

SEPARATION OF SULFONES BY GAS CHROMATOGRAPHY

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INTRODUCTION

Sulfones of the general formula R_2SO_2 are used for insecticides, fuel additives, plasticizers, anti-icing additives¹ and many other applications. With increasing use of the sulfones taking place the analysis of materials containing them is becoming more important. This study was made to determine the optimum column materials and conditions for effectively separating the sulfones by gas-liquid chromatography.

EXPERIMENTAL

Sulfones

Dimethyl sulfone was obtained from Crown Zellerbach Corporation, *n*-propyl, *n*-butyl and phenyl sulfone from Eastman, ethyl, isopropyl, isobutyl, *sec*.-butyl, *n*-amyl, isoamyl, *n*-hexyl, butadiene, tetramethylene (sulfolane) and *sym*.-trimethylene trisulfone from Wateree Chemical Co., ethyl 2-hydroxyethyl, 2-hydroxyethyl, 4-chlorophenyl, 3-aminophenyl, 4-aminophenyl, 4-hydroxyphenyl, dibenzothiophene, 2,4-dimethylsulfolane, and 2,4-dimethyl-3-sulfolene from Aldrich Chemical Co., 3-methylsulfolane, sulfolene, and 3-methylsulfolene from Phillips Petroleum Co., and methyl sulphonal from British Drug Houses Ltd. The *tert*.-butyl and methyl *p*-nitrophenyl sulfones were prepared in this laboratory.

Since a solid sample vaporizer was not available, the solid sulfones were injected into the gas chromatograph as a solution in an organic solvent. Acetone was found to be a very good solvent for most of the sulfones and was generally used to facilitate injection into the gas chromatograph. Chloroform was used for dibenzothiophene sulfone since it is a better solvent for this compound. Both solvents emerged from the column quickly and did not interfere with further study of the chromatogram.

Equipment

One of the instruments used for this study was constructed in this laboratory, the other was an F and M Model 609. The detector system for the former (Figs. 1 and 2) was similar to that of FELTON AND BUEHLER² using direct flow of the gas stream past Veco model airplane glo-plugs, type No. 109 with 7/32 in. reach. The connecting wire was silver soldered to the cap of the glo-plug. The power supply was a 4 V rechargeable lead storage battery which gave 2.4 V at the detector terminals. This voltage gave

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considerable greater sensitivity than the 1.5 V recommended by Veco, however, it was a practice to flush the system with helium before turning on the detector switch in order to prolong the life of the glo-plugs. The D.C. source gave more stable operation than an A.C. power supply.

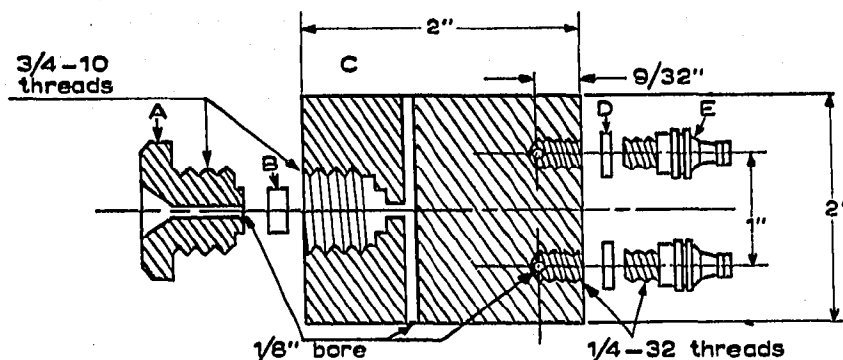


Fig. 1. Injector-detector block cross section. A. Section of a 3/4 in. 10 threads/in. machine bolt. B. Silicone rubber disc septum, 3/8 in. diameter, 1/8 in. thick. C. 2 in. cube piece of stainless steel. D. Copper glo-plug gasket, 1/4 in. I.D. E. Veco No. 109 glo-plug.

The temperature of the isothermal oven constructed by BEUERMAN AND MELOAN³ was controlled to within 1 degree during a days use by heating tapes and a powerstat variable transformer. The injector-detector block was maintained at a slightly higher temperature than the oven by means of a separate heating tape and powerstat.

Column materials and preparation

The columns were 3 ft. long and made of 1/4 in. O.D. aluminum tubing obtained from the Ben McKalip Co., the support was coated by covering 100 g of solid support with

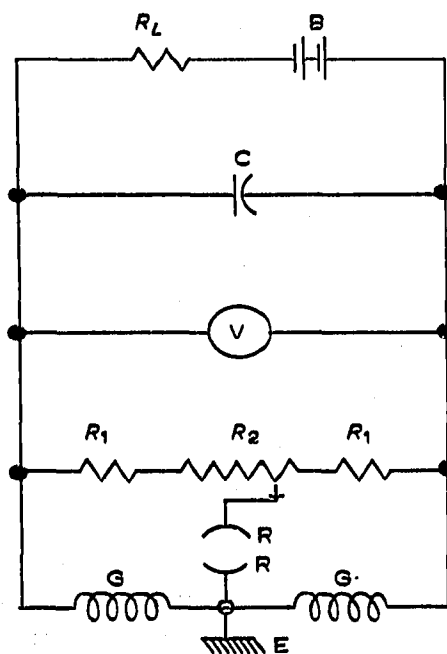


Fig. 2. Electrical circuit for the detector system. B = 2 V Gould National Battery Co. type EP 9 rechargeable lead-acid storage batteries. C = 500 mF 50 V D.C. capacitor. G = Veco No. 109 glo-plug. R = recorder leads. $R_1 = 47 \Omega$, 1 W resistor. $R_2 = 25 \Omega$, 10 turn helipot. R_L = resistance of trunk line cables. V = voltmeter, 0 to 3 V.

20 g of the liquid phase. Acetone was used as the solvent for the Carbowaxes and benzene for the silicones and Apiezon greases.

Column conditions

The columns were compared at 200°, as this is the temperature limit for the Carbowax 1500, with 15 p.s.i.g. of helium pressure at the inlet and atmospheric pressure at the outlet. The helium flow rate was measured with a soap bubble flow meter at the exhaust. Temperatures of 225° and 250° were used on those columns with higher temperature limits than 200°.

RESULTS AND DISCUSSION

The identification of the sulfones was verified by plotting the logarithm of the adjusted retention volume, V_R' , (the retention volume from air) vs. the number of carbon atoms as shown in Figs. 3, 4 and 5, and mentioned by PECSOK⁴. The numbers refer to similar numbers on Table I. The members of homologous structural type formed a straight or slightly curved line on these plots. The branched alkyl sulfones had shorter retention times than the straight chain compounds. The sulfone group is very polar and groups which tended to shield this group produced sulfones which had shorter retention times.

Thermal stability

No difficulty was observed due to possible thermal decomposition of any of the sulfones within the injection port or the column at operating temperature of 250°. This would be expected because of their great stability and very low reactivity⁵. This is contrary to experience with the sulfoxides and their disproportionation reactions which caused considerable trouble⁶.

Column characteristics

Liquid phases giving satisfactory results were Carbowax 1500, Carbowax 20-M, Dow Corning silicone oil 550, Silicone gum rubber (Fisher Scientific), and Apiezon L and M greases from James G. Biddle Co. These liquid phases have high temperature limits which are necessary for several of the sulfones, particularly the aryl sulfones.

Solid supports found to be satisfactory were Haloport F, 60-80 mesh Gas-Chrom P (acid and alcoholic base washed), Gas-Chrom Z (acid washed and silanized), and 35-80 mesh Chromosorb (silver plated as described by ORMEROD AND SCOTT)⁷, which gave only moderately acceptable results. Untreated Chromosorb and Chromosorb W were found to be unsatisfactory due to tailing of these polar compounds and of the water sometimes present in the sample. The most nearly symmetrical and sharpest peaks with the least amount of tailing for a given partition liquid were obtained when Gas-Chrom Z was used as the solid support.

The shape of the peaks was quite good when using any of the listed liquid phases except when the compounds had large retention volumes, such as phenyl and 4-chlorophenyl sulfones. These had a sloping leading edge and steeper backsides, which were considerably improved by raising the column temperature. Our instrument did not allow us to push this to the limit to see if good symmetrical peaks could eventually be obtained although it seemed possible that it could be done.

Fig. 3. The adjusted retention volume, V_R' , plotted against the number of carbon atoms in the molecule for the sulfones. The column was 3 ft. long and contained Apiezon L grease on Gas-Chrom Z. The points represent the sulfones having the corresponding numbers in Table I, and the volumes are those given in the table for the above column.

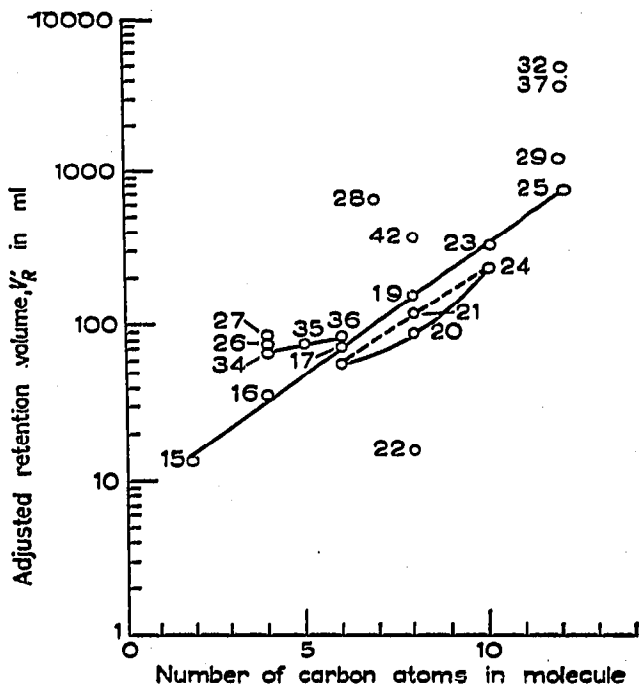
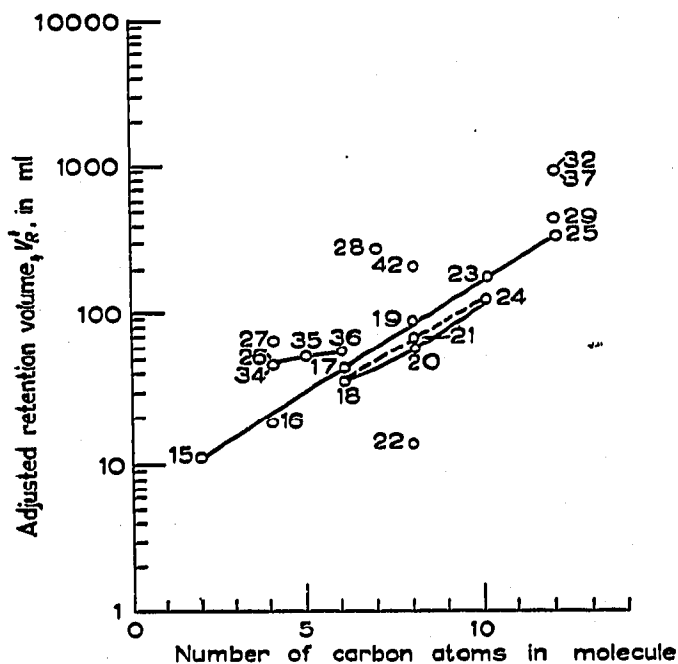


Fig. 4. The adjusted retention volume V_R' , plotted against the number of carbon atoms in the molecule for the sulfones. The column was 3 ft. long and contained Silicone gum rubber on Gas-Chrom Z. The points represent the sulfones having the corresponding numbers in Table I, and the volumes are those given in the table for the above column.

Fig. 5. The adjusted retention volume, V_R' , plotted against the number of carbon atoms in the molecule for the sulfones. The column was 3 ft. long and contained Carbowax 20-M on Gas-Chrom Z. The points represent the sulfones having the corresponding numbers in Table I, and the volumes are those given in the table for the above column.

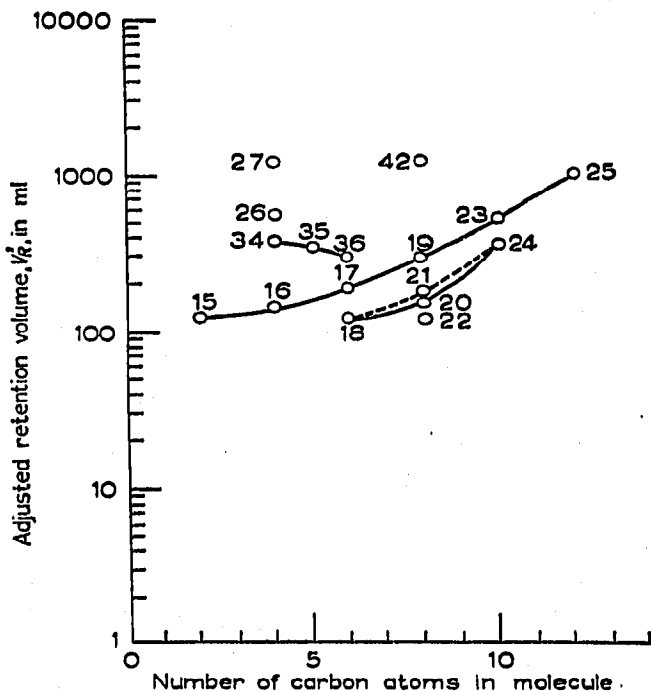


TABLE I
ADJUSTED RETENTION VOLUMES, V_R' , OF THE SULFOXIDES IN ml

Column No.	1		2		3		4		5		6		
	°C	He flow ml/min	300	250	300	250	300	250	300	225	300	250	300
		165	165	200	200	140	110	143	143	165	165	130	
	<i>Sulfone</i>												
15	Methyl		11		14		11		23		122		109
16	Ethyl		25		36		19		49		141		122
17	<i>n</i> -Propyl		46		74		43		91		193		162
18	Isopropyl		38		58		36		69		123		105
19	<i>n</i> -Butyl		95		156		92		192		298		286
20	Isobutyl		58		94		61		105		153		135
21	<i>sec.</i> -Butyl		77		124		72		133		178		157
22	<i>tert.</i> -Butyl		13		16		14		26		122		111
23	<i>n</i> -Amyl		211		346		189		393		525		495
24	Isoamyl		147		242		134		287		359		325
25	<i>n</i> -Hexyl		495	110	790	206	368	89	882	318	1000	195	891
26	2-Hydroxyethyl		61	26	76	34	47	38	109	60	541	122	417
27	Ethyl 2-hydroxyethyl		71	28	86	36	67	41	144	87	1210	198	1270
28	Methyl <i>p</i> -nitrophenyl		570	123	680	196	281	87	882	353		905	5400
29	Phenyl		775	187	1250	328	478	114	1780	565		695	4630
30	3-Aminophenyl*												
31	4-Aminophenyl*												
32	4-Chlorophenyl		520	5000	980	1010	197		1370		1630		
33	4-Hydroxyphenyl*												
34	Sulfolane		44		70		46		109		370		300
35	3-Methylsulfolane		54		78		54		128		343		267
36	2,4-Dimethylsulfolane		58		86		58		123		297		215
37	Dibenzothiophene	2300	445	3730	670	1000	167	4300	1330		2040		
38	Sulfolene*												
39	3-Methylsulfolene*												
40	2,4-Dimethyl-3-sulfolene*												
41	Butadiene*												
42	Methyl sulphonal	240	72	386	128	215	70	608	218	1210	215	900	
43	<i>sym.</i> -Trimethylene trisulfone**												

Columns: 1 = Apiezon M

2 = Apiezon L

3 = Silicone gum rubber

4 = Silicone oil 550

5 = Carbowax 20-M

6 = Carbowax 1500.

* Did not emerge in 30 min at 250° on Silicone gum rubber column.

** A suitable solvent in which this compound is soluble could not be found.

No retention volumes are given for the aminophenyl, hydroxyphenyl, and butadiene sulfones or any of the sulfolenes as these were not observed to emerge in 30 min. at 250°, the maximum operating temperature of the chromatograph, on the silicone gum rubber column.

Table I shows that the silicone gum rubber column generally gave the smallest retention volumes and Carbowax 20-M gave the longest. The carbowaxes gave the best separations of the sulfones from other components; however, the silicones and Apiezon greases give better separation and more linear curves of the log of retention volume vs. the number of carbon atoms for homologous sulfones.

By using flow rates less than those in Table I and varying the column temperatures to obtain the desired retention times, while using a liquid phase with a higher

temperature limit than the column temperature, quite satisfactory separations can be obtained. It may also be desired to use greater column lengths to increase the resolution of the components. The use of programmed temperature gas chromatography has considerable advantage with these compounds as can be seen by Figs. 6 and 7, the

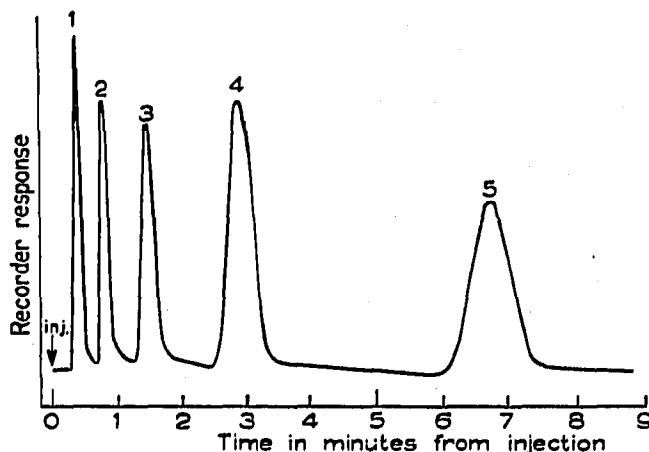


Fig. 6. Isothermal gas chromatogram of a mixture of sulfones. Instrument = F & M 609. Injection port temperature = 230° . Column temperature = 175° . Helium flow = 100 ml/min. Sample size = $0.5 \mu\text{l}$. Attenuator setting: peak 1 at 64, others at 32. Column = 3 ft. long, Carbowax 20-M on Gas-Chrom Z. Peak 1 = acetone solvent. Peak 2 = dimethyl sulfone = 13 % by weight. Peak 3 = diethyl sulfone = 15 % by weight. Peak 4 = *n*-propyl sulfone = 37 % by weight. Peak 5 = *n*-butyl sulfone = 35 % by weight.

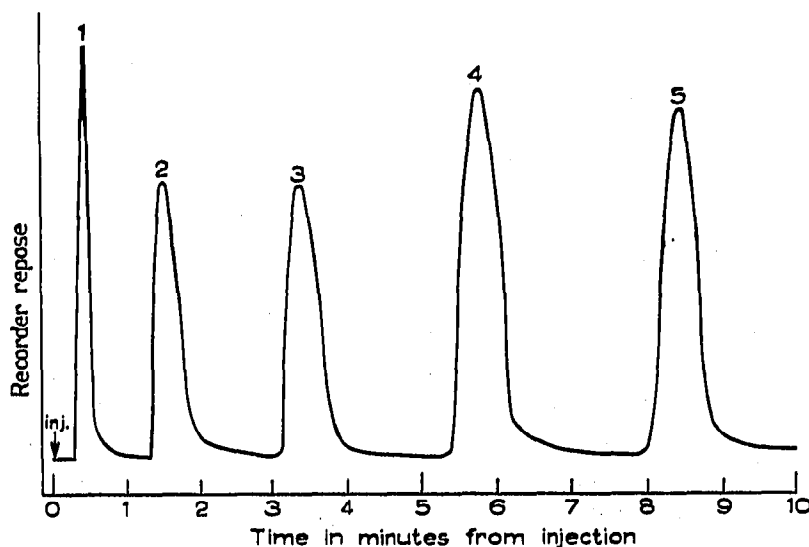


Fig. 7. Programmed temperature gas chromatogram of a mixture of sulfones. Instrument = F & M 609. Injection port temperature = 230° . Column temperature at start = 125° . Temperature programming rate = 13° per min. Helium flow = 100 ml/min. Sample size = $0.5 \mu\text{l}$. Attenuator setting = peak 1 at 64, others at 32. Column = 3 ft. long, Carbowax 20-M on Gas-Chrom Z. Peak 1 = acetone solvent. Peak 2 = dimethyl sulfone = 13 % by weight. Peak 3 = diethyl sulfone = 15 % by weight. Peak 4 = *n*-propyl sulfone = 37 % by weight. Peak 5 = *n*-butyl sulfone = 35 % by weight.

separation of four homologous sulfones. A weight percent standard should be used for calibration and quantitative analysis.

Fig. 8 shows the separation of a sulfide, a sulfoxide and a sulfone since this combination occurs together quite frequently in commercial products.

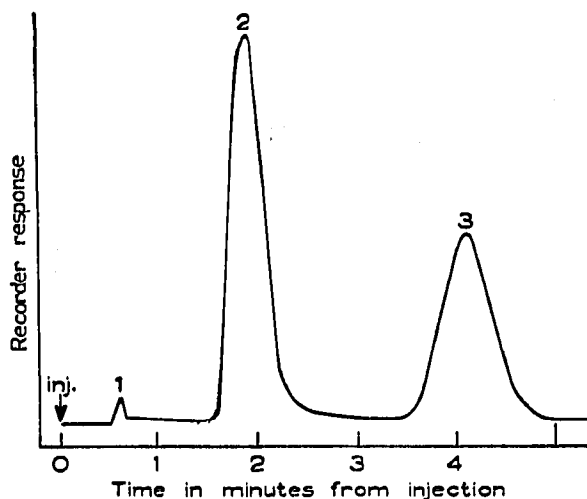


Fig. 8. Gas chromatogram of a mixture containing a sulfide, a sulfoxide and a sulfone having the same R groups. Instrument = F & M 609. Injection port temperature = 160°. Column temperature = 150°. Helium flow = 90 ml/min. Sample size = 0.4 μ l. Attenuator setting = 64. Column = 3 ft. long, Carbowax 20-M on Gas-Chrom Z. Peak 1 = *tert.*-butyl sulfide. Peak 2 = *tert.*-butyl sulfoxide. Peak 3 = *tert.*-butyl sulfone.

ACKNOWLEDGEMENT

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SUMMARY

Sulfones were separated by gas-liquid chromatography; the best separations were obtained using Carbowax 1500 and 20-M on Gas-Chrom-Z, a silanized diatomaceous solid support. The results are compared and discussed for other liquid phases and supports. The sulfones studied were: dimethyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec.*-butyl, *tert.*-butyl, butadiene, *n*-amyl, isoamyl, *n*-hexyl, phenyl, methyl *p*-nitrophenyl, tetramethylene, *sym.*-trimethylene trisulfone, ethyl 2-hydroxyethyl, 2-hydroxyethyl, 4-chlorophenyl, 3-aminophenyl, 4-aminophenyl, 4-hydroxyphenyl, dibenzothiophene, 2,4-dimethylsulfolane, 2,4-dimethyl-3-sulfolene, 3-methylsulfolane, sulfolene, 3-methylsulfolene and methyl sulfonyl.

REFERENCES

- ¹ *Technical Bulletin on Dimethyl Sulfone*, Crown Zellerbach Corporation, Camas, Washington.
- ² H. R. FELTON AND A. A. BUEHLER, *Anal. Chem.*, 30 (1958) 1163.
- ³ D. R. BEURMAN AND C. E. MELOAN, *Anal. Chem.*, 34 (1962) 319.
- ⁴ R. L. PECSOK, *Principles and Practice of Gas Chromatography*, Wiley, New York, 1959, pp. 137-8.
- ⁵ N. KHARASCH, *Organic Sulfur Compounds*, Vol. 1, Pergamon Press, New York, 1961, p. 148.
- ⁶ V. E. CATES AND C. E. MELOAN, *Anal. Chem.*, 35 (1963) 658.
- ⁷ E. C. ORMEROD AND R. P. W. SCOTT, *J. Chromatog.*, 2 (1959) 65.