Journal of Chromatography, 112 (1975) 111–120

CHROM. 8495

HIGH-TEMPERATURE GAS–LIQUID CHROMATOGRAPHY WITH A POLYPHENYL ETHER SULFONE

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SUMMARY

The applicability of polyphenyl ether sulfone liquid phases for the separation of moderately "polar" materials, at temperatures of 200–400°, has been evaluated. A variety of samples was separated and typical chromatograms are presented for the resolution of a synthetic lubricant, long-chain alcohol derivatives, triglycerides, cholesteryl esters, bile acid esters, and pesticides.

In order to extend the utility of sulfone phases to temperatures below their melting points, columns were prepared with a porous thermally stable polymer as the support. The results obtained indicate that these columns are useful for the separation of wide-boiling mixtures of "polar" materials.

INTRODUCTION

The synthesis, properties, and an initial evaluation of polyphenyl ether sulfones as thermally stable, moderately "polar", liquid phases for gas chromatography was presented in a previous paper[1]. Also, two papers[2,3] describing separations obtained with glass capillary columns, coated with polyphenyl ether sulfone, have been published. The objective of this investigation was to extend the evaluation of sulfone-coated columns to the high-temperature separation of other mixtures.

Although the sulfones we prepared have melting ranges of 85–165°, they do not provide low liquid viscosities and good column efficiencies at these temperatures. Therefore, we have prepared and evaluated packed columns containing the sulfone on an adsorbent. These columns provide separation, based on gas–solid chromatography, at temperatures where the sulfone is a solid. However, at higher temperatures, the separations are based upon gas–liquid phenomena.

EXPERIMENTAL

Equipment

Work at the Pennzoil Company Research Laboratory was done on a Barber-

Colman Series 5000 gas chromatograph equipped with a hydrogen flame ionization detector.

The portion of this investigation conducted at the Institute for Lipid Research, Baylor College of Medicine, utilized a Barber-Colman Series 5000 gas chromatograph equipped with a Keithley Model 417 picoammeter, Texas Instruments recorder and a flame ionization detector.

The instrument used at Applied Science Laboratories was a Hewlett-Packard Model 7620 with a flame ionization detector.

Reagents

The polyphenyl ether sulfones, PZ-176 and PZ-179, were synthesized as described in our previous paper[1]; Poly-S-179 is available from Applied Science Labs. (State College, Pa., U.S.A.). Tenax-GC was purchased from Applied Science Labs. Solvents used in preparing packed columns, chloroform, tetrahydrofuran, dimethylformamide, and acetone were procured from Aldrich (Milwaukee, Wisc., U.S.A.). Cholesteryl esters, triglycerides, bile acid methyl esters, and pesticides were obtained from Applied Science Labs.

Column preparation

The metal columns (Pennzoil) were prepared from Type 304 stainless-steel, 0.125 in. O.D. (0.062 in. I.D.) from Handy and Harman (Norristown, Pa., U.S.A.). The support was 100–120 mesh Gas-Chrom Q. The polyphenyl ether sulfones were coated onto this support from a tetrahydrofuran solution. Columns were conditioned by programming from ambient temperature to 300° at 0.5–1.0°/min and then holding overnight. The columns were then programmed to 350° or 400° at 1°/min, the temperature being held until the baseline stabilized. Glass W columns (Baylor) were prepared as described earlier[1]. Glass columns (Applied Science Labs.) were prepared by standard procedures.

RESULTS

Separation of synthetic lubricants

A variety of materials is produced and utilized as synthetic lubricants. In fact, a number of synthetic lubricants such as the phosphate esters and the silicones are often employed as liquid phases for gas chromatography. Because of its "polar" character, and its high-temperature stability, the polyphenyl ether sulfone (PZ-179) was evaluated for the separation of a number of synthetic lubricant materials. Fig. 1 shows the separation of Herculube A, a pentaerythritol-based synthetic lubricant. The column was programmed from 250–350° at a rate of 5°/min. The results obtained indicate that a suitable separation, with negligible "bleed" is provided by the polyphenyl ether sulfone-coated column.

Separation of alcohol derivatives

The separation of a C_{16}–C_{24} alcohol mixture, as both trimethylsilyl (TMS) ether derivatives and as acetate derivatives, was performed at Baylor Medical School by Drs. E. C. Horning, C. D. Pfaffenberger, and S.-N. Lin. Also, a C_{20}–C_{28} mixture was

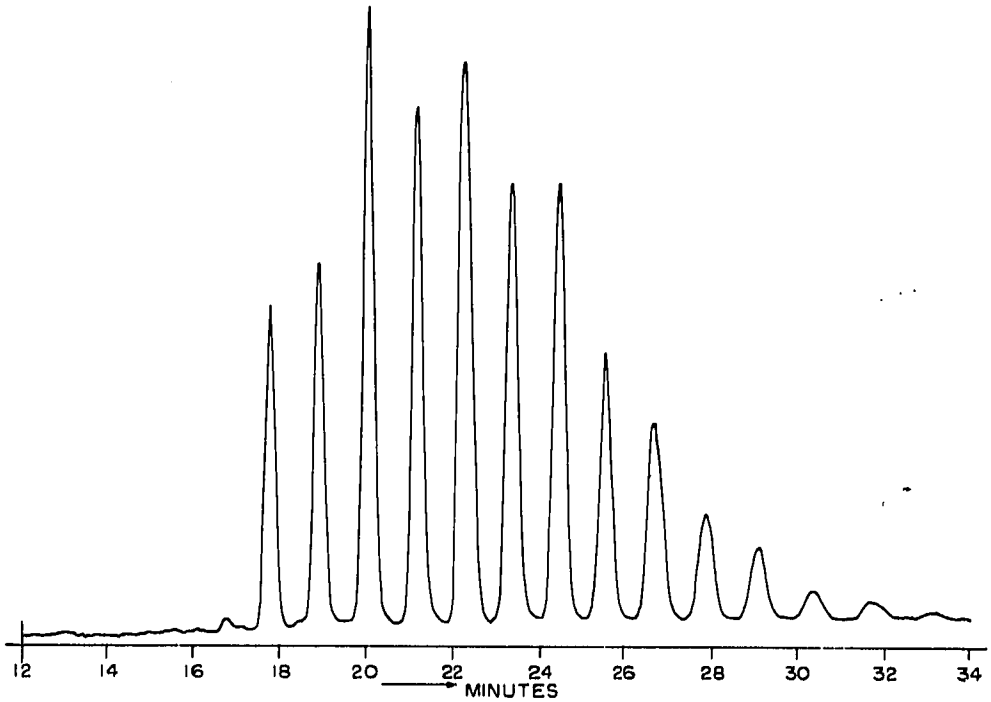

Fig. 1. Separation of Herculube A. Column, 20 ft. × 1/8 in. O.D. stainless steel, 5% PZ-179 on 100–120 mesh Gas-Chrom Q; temperature programmed at 5°/min from 250–350°.

separated as the bromide derivatives. The results obtained, for a 3% loading of the polyphenyl ether sulfone, are shown as Figs. 2–4.

Separation of pesticides

Poly-S-179 columns were tested for the separation of pesticides using an electron capture detector. Fig. 5 shows the separation of a seven-component mixture containing 1 ng of each pesticide. The column temperature was 200°.

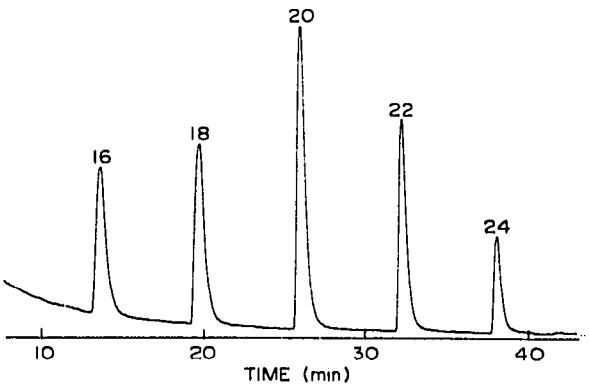

Fig. 2. Separation of long-chain acetates. Column, 4 m × 3.4 mm I.D. glass, 3% PZ-176 on 80–100 mesh silanized Gas-Chrom P; temperature programmed at 2°/min from 180°.

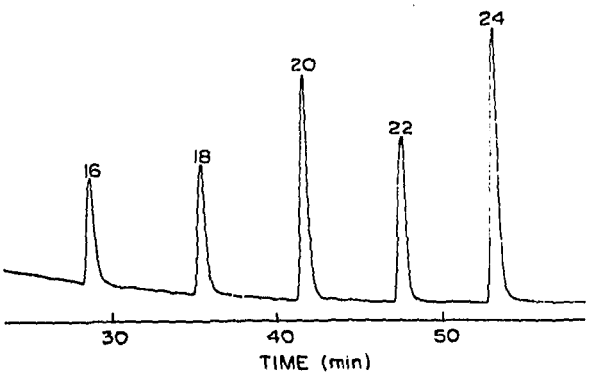

Fig. 3. Separation of long-chain TMS ethers. Column and programming, as in Fig. 2.

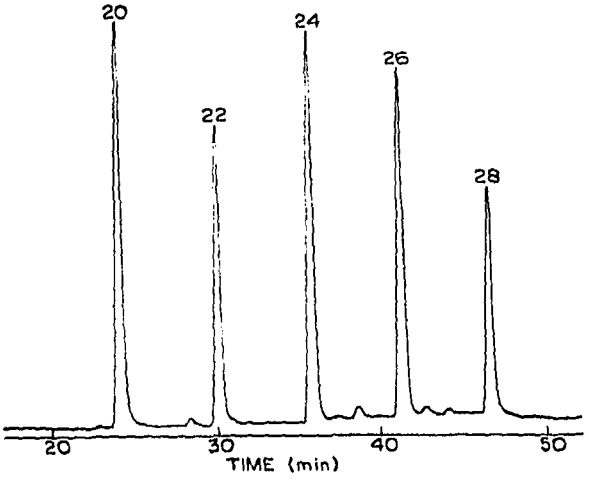

Fig. 4. Separation of long-chain bromides. Column, as in Fig. 2; temperature programmed at 2°/min from 200°.

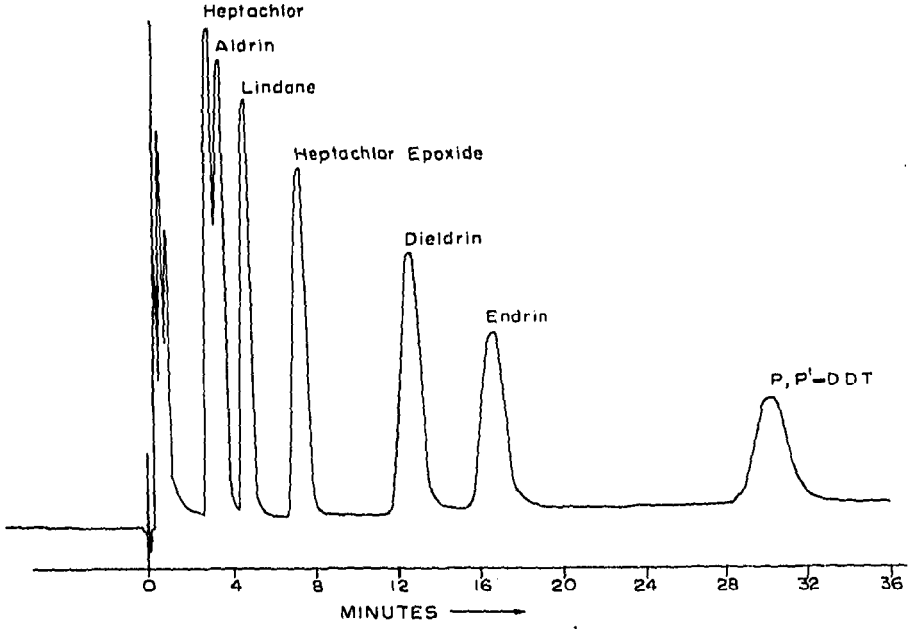

Fig. 5. Separation of pesticides. Column, 2 ft. × 4 mm I.D. glass, 1% Poly-S-179 on 100–120 mesh Gas-Chrom Q; temperature, 200°.

Separation of bile acid methyl esters

A mixture of bile acid methyl esters containing methyl lithocholate, methyl desoxycholate, methyl hyodesoxycholate, and methyl cholate was separated with the 1% Poly-S-179 column in less than 10 min. The column and injector temperatures were 350°. The results are shown as Fig. 6.

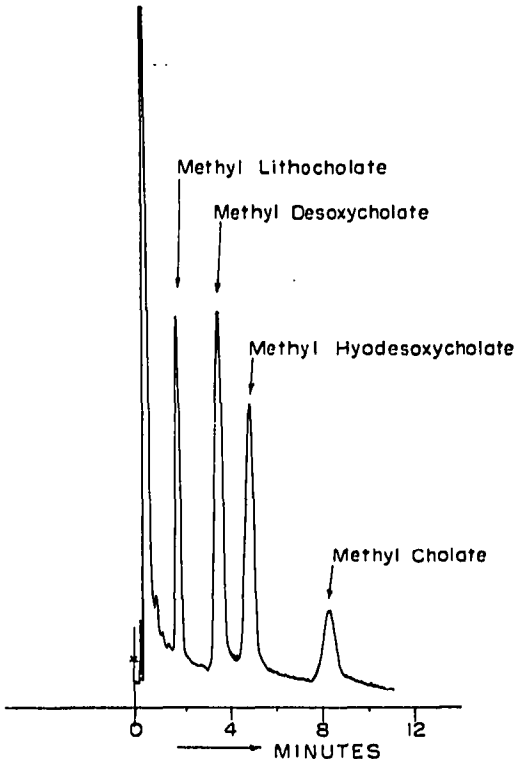

Fig. 6. Separation of bile acid methyl esters. Column, as in Fig. 5; temperature, 350°.

Separation of triglycerides[4]

Glass columns, coated with Poly-S-179, connected with Vespel or graphite ferrules, can be used to temperatures of 400°. However, the usual injection septums cannot be used above 300°.

Initial tests, with a 1% Poly-S-179 on 100–120 mesh Gas-Chrom Q column were not satisfactory. With an injection temperature of 300°, and column temperature of 250–275°, tailing was noticeable for trimyristen, and excessive tailing and low response were obtained for tripalmitin. The tristearin gave a very small peak. Thus, higher column temperatures did not seem to help, except to shorten the time of separation to 12 min.

The authors (Applied Science Labs.) had long considered that the problem of eluting higher triglycerides was related to their volatility and specifically to the injection conditions. Thermal or catalytic decomposition is another possibility. Triglycerides are not highly "polar", therefore, support adsorption effects should not be important.

In a later test, the injector was heated to 390°. An unexpected result was that

the septum (W-13) withstood eleven injections over a 4-h period without leaking. Not quite so unexpected were much improved results, though not perfect.

Fig. 7 shows the results of dual-column operation from 250–375° at 10°/min but with the injector at 390°. The sample size was 0.1 μl containing 2 μg of each triglyceride and the electrometer setting was 2×10^{-9} a.f.s. The injector temperature of 390° gave a definite tristearin peak, though the response is low, a much improved tripalmitin peak, sharper peaks in general, and no tailing.

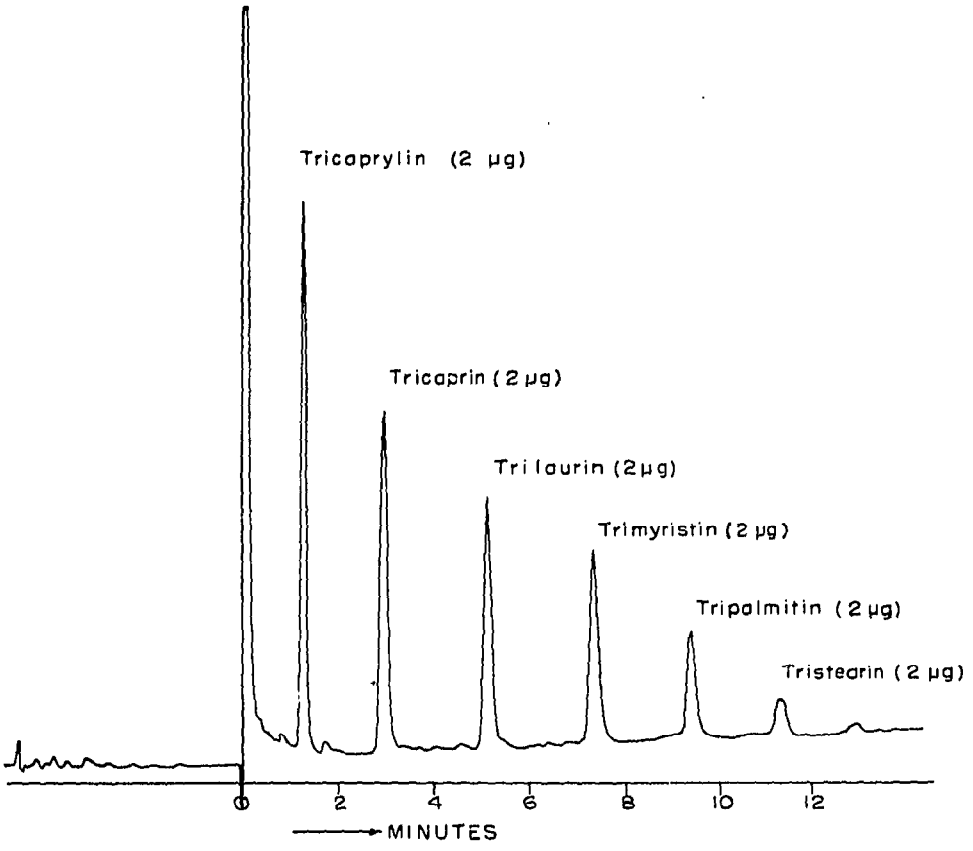

Fig. 7. Separation of triglycerides. Column, as in Fig. 5; temperature programmed at 10°/min from 250–375°. Dual-column operation.

Fig. 8 is a repeat of the separation shown in Fig. 7, but with single-column operation to show the degree of actual baseline rise from 250–370° due to phase bleed. The baseline rise is not excessive at 2×10^{-9} a.f.s.

In another test, the column was programmed from 270–395° at 20°/min with the injector at 390°. Fig. 9 shows the results, for single-column operation, at an electrometer setting of 16×10^{-9} a.f.s. The baseline rise between trilaurin and tristearin and the drop in baseline after tristearin indicate some decomposition of the tristearin and possibly of the tripalmitin. These effects are not so obvious in the other figures but they can be seen if scrutinized closely. This may account for the low tristearin response, even though the peak is sharp. Partial decomposition may be due to the high injector

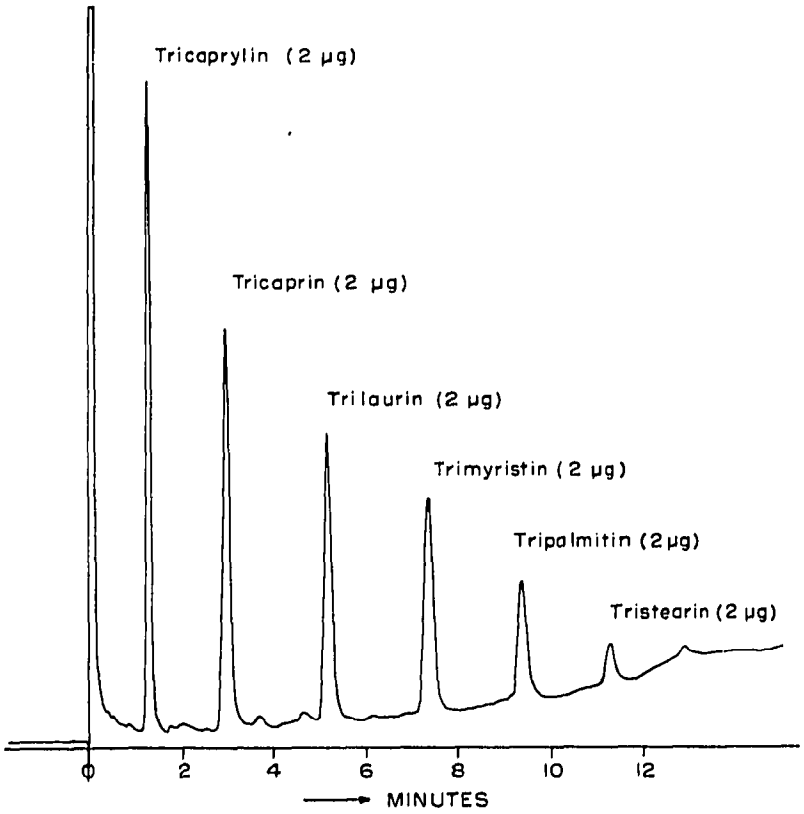

Fig. 8. Separation of triglycerides. Column, as in Fig. 5; temperature programmed at 10°/min from 250–375°. Single-column operation.

temperature. Future tests will evaluate the results obtained at other injection temperatures in the 300–390° range.

Extraneous peaks, and baseline rise, under these conditions can also be caused by septum bleed. Tests indicated a stable baseline for a column temperature of 250° and an injector temperature of 300° at an electrometer setting of 1×10^{-10} a.f.s. Under the same conditions, with the injector at 390°, the baseline was noisy.

As an extension of these tests, a sample of coconut oil triglycerides was separated on a 1% Poly-S-179 column programmed from 250–350° at 6°/min. The injector temperature was 350°. Results are shown as Fig. 10.

Separation of cholesteryl esters

Cholesteryl esters are found in the adrenals, liver, and plasma. Their relationship to atherosclerosis is well known in biochemistry. Cholesterol levels in plasma, and the influence of various polyunsaturated fatty acids in the diet, are interrelated to cholesteryl esters in the plasma.

A previous report[5] on the separation of cholesteryl esters, with a Dexsil liquid phase, does not seem satisfactory because of peak tailing. A standard sample containing eight cholesteryl esters was separated on a 2-ft. glass column, 4 mm I.D., packed with 1% of Poly-S-179 on 100–120 mesh Gas-Chrom Q. The column temperature was programmed from 270–350° at 2°/min. Fig. 11 shows the separation of cholesteryl

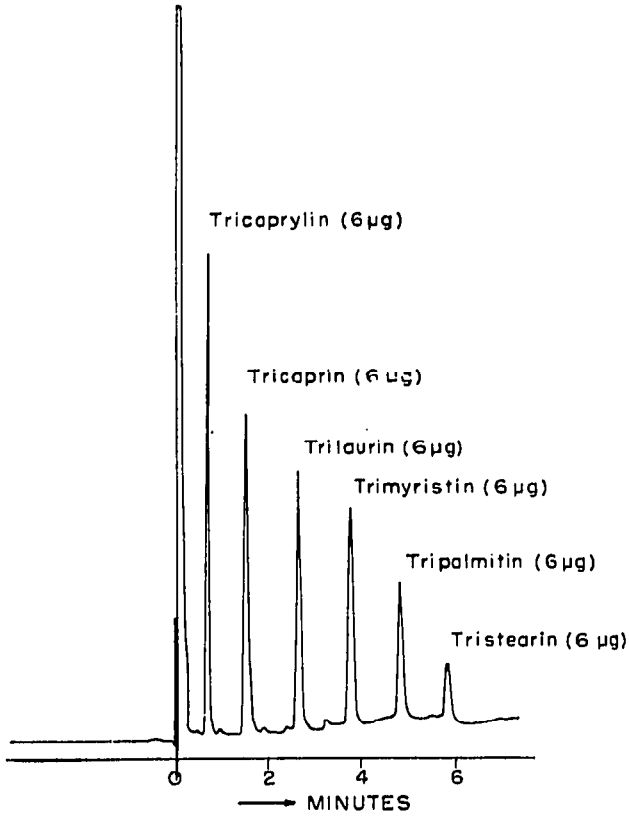

Fig. 9. Separation of triglycerides. Column, as in Fig. 5; temperature programmed at 20°/min from 270–395°. Single-column operation.

derivatives from the undecanoate to the stearate. A small artifact, or unknown peak, eluted immediately after the solvent front. Variation of the injection port temperature did not prevent the formation of this artifact. This artifact may be due to decomposition of cholesteryl esters into free cholesterol and free acid by a thermal rearrangement of the molecule. Further work will be required for the characterization of the artifact.

Sulfone-modified Tenax materials

Tenax[6] is a thermally stable porous polymer which has several uses in gas chromatography. It has been utilized as a trap for volatile materials and as a column packing for the separation of "polar" compounds.

The chemical structure of Tenax —poly-(*p*-2,6-diphenylphenylene oxide)— is closely related to the polyphenyl ether component of polyphenyl ether sulfones. Therefore, it appeared that sulfonylation of Tenax or addition of a sulfone to Tenax would provide interesting, thermally stable, materials for evaluation in high-temperature gas chromatographic systems. Tenax was reacted with excess benzene sulfonyl chloride under Friedel–Crafts conditions. The object of this experiment was to introduce some "polarity" (sulfone groups) to the Tenax without sacrificing the thermal stability. The reacted Tenax was recovered in the same physical form (irregular granules), and is being evaluated for high-temperature applications.

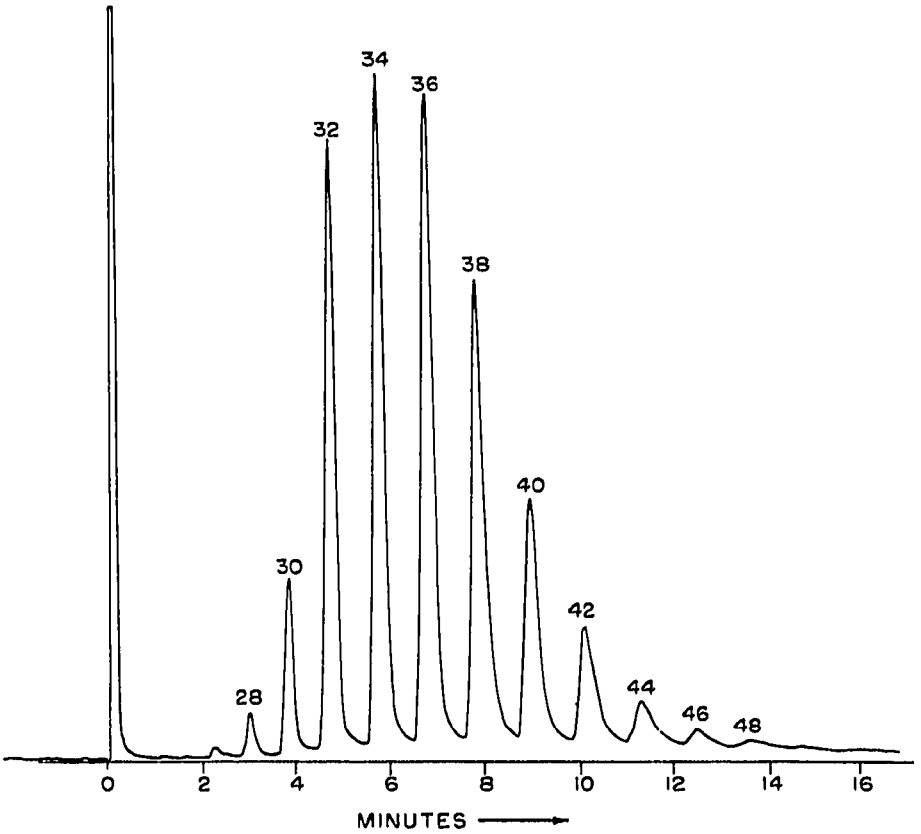

Fig. 10. Separation of coconut oil triglycerides. Column, as in Fig. 5; temperature programmed at 6°/min from 250–350°. Numbers on top of each peak denote the number of carbon atoms in the fatty acid moiety of the triglyceride molecule.

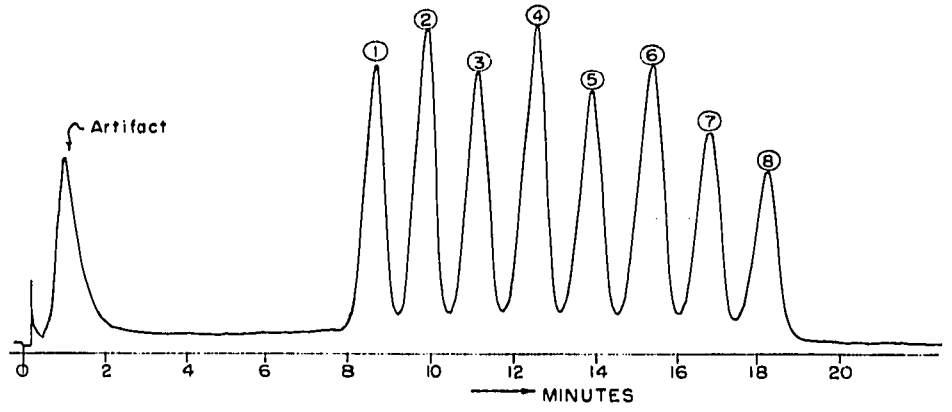

Fig. 11. Separation of cholesteryl esters. Column, as in Fig. 5; temperature programmed at 2°/min from 270–330°. 1 = Cholesteryl undecanoate; 2 = cholesteryl laurate; 3 = cholesteryl tridecanoate; 4 = cholesteryl myristate; 5 = cholesteryl pentadecanoate; 6 = cholesteryl palmitate; 7 = cholesteryl heptadecanoate; 8 = cholesteryl stearate.

In order to prepare a sulfone-coated column which could be programmed from temperatures below 200° to 400°, the polyphenyl ether sulfone was coated onto Tenax. A slurry technique, with a 1:1 dimethylformamide–acetone mixture was employed to prepare a Tenax coated with 10% (by weight) of the polyphenyl ether sulfone. The mixture was air-dried and then dried overnight at 100°.

Two 6-ft. × 1/8-in. O.D. stainless-steel columns were prepared. One was packed with 60–80 mesh Tenax and the other was packed with 60–80 mesh Tenax containing 10% of the polyphenyl ether sulfone. The columns were evaluated for the separation of a benzene–ethanol mixture at 100° and for the separation of a diethylene glycol–dimethylnaphthalene mixture at 200°. The ratio of the retention time for benzene to that for ethanol at 100° was 7.4 on the Tenax and 6.9 for the Tenax plus sulfone. Further, the peaks were sharper and more symmetrical on the sulfone-modified column. This is somewhat surprising because the sulfone is not melted at 100°. At 200°, the ratio of the retention time for the dimethylnaphthalene to that for diethylene glycol was 6.6 for the Tenax column and 5.0 for the sulfone-modified Tenax. At 200° the sulfone is fluid, and as expected sharper, more symmetrical peaks were obtained.

We plan to continue evaluation of sulfonylated Tenax and Tenax plus sulfone columns for the separation of high-boiling "polar" materials.

CONCLUSIONS

Packed columns, coated with polyphenyl ether sulfones are suitable for the separation of certain synthetic lubricants, alcohol derivatives, pesticides, bile acid methyl esters, triglycerides, and cholesteryl esters.

Sulfone-modified porous polymers have been prepared and tested for the separation of "polar" compounds. These columns permit temperature-programmed operation at temperatures below the melting point of the sulfone. Since they contain a uniform organic support material, adsorption effects are reduced.

ACKNOWLEDGEMENTS

The authors thank Drs. Horning, Pfaffenberger, and Lin, of Baylor College of Medicine, Houston, Texas for providing the separations of the long-chain acetates, ethers and bromides. We also thank Alfred J. Webber of Applied Science Labs. for his active participation and suggestions during this work.

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