Analyses of Sulfur Gases at Trace and Low Percent Levels, Using Packed Column GC

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% H_3PO_4

12% polyphenyl ether/0.5% H_3PO_4 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

	Column					
Compound	**A**	**B**	**C**	**D**	**E**	**F**
Methane	100	100	100	100	100	100
Sulfur hexafluoride	—	—	—	105	200	—
Ethane	200	200	200	200	200	200
Ethylene	239	200	174	167	200	186
Propane	300	300	300	300	300	300
Propylene	406	310	294	289	317	296
Hydrogen sulfide	364	310	174	78	327	257
Carbonyl sulfide	343	291	245	151	327	284
Isobutane	391	375	375	377	348	—
n-Butane	400	400	400	400	400	400
Butene-1	510	410	386	384	407	400
cis-Butene-2	562	415	417	415	433	—
trans-Butene-2	548	415	417	415	433	—
Sulfur dioxide	539	—	254	187	445	355
Isobutylene	406	400	396	397	445	—
n-Pentane	500	500	500	500	500	500
Methyl mercaptan	—	443	298	235	507	500
Isopentane	489	485	474	472	507	—
Pentene-1	—	507	483	480	507	488
2-Methylpentane	—	580	—	—	537	585
Ethyl mercaptan	—	529	390	343	588	400
n-Hexane	600	600	600	600	600	600
Hexene-1	—	607	571	—	604	600
Dimethyl sulfide	—	513	395	349	611	500
Carbon disulfide	450	472	406	357	617	488
n-Propyl mercaptan	—	631	490	474	656	618
2,4-Dimethylpentane	—	652	—	—	660	668
Diethyl sulfide	—	—	566	—	696	—
n-Heptane	700	700	700	700	700	700
n-Butyl mercaptan	—	734	580	502	702	735
Dimethyl disulfide	—	743	536	—	736	735
Toluene	—	773	—	—	741	751
n-Octane	800	800	800	800	800	800

Column Packings

A Chromosil 310

B Chromosil 330

C 40/60 Carbopack B HT 100

D Carbopack B/1.5% XE-60/1.0% H_3PO_4

E 12% Polyphenyl ether/0.5% H_3PO_4 on 40/60 Chromosorb T

F Supelpak-S

* 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, H_2S, CS_2, and SO_2, using Chromosil 310 in an 8' x 1/8" Teflon® (FEP) column (6' packed). Because COS is eluted before H_2S, you can use this column to monitor traces of COS in the presence of larger amounts of H_2S. Figure B shows the separation of percent concentrations of COS, H_2S, SO_2, and CO_2 in air. To improve the separation of the sulfur gases from CO_2 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.

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

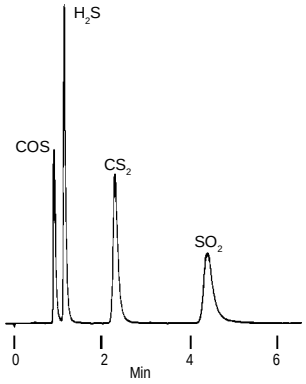

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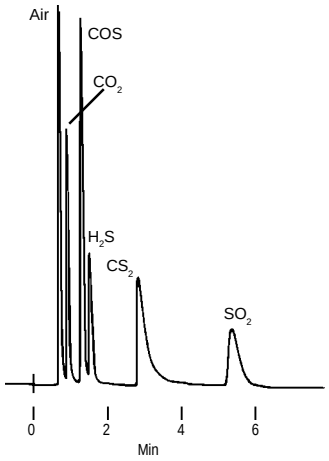
Figure B. Light Sulfur Gases at Percent Concentrations

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



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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, H_2S, SO_2, CS_2, and C1-C3 mercaptans (Figure C). COS elutes before H_2S, 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 H_2S/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 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

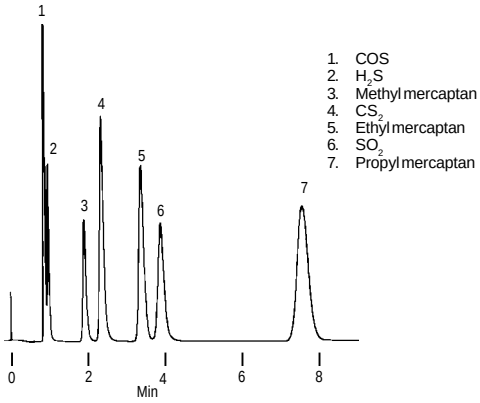

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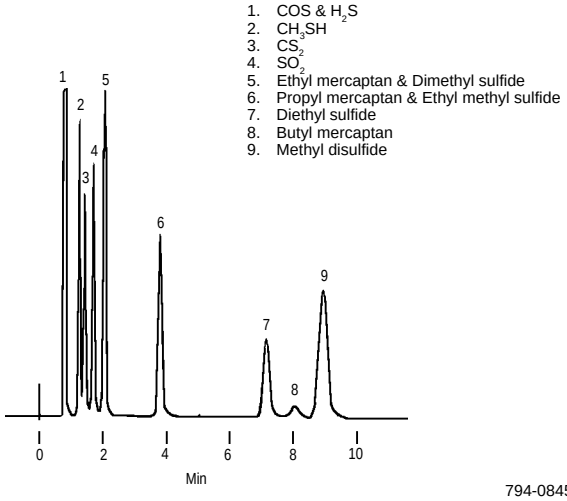
Figure D. Alkyl Sulfides and Mercaptans

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



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40/60 Carbopack B HT 100

This packing was developed by Bruner *et al.* (1) to separate H_2S, SO_2, COS, and CH_3SH at ppm and ppb levels (Figure E). HT indicates the packing has been deactivated with hydrogen (at 1000°C). Carbopack B HT 100 includes H_3PO_4, 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% H_3PO_4

Figure E. Trace Sulfur Gases

Column: **40/60 Carbopack B HT 100, 1.4m x 1/8" OD Teflon (FEP)**
Cat. No.: **11502-U**
Oven: 35°C
Carrier: nitrogen, 20mL/min
Det.: FPD
Inj.: 0.3mL

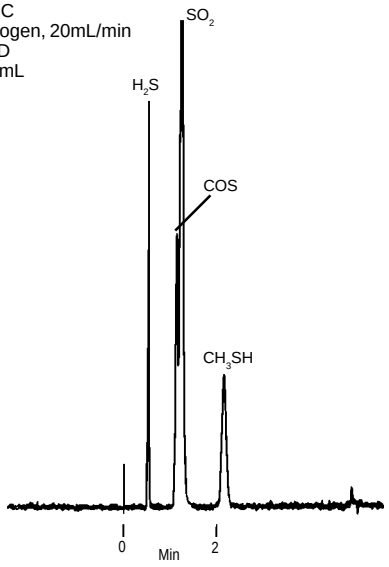

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Figure F. Trace H_2S, SO_2, & CH_3SH

Packing: **40/60 Carbopack B HT 100**
Cat. No.: **20272** (15g)
Column: 5' x 4mm ID glass
Oven: 25°C
Carrier: nitrogen, 125mL/min
Det.: FPD
Inj.: 0.5mL synthetic mix

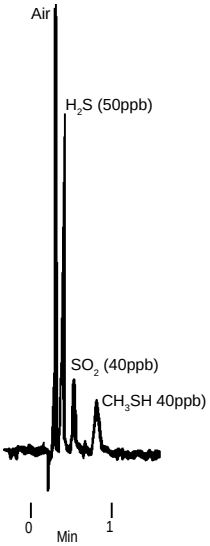

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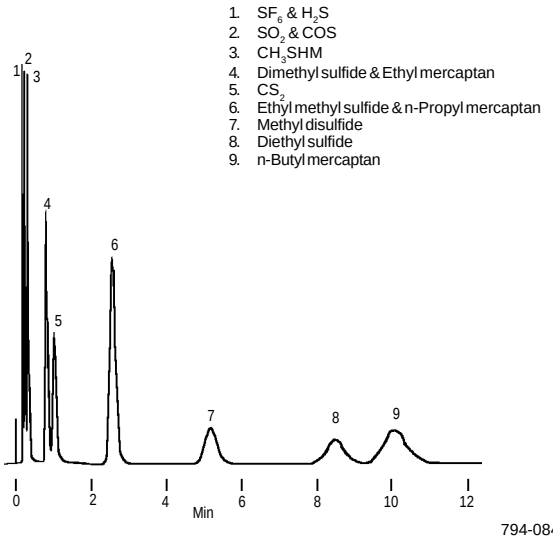
Figure G. Light Sulfur Gases, Alkyl Sulfides, and Mercaptans

Column: **40/60 Carbopack B HT 100, 1.4m x 1/8" OD Teflon (FEP)**
Cat. No.: **11502-U**
Oven: 100°C
Carrier: nitrogen, 70mL/min
Det.: FPD
Inj.: 0.5mL synthetic mix



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C_2 Sulfur Isomers

Carbopack B coated with 1.5% XE-60/1.0% H_3PO_4 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.

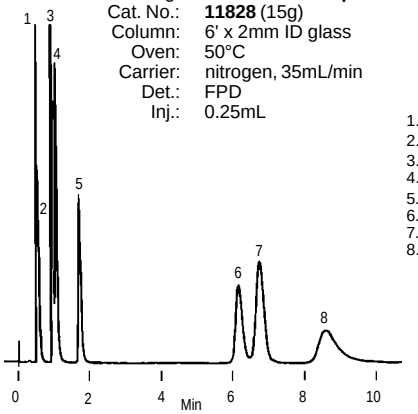
SF_6, H_2S, COS

Sulfur hexafluoride is commonly used as a tracer gas in pollution monitoring. Until now a 36-foot polyphenyl ether column was used to monitor SF_6, along with other light sulfur gases. Carbopack B/1.5% XE-60/1.0% H_3PO_4 separates SF_6, H_2S, and COS at ambient temperature – a separation impossible with the PPE column. Figure I shows the separation of H_2S, SF_6, COS, SO_2, and CH_3SH, 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% H_3PO_4 on 40/60

Figure H. Trace Sulfur Gases with C_2 Isomeric Sulfur Compounds

Packing: **GP 60/80 Carbopack B/1.5% XE-60/1.0% H_3PO_4**
Cat. No.: **11828** (15g)
Column: 6' x 2mm ID glass
Oven: 50°C
Carrier: nitrogen, 35mL/min
Det.: FPD
Inj.: 0.25mL



1. H_2S
2. SF_6
3. COS
4. SO_2
5. Methyl mercaptan
6. Ethyl mercaptan
7. Dimethyl sulfide
8. CS_2

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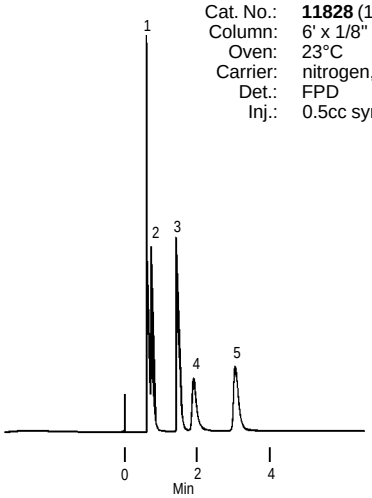
Figure I. SF_6 from Other Light Sulfur Gases

Packing: **GP 60/80 Carbopack B/1.5% XE-60/1.0% H_3PO_4**
Cat. No.: **11828** (15g)
Column: 6' x 1/8" OD Teflon (FEP)
Oven: 23°C
Carrier: nitrogen, 35mL/min
Det.: FPD
Inj.: 0.5cc synthetic mix



1. H_2S
2. SF_6
3. COS
4. SO_2
5. CH_3SH

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Chromosorb T

A 36' x 1/8" OD Teflon (FEP) column packed with 12% polyphenyl ether/0.5% H_3PO_4 on 40/60 Chromosorb T was developed to separate H_2S, SO_2, methyl and ethyl mercaptans, and dimethyl sulfide at ppm and ppb concentrations, for air pollution studies (4). Development of this column involved a careful study of factors that cause adsorption of the sulfur gases. Stainless steel and glass tubing and conventional diatomite supports adsorbed these compounds, but Teflon supports were more nearly inert. H_3PO_4 eliminated the last trace of activity from the column. Figure J shows a separation of sulfur compounds on this column. H_2S and COS are not separated. The same column can be used to separate a variety of mercaptans, sulfides, and disulfides (3) at 50°C (Figure K) and 100°C. Methyl ethyl sulfide and n-propyl mercaptan are not separated at 100°C. The maximum operating temperature for this column is 150°C.

Supelpak-S

Figure J. Trace Sulfur Gases

Column: **12% polyphenyl ether/0.5% H_3PO_4 on 40/60 Chromosorb T, 36' x 0.085" ID Teflon**
Cat. No.: **11500**
Oven: 50°C
Carrier: nitrogen, 100mL/min; oxygen, 15mL/min; hydrogen, 75mL/min
Det.: FPD (100°C)

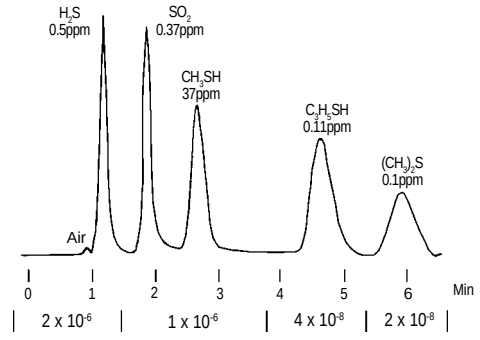

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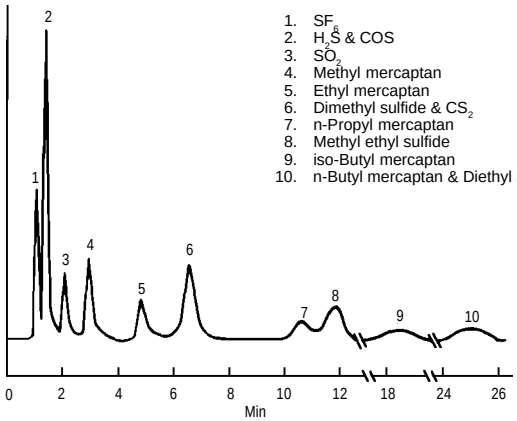
Figure K. Mercaptans, Sulfides, and Disulfides

Column: **12% polyphenyl ether/0.5% H_3PO_4 on 40/60 Chromosorb T, 36' x 0.085" ID Teflon**
Cat. No.: **11500**
Oven: 50°C
Carrier: nitrogen, 80mL/min
Det.: FPD
Inj.: 0.5cc synthetic mix



1. SF_6
2. H_2S & COS
3. SO_2
4. Methyl mercaptan
5. Ethyl mercaptan
6. Dimethyl sulfide & CS_2
7. n-Propyl mercaptan
8. Methyl ethyl sulfide
9. iso-Butyl mercaptan
10. n-Butyl mercaptan & Diethyl sulfide

794-0850

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A specially prepared Porapak® QS packing, Supelpak-S, was developed to separate H_2S, COS, SO_2, CH_3SH, $(CH_3)_2S$, and $(CH_3)_2S_2$ – 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:

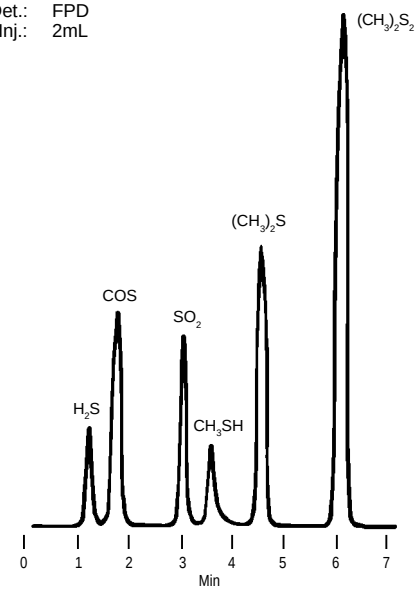
- water in the stack gas is quickly eluted from the column and does not interfere with the separation of the sulfur gases
- the short length ensures low back pressure
- samples are resolved well
- the column can be temperature programmed to 210°C
- because no liquid phase is used, there is no bleed
- the column can separate H_2S 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

Column: **Supelpak-S, 30" (18" packed) x 1/8" OD Teflon (FEP)**
Cat. No.: **12255-U**
Oven: 30°C (1 min) to 210°C at 40°C/min
Carrier: helium, 30mL/min
Det.: FPD
Inj.: 2mL



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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

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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 Carbopack B HT 100, 15g	**20272**
Carbopack B HT 100, 1.4m (4.6') x 1/8" OD Teflon (FEP) Column	**11502-U**
Carbopack B/1.5% XE-60/1.0% H_3PO_4, 15g	**11828**
12% Polyphenyl ether/0.5% H_3PO_4 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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