

## Analyze Sulfur Compounds at ppb Levels, Using an Rt-XLSulfur Micropacked GC Column or an Rtx<sup>fi</sup>-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 sulfurs is of significant environmental importance. In short, to protect both processing equipment and the environment, ability to quantify sulfur compounds to ppb levels is imperative.

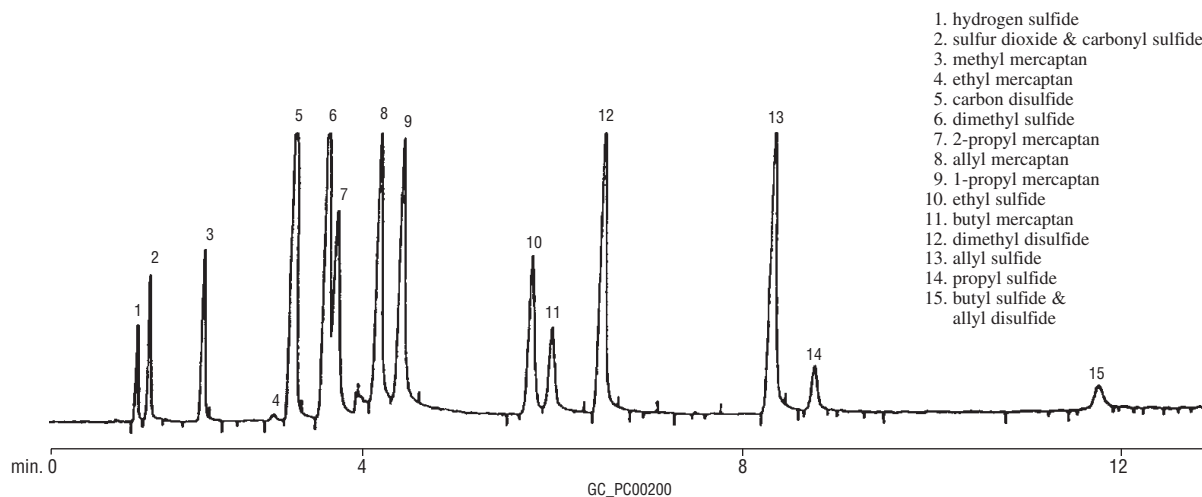
Gas chromatography is the method of choice for the analysis of sulfur compounds. Both packed and capillary GC columns have been successfully used for this application. Although gas chromatographic analysis of the sulfur compounds in petroleum streams is important, this often is a difficult application. With packed columns, the choice of column tubing is critical for accurate determination of sulfur compounds, particularly at low concentrations. Analyses on glass, Teflon<sup>®</sup>, 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. Teflon<sup>®</sup> 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; 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 sulfur compounds by GC is to use a thick film, 100% polydimethylsiloxane Rtx<sup>®</sup>-1 capillary column. Figure 1 illustrates the analysis of sulfur compounds on a 60-meter x 0.53mm ID x 7µm Rtx<sup>®</sup>-1 column. The thick film is needed to resolve the volatile sulfur compounds, but makes for long retention times for higher molecular weight

Figure 1

*Sulfur compounds on a thick film Rtx<sup>®</sup>-1 capillary column.*

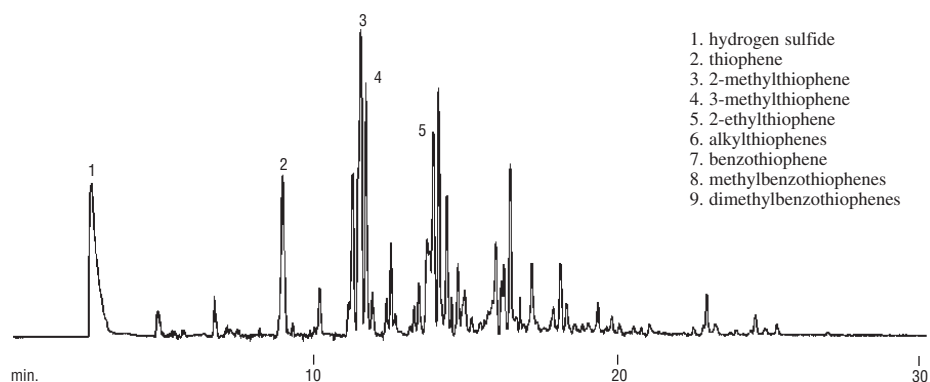


1. hydrogen sulfide
2. sulfur dioxide & carbonyl sulfide
3. methyl mercaptan
4. ethyl mercaptan
5. carbon disulfide
6. dimethyl sulfide
7. 2-propyl mercaptan
8. allyl mercaptan
9. 1-propyl mercaptan
10. ethyl sulfide
11. butyl mercaptan
12. dimethyl disulfide
13. allyl sulfide
14. propyl sulfide
15. butyl sulfide & allyl disulfide

60m, 0.53mm ID, 7.0µm Rtx<sup>®</sup>-1 (cat.# 10193)  
 100µL direct injection of sulfur compounds, approximately 10ppm each.  
**Oven temp.:** 50°C to 200°C @ 15°C/min.; **Inj. / det. temp.:** 50°C / 230°C;  
**Carrier gas:** helium; **Linear velocity:** 30cm/sec. set @ 50°C; **Det.:** FPD

Figure 2

Higher weight sulfur compounds on a 30-meter Rt<sup>x</sup>-1 column with a 4.0 $\mu$ m phase film.



- 1. hydrogen sulfide
- 2. thiophene
- 3. 2-methylthiophene
- 4. 3-methylthiophene
- 5. 2-ethylthiophene
- 6. alkylthiophenes
- 7. benzothiophene
- 8. methylbenzothiophenes
- 9. dimethylbenzothiophenes

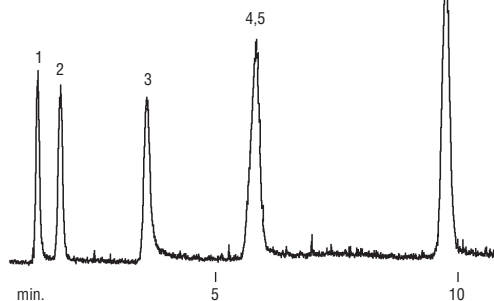
30m, 0.32mm ID, 4.0 $\mu$ m Rt<sup>x</sup>-1 (cat.# 10198), 1.0 $\mu$ L split injection of naphtha containing 500ppm total sulfur compounds.

Oven temp.: 35°C to 275°C @ 10°C/min. (hold 5 min.);  
Inj./det. temp.: 275°C; Det.: atomic emission detector (181nm);  
Carrier gas: helium; Linear velocity: 24cm/sec. (0.8mL/min.); Split ratio: 10:1

Figure 3

An Rt-XLSulfur<sup>TM</sup> micropacked column exhibits excellent inertness for low ppbv-levels of sulfur compounds.

- 1. hydrogen sulfide
- 2. carbonyl sulfide
- 3. methyl mercaptan
- 4. ethyl mercaptan
- 5. dimethyl sulfide
- 6. dimethyl disulfide

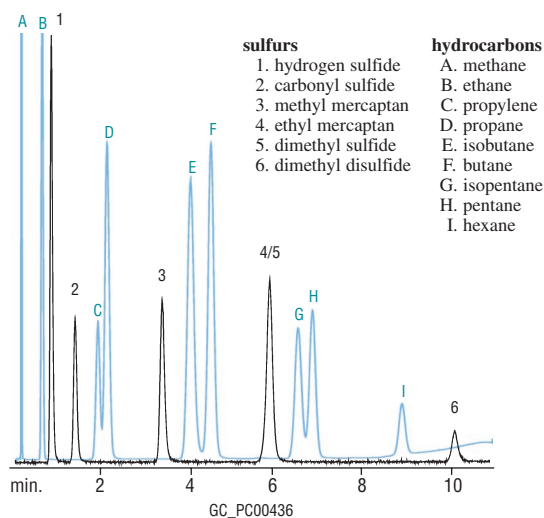


1m, 0.75mm ID Rt-XLSulfur<sup>TM</sup> micropacked column (cat.# 19806)

Conc.: 1mL of 50ppbv each sulfur compound; Oven temp.: 60°C to 230°C @ 15°C/min.; Carrier gas: helium; Flow rate: 9mL/min.; Det.: sulfur chemiluminescence detector (SCD)

Figure 4

Sulfur compounds resolved from C1-C6 hydrocarbons, using an Rt-XLSulfur<sup>TM</sup> micropacked column.



- 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

1m, 0.75mm ID Rt-XLSulfur<sup>TM</sup> micropacked column (cat.# 19806)

Conc.: 50ppb each analyte; Oven temp.: 60°C to 230°C @ 15°C/min.; Carrier gas: helium; Flow rate: 9mL/min.; Det.: SCD/FID

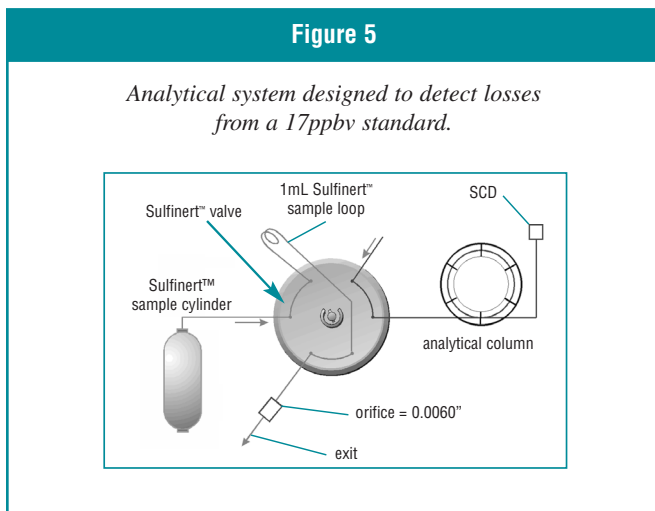
Sulfur standard courtesy of DCG Partnership 1 Ltd., Pearland, TX.

sulfur compounds. Alternatively, a 30-meter, 0.32mm ID, 4µm Rtx®-1 column can be used to analyze higher molecular weight sulfur compounds, such as thiophenes (Figure 2).

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 Restek's state-of-the-art 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 10ppb. Moreover, the Rt-XLSulfur™ micropacked column displays minimal bleed, well within 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<sub>2</sub>S), carbonyl sulfide (COS), and sulfur dioxide (SO<sub>2</sub>), as defined in the International Society of Beverage Technologists (ISBT) Procedure 14.0. Figure 3 shows the highly volatile H<sub>2</sub>S and COS separated using a 1-meter, 0.75mm 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 4).

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 sleeve. Sample pathways in the analyses shown in Figures 1 through 4 were passivated using Restek's Sulfinert™ deactivation process. Figure 5 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 sulfur compounds.

For more information about the Sulfinert™ passivation technique, request a copy of Restek's brochure on Sulfinert™ coatings (Lit. cat.# 59203).



## Product Listing

### Rt-XLSulfur™ Micropacked Columns

Other column dimensions can be prepared on a custom basis. Please inquire. Purchase installation kit separately.

| OD     | ID (mm) | 1-Meter | 2-Meter |
|--------|---------|---------|---------|
| 1/16"  | 1.0mm   | 19804   | 19805   |
| 0.95mm | 0.75mm  | 19806   | 19807   |

### Installation Kits

|                        | for 0.75mm ID col. | for 1mm ID col. | for 2mm ID col. |
|------------------------|--------------------|-----------------|-----------------|
| For valve applications | 21062              | 21065           | 21067           |
| For split applications | 21063              | —               | —               |
| For all Agilent GCs    | 21064              | —               | —               |
| For direct injections  | —                  | 21066           | —               |

### Rtx®-1 Capillary Columns (Fused Silica)

(Crossbond® 100% dimethyl polysiloxane)

| ID     | df (µm) | temp. limits     | 15m   | 30m   | 60m   | 75m   | 105m  |
|--------|---------|------------------|-------|-------|-------|-------|-------|
| 0.32mm | 3.00    | -60 to 280/300°C | 10181 | 10184 | 10187 |       | 10190 |
|        | 4.00    | -60 to 280/300°C |       | 10198 |       |       |       |
|        | 5.00    | -60 to 260/280°C | 10176 | 10178 | 10180 |       |       |
| 0.45mm | 2.55    | -60 to 270/290°C |       |       |       | 10992 |       |
| 0.53mm | 3.00    | -60 to 270/290°C | 10182 | 10185 | 10188 |       | 10189 |
|        | 5.00    | -60 to 270/290°C | 10177 | 10179 | 10183 |       | 10194 |
|        | 7.00    | -60 to 240/260°C | 10191 | 10192 | 10193 |       |       |

The maximum temperatures listed are for 15- and 30-meter lengths. Longer lengths may have a slightly reduced maximum temperature.

### Sulfinert™ Welded 304 Grade Stainless Steel Tubing

Available in lengths from 5—400 feet. Call for details.

| ID              | OD              | cat.# |
|-----------------|-----------------|-------|
| 0.011" (0.28mm) | 0.022" (0.56mm) | 22500 |
| 0.021" (0.53mm) | 0.029" (0.74mm) | 22501 |
| 0.010" (0.25mm) | 1/16" (1.59mm)  | 22502 |
| 0.020" (0.51mm) | 1/16" (1.59mm)  | 22503 |
| 0.030" (0.76mm) | 1/16" (1.59mm)  | 22504 |
| 0.040" (1.02mm) | 1/16" (1.59mm)  | 22505 |
| 0.085" (2.16mm) | 1/8" (3.18mm)*  | 22506 |
| 0.210" (5.33mm) | 1/4" (6.35mm)*  | 22507 |

\*0.020" wall thickness

### Sulfinert™ Seamless 316 Grade Stainless Steel Tubing

Available in lengths from 5—400 feet. Call for details.

| ID              | OD              | cat.# |
|-----------------|-----------------|-------|
| 0.055" (1.40mm) | 1/8" (3.18mm)** | 22508 |
| 0.180" (4.57mm) | 1/4" (6.35mm)** | 22509 |

\*\*0.035" wall thickness

### Sulfinert™-Treated Sample Cylinders

- Sizes from 75cc to 2250cc.
- Durable 316 stainless steel.
- 1/4-inch female NPT threaded ends.
- D.O.T. rated to 1800psi at room temperature.



| Size   | qty. | cat.# |
|--------|------|-------|
| 75cc   | ea.  | 24130 |
| 150cc  | ea.  | 24131 |
| 300cc  | ea.  | 24132 |
| 500cc  | ea.  | 24133 |
| 1000cc | ea.  | 24134 |
| 2250cc | ea.  | 21394 |

### Sulfinert™ Sample Cylinder Valves

- Maximum operating pressure: 5000psig.
- Temperature range for KEL-F® stem tip: -20°F to 250°F (-29°C to 121°C).



| Description  | qty. | cat.# |
|--|------|-------|
| (A) 1/4" NPT Exit, KEL-F® Stem Tip                 | ea.  | 24127 |
| (B) 1/4" Compression Exit, KEL-F® Stem Tip         | ea.  | 24128 |
| (C) 1/4" Female NPT Outlet (built-in rupture disc) | ea.  | 21395 |

### Sulfinert™-Treated Gas Sampling Valves and Sample Loops

- Ideal for samples containing low-concentration sulfur compounds.
- Sample loop sizes from 5µL to 5cc.



### “W Type” Sulfinert™ Gas Sampling Valves 1/16" fittings, 0.40mm port diameter

| Description                            | qty. | cat.# |
|--|------|-------|
| Sulfinert™ Gas Sampling Valve; 4-Port  | ea.  | 20584 |
| Sulfinert™ Gas Sampling Valve; 6-Port  | ea.  | 20585 |
| Sulfinert™ Gas Sampling Valve; 10-Port | ea.  | 20586 |

### Replacement Rotors

| Description   | qty. | cat.# |
|---|------|-------|
| Replacement Rotor for 4-Port Sulfinert™ Gas Sampling Valve  | ea.  | 20587 |
| Replacement Rotor for 6-Port Sulfinert™ Gas Sampling Valve  | ea.  | 20588 |
| Replacement Rotor for 10-Port Sulfinert™ Gas Sampling Valve | ea.  | 20589 |

### Sulfinert™ Gas Sample Loops for “W Type” valves 1/16" fittings





| Sizes | qty. | cat.# |
|-------|------|-------|
| 5µL   | ea.  | 22840 |
| 10µL  | ea.  | 22841 |
| 20µL  | ea.  | 22842 |
| 25µL  | ea.  | 22843 |
| 50µL  | ea.  | 22844 |
| 100µL | ea.  | 22845 |
| 250µL | ea.  | 22846 |
| 500µL | ea.  | 22847 |
| 1cc   | ea.  | 22848 |
| 2cc   | ea.  | 22849 |
| 5cc   | ea.  | 22850 |

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**Other Trademarks:** KEL-F (3M Co.), Teflon (E.I. du Pont de Nemours & Co., Inc.)

### Sulfinert™-Treated Fittings

These are example products—a full line of 1/16", 1/8", and 1/4" fittings is available. Please refer to our catalog.

|   | Size          | qty. | cat.# |
|---|---------------|------|-------|
| <br><b>union</b>          | 1/16"         | ea.  | 22520 |
|   | 1/8"          | ea.  | 22521 |
|   | 1/4"          | ea.  | 22522 |
| <br><b>tee</b>            | 1/16"         | ea.  | 22526 |
|   | 1/8"          | ea.  | 22527 |
|   | 1/4"          | ea.  | 22528 |
| <br><b>reducing union</b> | 1/8" to 1/16" | ea.  | 22523 |
|   | 1/4" to 1/16" | ea.  | 22524 |
|   | 1/4" to 1/8"  | ea.  | 22525 |
| <br><b>elbow</b>         | 1/16"         | ea.  | 22529 |
|   | 1/8"          | ea.  | 22530 |
|   | 1/4"          | ea.  | 22531 |

**For information about having system components custom Sulfinert™-treated, contact our Technical Service group, 800-356-1688 or 814-353-1300, ext. 4, or contact your Restek representative.**

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