This bulletin describes the relative advantages, and some limitations, of six gas chromatography packings developed specifically for separating hydrogen sulfide, sulfur dioxide, carbonyl sulfide, and other sulfur gases at ppm and ppb concentrations in air. Retention indices for many analytes are tabulated for easy comparison. Example applications for each packing are shown.

Key Words:
- sulfur gases
- Kraft gases
- hydrogen sulfide
- sulfur dioxide
- carbonyl sulfide
- mercaptans

Sulfur gases are a challenging gas chromatographic analysis because they are both highly mobile and chemically very active molecules. Six gas chromatography packings developed specifically for separating hydrogen sulfide, sulfur dioxide, carbonyl sulfide, and other sulfur gases at ppm and ppb concentrations in air are described here. In order of description, these packings are:

- Chromosil 310*
- Chromosil 330*
- 40/60 Carbopack™ B HT 100
- Carbopack B/1.5% XE-60/1.0% H₃PO₄
- 12% polyphenyl ether/0.5% H₃PO₄ on 40/60 Chromosorb T
- Supelpak™-S

Relative advantages of each packing, and some limitations, are discussed.

Retention data for many sulfur compounds on these packings are listed in Table 1. Descriptions of the packings, and typical separations, are presented on pages 2-5. Ordering information is given on the back page.

### Table 1. Kovats Retention Indices for Sulfur Compounds

<table>
<thead>
<tr>
<th>Column</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>Methane</td>
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<td>100</td>
<td>100</td>
<td>100</td>
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<td>100</td>
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<tr>
<td>Sulfur hexafluoride</td>
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<td>—</td>
<td>—</td>
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<td>200</td>
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<td>Propylene</td>
<td>406</td>
<td>310</td>
<td>294</td>
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<td>Hydrogen sulfide</td>
<td>364</td>
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<td>174</td>
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<td>Carbonyl sulfide</td>
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<td>291</td>
<td>245</td>
<td>151</td>
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<td>377</td>
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<td>400</td>
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<td>400</td>
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<td>384</td>
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<tr>
<td>cis-Butene-2</td>
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<td>417</td>
<td>415</td>
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<td>trans-Butene-2</td>
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<td>Diethyl sulfide</td>
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<td>696</td>
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<td>n-Heptane</td>
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<td>n-Butyl mercaptan</td>
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<td>734</td>
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<td>502</td>
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<td>735</td>
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<tr>
<td>Dimethyl disulfide</td>
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<td>536</td>
<td>—</td>
<td>736</td>
<td>735</td>
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<td>Toluene</td>
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<td>—</td>
<td>741</td>
<td>751</td>
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<td>n-Octane</td>
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<td>800</td>
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</tbody>
</table>

* Because high injector and detector temperatures can affect Chromosil packings, 1 foot (25cm) of tubing is left unpacked at the column inlet and the column outlet (e.g., an 8-foot column contains 6 feet of packing).
Chromosil 310
Chromosil 310 is a silica gel that has been specially treated to separate both trace (ppm/ppb) and percent concentrations of sulfur compounds. Figure A shows the separation of ppm levels of COS, H₂S, CS₂, and SO₂ using Chromosil 310 in an 8’ x 1/8” Teflon® (FEP) column (6’ packed). Because COS is eluted before H₂S, you can use this column to monitor traces of COS in the presence of larger amounts of H₂S. Figure B shows the separation of percent concentrations of COS, H₂S, SO₂, and CO₂ in air. To improve the separation of the sulfur gases from CO₂ and air, a 6’ x 4mm ID glass column was used, instead of a Teflon column. The maximum operating temperature for Chromosil 310 columns is 100°C.

Chromosil 330
Chromosil 330 is a modified silica gel specifically treated for separating ppb concentrations of light sulfur gases, mercaptans, and alkyl sulfides. At 40°C, an 8’ Teflon (FEP) column (6’ packed) packed with Chromosil 330 will separate COS, H₂S, SO₂, CS₂, and C₁-C₃ mercaptans (Figure C). COS elutes before H₂S, as it does on Chromosil 310. Higher molecular weight mercaptans and alkyl sulfides can be separated by raising the column temperature to 65°C (Figure D). Under these conditions the pairs H₂S/COS, ethyl mercaptan/dimethyl sulfide, and propyl mercaptan/ethyl methyl sulfide will not be separated, however. The maximum operating temperature for Chromosil 330 columns is 100°C.

Figure A. Trace Light Sulfur Gases

Column: Chromosil 310, 8' (6' packed) x 1/8" OD Teflon (FEP)
Cat. No.: 11501
Oven: 50°C
Carrier: nitrogen, 20mL/min
Det.: FPD
Inj.: 0.5mL nitrogen, approx. 1ppm each analyte

Figure B. Light Sulfur Gases at Percent Concentrations

Column: Chromosil 310, 6’ x 4mm ID glass
Cat. No.: prepared on request
Oven: 40°C
Carrier: helium, 50mL/min
Det.: TCD
Inj.: 0.3mL synthetic mix

Figure C. Trace Light Sulfur Gases & C₁-C₃ Mercaptans

Column: Chromosil 330, 8' (6' packed) x 1/8" OD Teflon (FEP)
Cat. No.: 11496
Oven: 40°C
Carrier: nitrogen, 20mL/min
Det.: FPD
Inj.: 0.2mL nitrogen, approx. 1ppm each analyte

Figure D. Alkyl Sulfides and Mercaptans

Column: Chromosil 330, 8' (6' packed) x 1/8" OD Teflon (FEP)
Cat. No.: 11496
Oven: 65°C
Carrier: nitrogen, 20mL/min
Det.: FPD
Inj.: 0.5cc synthetic mix

1. COS & H₂S
2. CH₂SH
3. CS₂
4. SO₂
5. Ethyl mercaptan & Dimethyl sulfide
6. Propyl mercaptan & Ethyl methyl sulfide
7. Diethyl sulfide
8. Butyl mercaptan
9. Methyl disulfide
40/60 Carbopack B HT 100
This packing was developed by Bruner et al. (1) to separate H₂S, SO₂, COS, and CH₃SH at ppm and ppb levels (Figure E). HT indicates the packing has been deactivated with hydrogen (at 1000°C). Carbopack B HT 100 includes H₃PO₄ for additional deactivation.

In the original work (1) this packing was used in Teflon (FEP) tubing. Subsequently, Bruner et al. considerably improved column efficiency and reduced analysis time to 1 minute (Figure F) by using glass rather than Teflon tubing (2). Prior to preparing the column, the empty glass tubing must be thoroughly dried by conditioning it at 130°C for 6 hours (200mL/min carrier gas flow).

Carbopack B HT 100 can be used at 100°C to separate a variety of mercaptans, sulfides, and disulfides (Figure G and reference 3). The maximum operating temperature for this packing is 150°C.

Carbopack B/1.5% XE-60/1.0% H₃PO₄

Figure E. Trace Sulfur Gases

Figure F. Trace H₂S, SO₂, & CH₃SH

Figure G. Light Sulfur Gases, Alkyl Sulfides, and Mercaptans
C2 Sulfur Isomers

Carbopack B coated with 1.5% XE-60/1.0% H3PO4 is specifically tailored to separate ethyl mercaptan and dimethyl sulfide. Previously, only excessively long columns of polyphenyl ether (PPE) on Chromosorb T (described later) would separate these isomers. Figure H shows a separation of sulfur-containing compounds on this packing. A 6' x 2mm ID glass column was required to resolve ethyl mercaptan and dimethyl sulfide to the baseline. The empty glass column was dried as described in the Carbopack B HT 100 section. A Teflon column gave only 50% resolution of the isomers, at best, but resolution of the other compounds in Figure H was not impaired.

SF6, H2S, COS

Sulfur hexafluoride is commonly used as a tracer gas in pollution monitoring. Until now a 36-foot polyphenyl ether column was used to monitor SF6, along with other light sulfur gases. Carbopack B/1.5% XE-60/1.0% H3PO4 separates SF6, H2S, and COS at ambient temperature – a separation impossible with the PPE column. Figure I shows the separation of H2S, SF6, COS, SO2, and CH3SH, using this packing in a 6' x 1/8" Teflon (FEP) column. The maximum operating temperature for this packing is 150°C.

12% Polyphenyl Ether/0.5% H3PO4 on 40/60

Figure J. Trace Sulfur Gases

<table>
<thead>
<tr>
<th>Column: 12% polyphenyl ether/0.5% H3PO4 on 40/60 Chromosorb T, 36' x 0.085&quot; ID Teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.: 11500</td>
</tr>
<tr>
<td>Oven: 50°C</td>
</tr>
<tr>
<td>Carrier: nitrogen, 100mL/min; oxygen, 15mL/min; hydrogen, 75mL/min</td>
</tr>
<tr>
<td>Det.: FPD (100°C)</td>
</tr>
</tbody>
</table>

Figure K. Mercaptans, Sulfides, and Disulfides

<table>
<thead>
<tr>
<th>Column: 12% polyphenyl ether/0.5% H3PO4 on 40/60 Chromosorb T, 36' x 0.085&quot; ID Teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.: 11500</td>
</tr>
<tr>
<td>Oven: 50°C</td>
</tr>
<tr>
<td>Carrier: nitrogen, 80mL/min</td>
</tr>
<tr>
<td>Det.: FPD</td>
</tr>
<tr>
<td>Inj.: 0.5cc synthetic mix</td>
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</tbody>
</table>

Supelpak-S

Figure J. Trace Sulfur Gases

<table>
<thead>
<tr>
<th>Column: 12% polyphenyl ether/0.5% H3PO4 on 40/60 Chromosorb T, 36' x 0.085&quot; ID Teflon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. No.: 11828 (15g)</td>
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<tr>
<td>Column: 6' x 1/8&quot; OD Teflon (FEP)</td>
</tr>
<tr>
<td>Oven: 23°C</td>
</tr>
<tr>
<td>Carrier: nitrogen, 35mL/min</td>
</tr>
<tr>
<td>Det.: FPD</td>
</tr>
<tr>
<td>Inj.: 0.5cc synthetic mix</td>
</tr>
</tbody>
</table>

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A specially prepared Porapak® QS packing, Supelpak-S, was developed to separate H₂S, COS, SO₂, CH₃SH, (CH₃)₂S, and (CH₃)₂S₂—compounds found in the stack gases of Kraft pulp mills, nylon plants, or petroleum refineries—at low ppm concentrations (5). Porapak QS does not give a suitable separation; the baseline is erratic and the peaks are not completely separated. The performance of Porapak QS is substantially improved with a special washing procedure.

The column consists of 30” of 1/8” Teflon tubing, 18” packed with Supelpak-S. The additional unpacked tubing makes it convenient to connect the column to the chromatograph. Separation of a standard gas mixture is shown in Figure L. We recommend using this column with a flame photometric detector.

In analyses of sulfur compounds that might form in Kraft recovery furnaces, a Supelpak-S column offers several advantages:

- water in the stack gas is quickly eluted from the column and does not interfere with the separation of the sulfur gases
- the short length ensures low back pressure
- samples are resolved well
- the column can be temperature programmed to 210°C
- because no liquid phase is used, there is no bleed
- the column can separate H₂S from COS

A number of stack gas compounds are listed in Table 1. Many have retention times of less than 10 minutes on a Supelpak-S column.

Detection and Calibration

Figure L. Kraft Pulp Mill Stack Gases

The detector used for most of these analyses is a flame photometric detector (FPD), originally developed by Brody and Chaney (6). A number of investigators have studied its response to sulfur compounds (7-10). The detector is calibrated with samples of known concentration, using permeation tubes or exponential dilution. O’Keefe and Ortman (11) originally developed the permeation tube as a primary standard source. Stevens, O’Keefe and Ortman described calibration of the detector for volatile sulfur compounds at sub-ppm levels, using permeation tubes (12). Bruner et al. demonstrated the use of coupled permeation tubes and exponential dilution (13) and, more recently, described calibration for the sulfur gases in more detail (14).

Column Preparation

For longer column life and more effective separations of sulfur gases, follow the conditioning instructions and maximum temperature recommendations that accompany these packings and packed columns.

Ordering Information:

References


References not available from Supelco.
Chromosil 310,
8' (6' packed) x 1/8" OD Teflon (FEP) Column* 11501
Chromosil 330,
8' (6' packed) x 1/8" OD Teflon (FEP) Column* 11496
40/60 Carpack B HT 100, 15g 20272
Carpack B HT 100,
1.4m (4.6') x 1/8" OD Teflon (FEP) Column 11502-U
Carpack B/1.5% XE-60/1.0% H3PO4, 15g 11828
12% Polyphenyl ether/0.5% H3PO4 on
40/60 Chromosorb T,
36' x 1/8" OD Teflon (FEP) Column 11500
Supelpak-S,
30' (18" packed) x 1/8" OD Teflon Column 12255-U

* Because high injector and detector temperatures can affect Chromosil packings, the ends of these columns are not packed.

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Chromosorb – Celite Corp.
Porapak – Waters Associates, Inc.
Supelpak – Sigma-Aldrich Co.
Teflon – E.I. du Pont de Nemours & Co., Inc.

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