Petrochemical Applications

Analyze ppb Level Sulfur Compounds Using an Rt®-XLSulfur Micropacked GC Column or an Rtx®-1 Thick Film Capillary GC Column

Sulfur compounds in petroleum streams can have detrimental effects on the performance and longevity of the catalysts used in hydrocarbon processing. Furthermore, the toxicity and odor associated with sulfur compounds is of significant environmental importance. In short, to protect both processing equipment and the environment, the ability to quantify sulfur compounds to ppb levels is imperative.

Gas chromatography is the method of choice for analyzing ppb level sulfur compounds in petroleum streams. Both packed and capillary GC columns have been successfully used for analyzing sulfurs and hydrocarbons in petroleum, although this often is a difficult application. With packed columns, the choice of column tubing is critical for accurate determination of sulfur compounds, particularly at low concentrations. Analyses on glass, PTFE, or stainless steel columns all present distinct problems. Glass columns exhibit poor inertness and lack ruggedness for field or process control use, and results are subject to variability because of column-to-column variation in ID. PTFE tubing, although more robust than glass, is plagued by three significant problems: 1) shrinkage as the column cools causes back diffusion of oxygen and water into the packing material which, if not addressed, can cause retention times to vary by as much as 15%; 2) oxygen and water diffuse through the tubing wall, significantly decreasing column longevity and creating reproducibility problems; and 3) a maximum column temperature limit of only 210 °C makes it impossible to quickly elute high molecular weight sulfur compounds. Without specialized surface passivation, stainless steel columns simply do not offer the inertness needed to monitor active sulfur compounds at ppb levels.

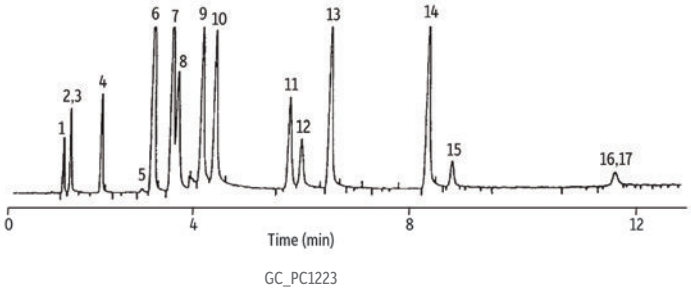
One of the proven approaches for analyzing ppb level sulfur compounds by GC is to use a thick film, 100% polydimethylsiloxane Rtx®-1 capillary column. Figure 1 illustrates the analysis of sulfur compounds on a 60 m x 0.53 mm ID x 7 µm Rtx®-1 column. The thick film is needed to resolve the volatile sulfur compounds, but makes for long retention times for higher molecular weight sulfur compounds. Alternatively, a 30 m x 0.32 mm ID x 4 µm Rtx®-1 column can be used to analyze higher molecular weight sulfur compounds, such as thiophenes.

Another excellent approach for analyzing low molecular weight sulfur compounds is the use of micropacked columns. The Rt®-XLSulfur micropacked column contains a specially deactivated divinylbenzene porous polymer in stainless steel tubing, deactivated through the Sulfinert® passivation process. The inertness of both the packing material and the tubing ensure a column that is capable of analyzing active sulfur compounds to 10 ppb. Moreover, the Rt®-XLSulfur micropacked column displays minimal bleed, well within the limits necessary for ppb level sulfur analysis, after a brief conditioning period (<30 minutes). The maximum temperature limit, 310 °C, allows rapid elution of the higher molecular weight analytes. This column achieves the critical separation of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and sulfur dioxide (SO_2), as defined in the International Society of Beverage Technologists (ISBT) Procedure 14.0. Figure 2 shows the highly volatile H_2S and COS separated using a 1 m x 0.75 mm ID Rt®-XLSulfur micropacked column. Additionally, these volatile sulfur compounds are well-retained and well-resolved from the hydrocarbons that could interfere with quantification on some sulfur-specific detectors (Figure 3).

RESTEK
Freude an Chromatografie

Note that to achieve this high level of sensitivity, every component of the sample pathway must be inert: the porous polymer, the column tubing, the column end fittings, and, additionally, the sample loop and/or inlet liner. Sample pathways in the analyses shown in Figures 1 through 3 were passivated using the Sulfinert® deactivation process. Figure 4 shows a schematic diagram of a system designed to analyze volatile and reactive sulfur compounds. From the Sulfinert®-treated sample cylinder used to collect and store the sample, to the Sulfinert®-treated valve and sample loop used to transfer the sample to the GC system, to either the inert capillary or packed column, Restek offers a complete line of products to ensure consistent and reliable analysis of ppb level sulfur compounds in petroleum streams.

Figure 1: Sulfur compounds on a thick film Rtx®-1 capillary column.

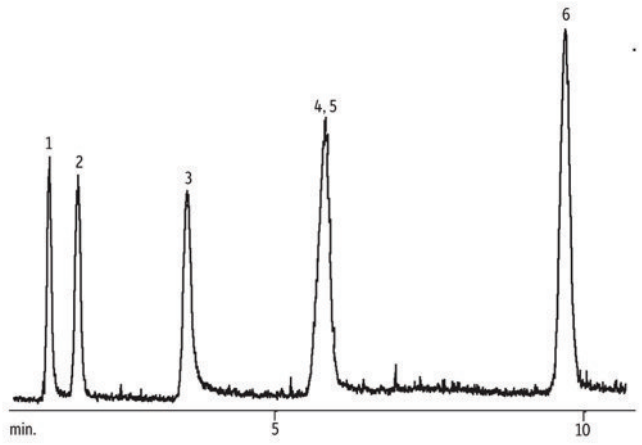


GC_PC1223

Peaks
1. Hydrogen sulfide
2. Sulfur dioxide
3. Carbonyl sulfide
4. Methyl mercaptan
5. Ethyl mercaptan
6. Carbon disulfide
7. Dimethyl sulfide
8. 2-Propyl mercaptan
9. Allyl mercaptan
10. 1-Propyl mercaptan
11. Ethyl sulfide
12. Butyl mercaptan
13. Dimethyl disulfide
14. Allyl sulfide
15. Propyl sulfide
16. Butyl sulfide
17. Allyl disulfide

Column	Rtx®-1, 60 m, 0.53 mm ID, 7.00 µm (cat.# 10193)
Sample	
Conc.:	~10 ppm each
Injection	
Inj. Vol.:	100 µL direct
Inj. Temp.:	50 °C
Oven	
Oven Temp:	50 °C to 200 °C at 15 °C/min.
Carrier Gas	He, constant linear velocity
Linear Velocity:	30 cm/sec. @ 50 °C
Detector	FPD @ 230 °C

Figure 2: An Rt®-XLSulfur micropacked column exhibits excellent inertness for low ppbv levels of sulfur compounds.

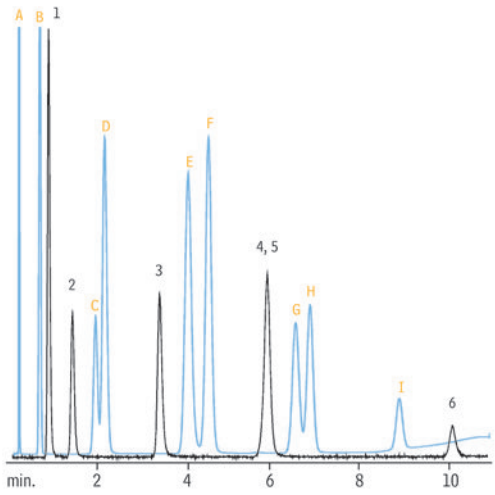


GC_PC1221

Peaks
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Column	Rt®-XLSulfur, 1 m, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	1 mL of 50 ppbv each sulfur compound
Injection	sample valve
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD

Figure 3: Sulfur compounds resolved from C1-C6 hydrocarbons, using an Rt®-XLSulfur micropacked column.



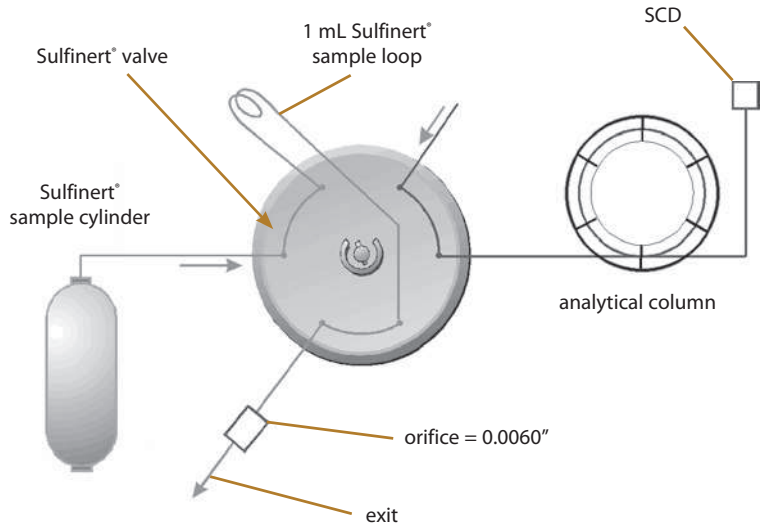
GC_PC00436

Sulfurs
1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Dimethyl sulfide
6. Dimethyl disulfide

Hydrocarbons
A. Methane
B. Ethane
C. Propylene
D. Propane
E. Isobutane
F. Butane
G. Isopentane
H. Pentane
I. Hexane

Column	Rt®-XLSulfur, 1m, 0.95mm OD, 0.75 mm ID (cat.# 19806)
Sample	
Conc.:	50 ppb each
Injection	packed not on-column
Oven	
Oven Temp:	60 °C to 230 °C at 15 °C/min.
Carrier Gas	He, constant flow
Flow Rate:	9 mL/min.
Detector	SCD/FID
Acknowledgement	Sulfur standards courtesy of DCG Partnership 1 Ltd., Pearland, TX.

Figure 4: Analytical system designed to analyze volatile and reactive sulfur compounds.



Lit. Cat.# PCAN1499-UNV

Restek U.S. • 110 Benner Circle • Bellefonte, PA 16823 • 1-814-353-1300 • 1-800-356-1688 • fax: 1-814-353-1309 • **www.restek.com**
Restek France • phone: +33 (0)1 60 78 32 10 • fax: +33 (0)1 60 78 70 90 • e-mail: restek@restekfrance.fr
Restek GmbH • phone: +49 (0)6172 2797 0 • fax: +49 (0)6172 2797 77 • e-mail: info@restekgmbh.de
Restek Ireland • phone: +44 (0)2890 814576 • fax: +44 (0)2890 814576 • e-mail: restekireland@aol.com
Restek Japan • phone: +81 (3)6459 0025 • fax: +81 (3)6459 0025 • e-mail: restekjapan@restek.com
Thames Restek U.K. LTD • phone: +44 (0)1494 563377 • fax: +44 (0)1494 564990 • e-mail: sales@thamesrestek.co.uk