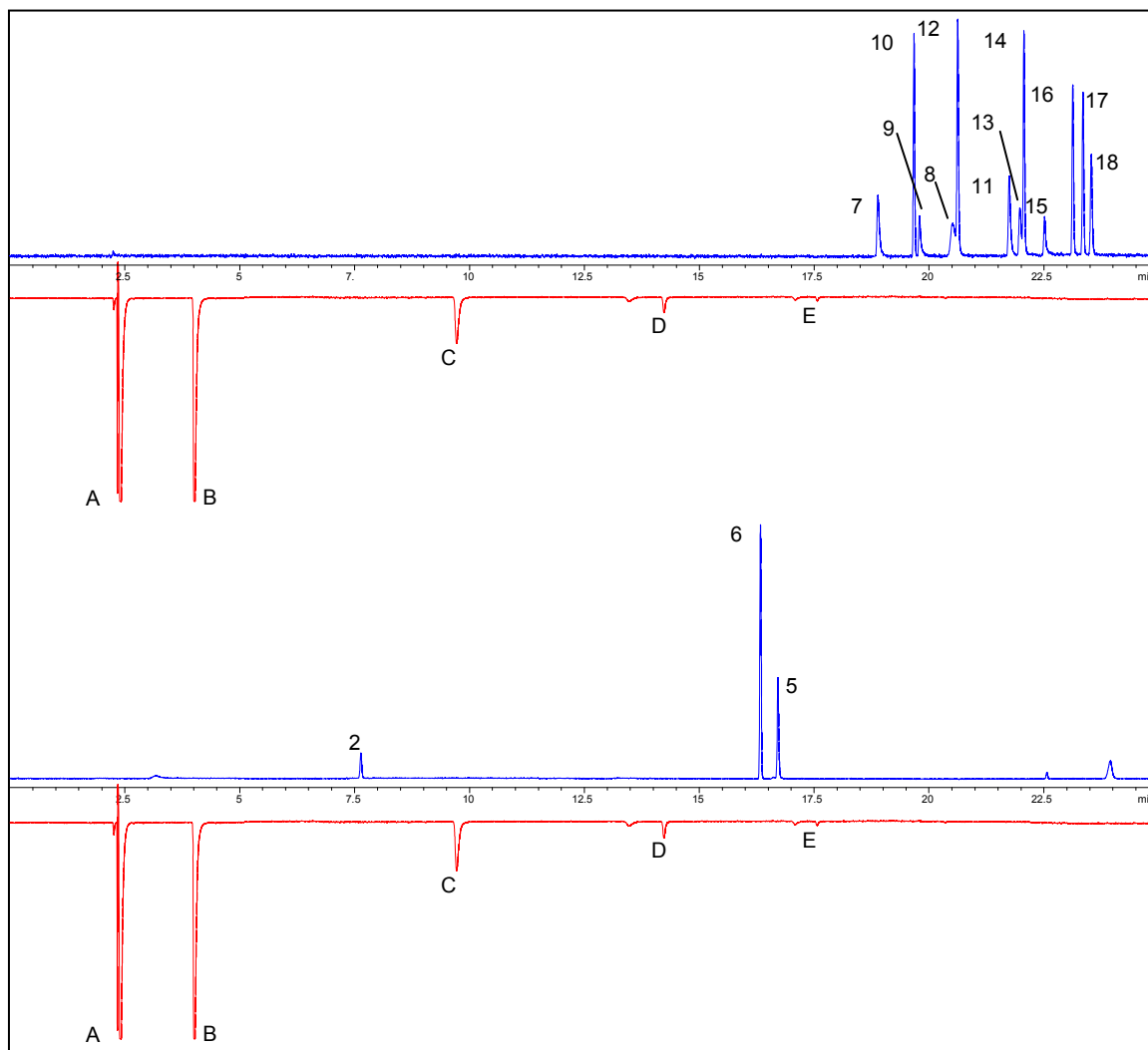


Figure 4 - Low and high molecular weight sulfur compounds on the Rt-S-BOND column

Sulfur compounds on Rt-U-BOND

The Rt-UBOND column is coated with a porous layer that incorporates ethylene glycol/dimethacrylate into the divinylbenzene substrate. The Rt-UBOND column provides excellent peak shape and response for polar compounds including the low molecular weight sulfur containing compounds (See Figure 5 below).

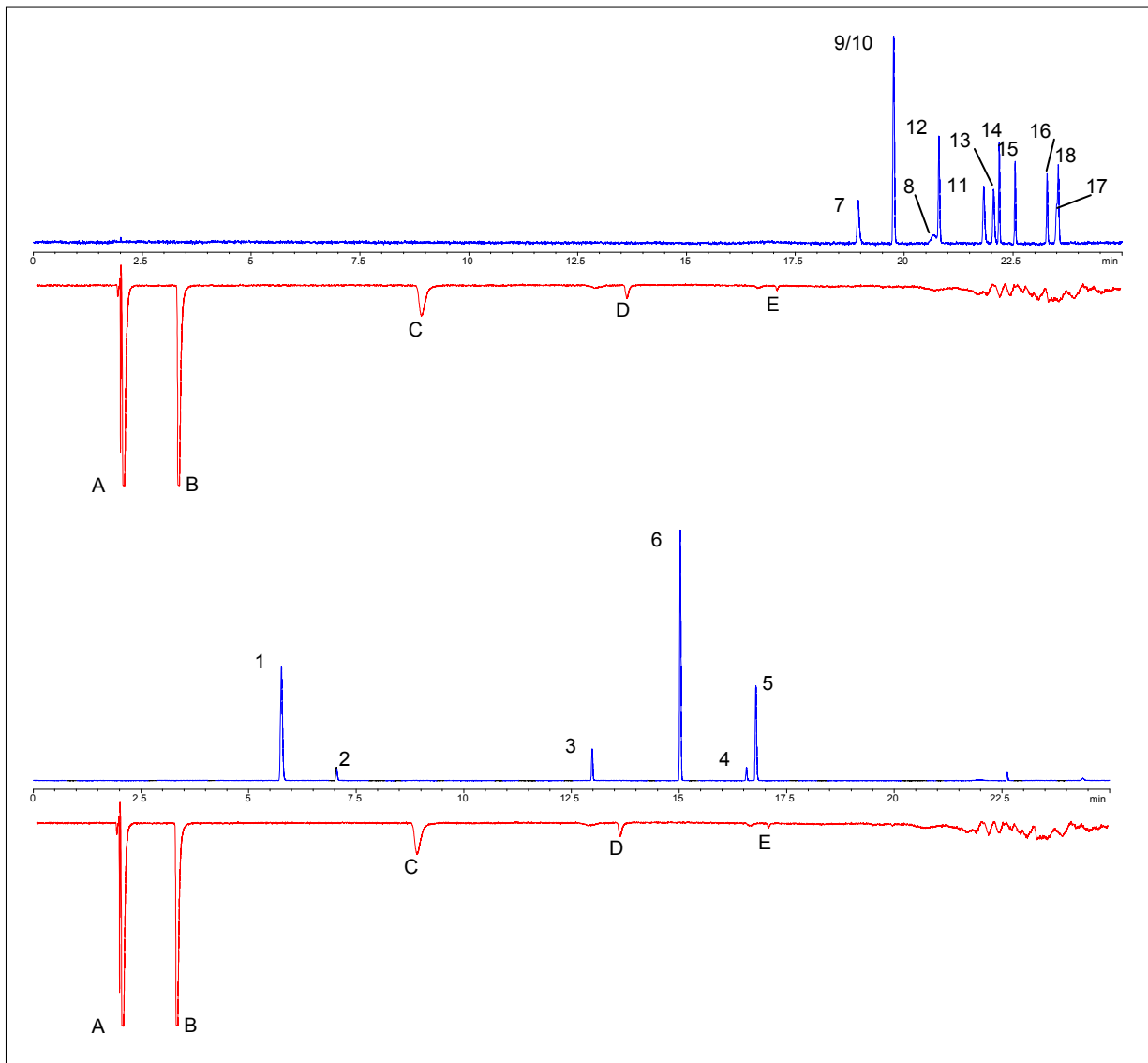


Fig. 5 - Low and high molecular weight sulfur compounds on the Rt-U-BOND column

The chromatogram in Figure 6 below shows an expanded view of the hydrogen sulfide and carbonyl sulfide peak shapes on the Rt-U-BOND column. Both compounds demonstrate good response and symmetrical peak shapes, which indicates that the Rt-U-BOND column has the best inertness performance out of all the PLOT columns in this study, even at low ppm concentrations.

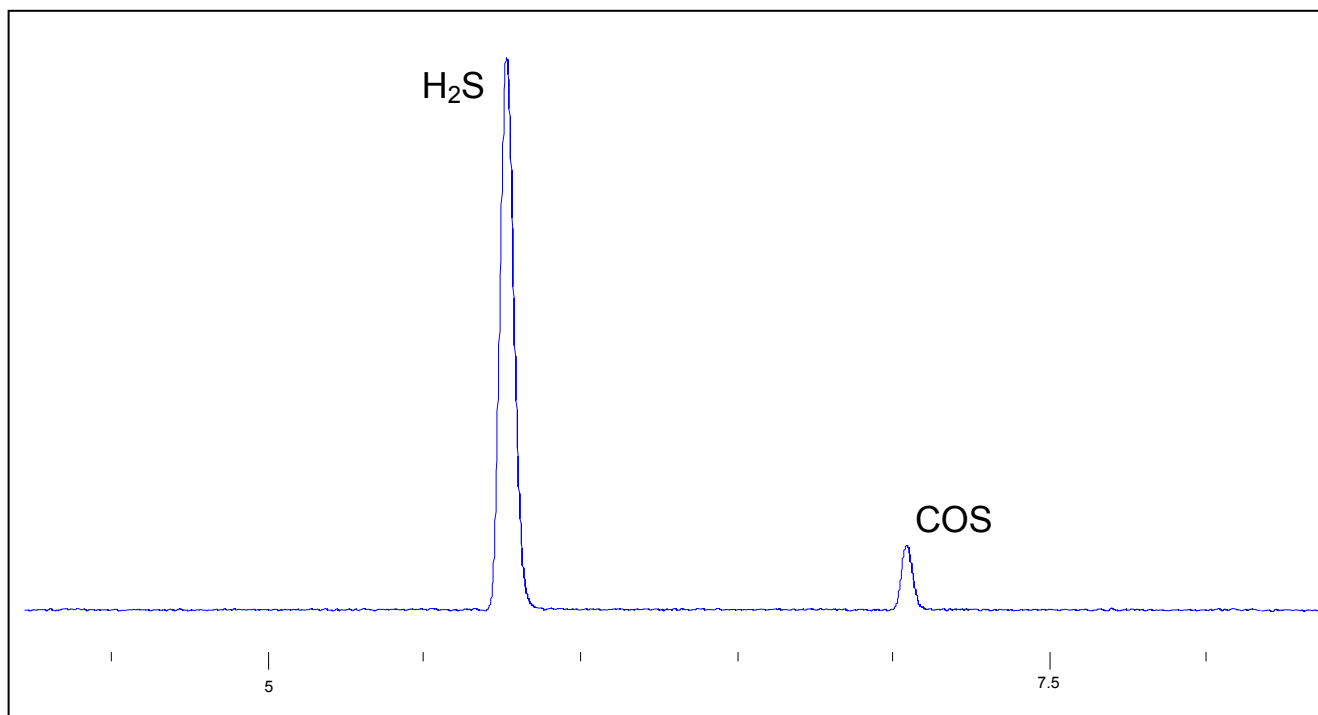


Figure 6 - H_2S and COS chromatograph with symmetrical peak shapes and excellent response on the Rt-U-BOND column.

The Rt-U-BOND column is an ideal candidate for analyzing low molecular weight sulfur compounds in light hydrocarbons streams. As demonstrated in Figure 7 below, H₂S and COS elute from the Rt-U-BOND column in between ethane and propane. The amount of separation between both the hydrocarbons and the sulfur compounds allows for trace amounts of these compounds to be analyzed in the presence of high concentrations of any of the other three. For samples of LNG or sour gas, or for purity analyses of ethylene, propylene or propane, the volatile sulfur gases should be well resolved from the large concentrations of hydrocarbons in these samples.

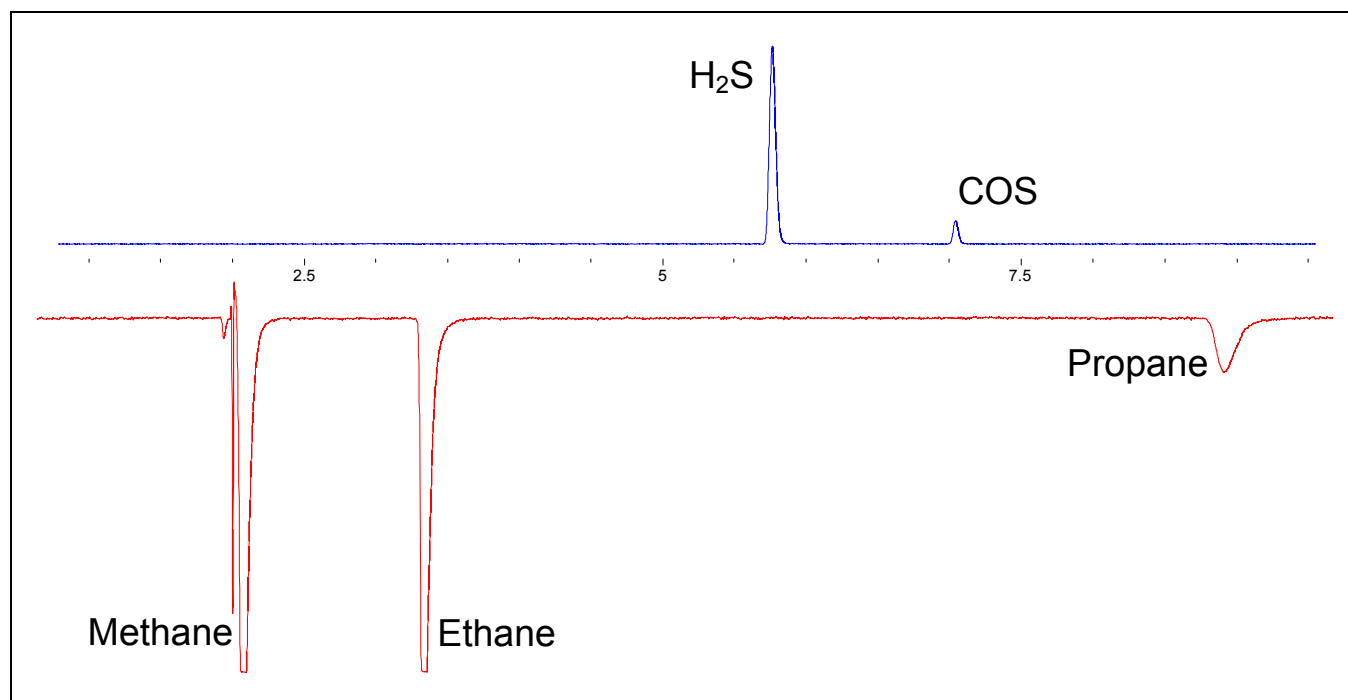


Figure 7 – Volatile sulfur gases are well resolved from low molecular weight hydrocarbons on the Rt-U-BOND column.

As noted in Figure 5 above, higher molecular weight sulfur containing compounds will elute from the Rt-U-BOND column, but only if the column is operated above the maximum recommended operating temperature. When used at elevated temperatures, the Rt-U-BOND column does exhibit higher than normal background as seen in the hydrocarbon trace in Figure 5. However, even though the column was used at higher than recommended temperatures, the peak shapes for high molecular weight sulfur containing compounds were still symmetrical indicating improved inertness performance for the Rt-U-BOND column compared to the other PLOT columns in this study.

System inertness

In addition to selecting a column for sulfur analysis which demonstrates superior inertness and resolution, consideration should also be given to instrument components and sample pathways. Sulfurs are highly reactive compounds and will adsorb onto untreated or non-passivated metal surfaces. When testing for trace levels of sulfur compounds, it is very important to use properly deactivated transfer lines, injection port liners, sample valves and sample loops. Sulfur standards should be manufactured and stored in specially deactivated cylinders. Samples for analysis should also be collected in properly deactivated air cans or sample cylinders.

Siltek[®] and Sulfinert[®] deactivation technology can significantly improve the recovery of volatile sulfur compounds. These treatments can be applied to tubing, valve parts and instrument parts and supplies. Any metal surface that comes in contact with the sample during collection, storage or analysis should be passivated with one of these treatments to maximize sulfur response.

Conclusions

Rtx-1 columns provide better thermal stability than porous polymer PLOT columns. The increased temperature range can be used to speed up the elution of higher molecular weight compounds as well as provide more flexibility in designing temperature ramps to improve resolution between minimally separated compounds.

Although methyl silicone columns like the Rtx-1 column are widely used for analyzing volatile sulfurs in light hydrocarbon stream, PLOT columns can offer a significant advantage in improved resolution.

PLOT columns offer increased separation between low molecular weight hydrocarbons and also provide a unique selective retention for low molecular weight sulfur compounds. The combination of these two features allows tuning of the separation to achieve complete resolution of the sulfur compounds in the presence of large concentrations of hydrocarbons.

The Rt-U-BOND column provides the best overall separation for all the sulfur compounds tested in this study. The selectivity and inertness of this PLOT column also provides the separation required for trace sulfur gas analysis in high purity propylene, propane and ethylene.

Potential co-elutions between hydrocarbons and sulfur containing compounds are well resolved on the Rt-U-BOND column allowing the use of a selective detector like the PFPD. This detector contains a dual mode capability for selective and separate detection of hydrocarbons and sulfur containing compounds.

Porous polymer PLOT columns may not be as suitable for analyzing higher molecular weight sulfur containing compounds as the Rtx-1 WCOT columns. The maximum operating temperature for many PLOT columns is at or near the elution temperature for many of these compounds.

When performing sulfur speciation in natural gas samples and other light hydrocarbon streams, understanding the potential sample composition will help determine column separation requirements relative to molecular weight and elution temperatures.

Acknowledgement

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