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PREPARATIVE CAPILLARY GAS CHROMATOGRAPHY

II. FRACTION COLLECTION ON TRAPS COATED WITH A VERY THICK FILM OF IMMOBILIZED STATIONARY PHASE

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SUMMARY

A new concept for preparative collection of volatile compounds is described, using an open-tubular trap coated with an 80- μm film of a cross-linked silicone stationary phase. Breakthrough volumes for a number of volatile organic compounds were calculated from their capacity factors and band broadening. The trap showed a very high retention, as expected from the low phase ratio, $\beta = 1.44$. Benzene for example had a capacity factor of 285 at room temperature. The retention of the thick-film trap is roughly comparable to the retention in an empty tube, kept at a temperature 80–90°C lower. Thus, it was shown to be possible to collect volatile fractions at room temperature from the eluent of a capillary column over an extended period. Recovery of the collected substances was carried out either by thermal desorption or by extraction with pentane. A nearly complete yield of the trapped material was obtained in both cases. The elimination of the need for cryotrapping greatly facilitates fraction collection in preparative capillary gas chromatography and subsequent sample handling.

INTRODUCTION

High-resolution preparative gas chromatography (GC) is a powerful technique for the isolation of volatile trace components from complex mixtures^{1–3}. Usually, better resolution is achieved when compared to high-performance liquid chromatography, and fractions free of mobile phase are obtained. We have recently shown that the technique can be used to collect milligram amounts of material, even when analytical capillary columns are employed⁴.

Unfortunately, fraction collection is not so straightforward. Varying recoveries are frequently experienced due to aerosol formation, inefficient trapping or inadequate handling and transfer of the collected material. In order to improve the collection efficiency for volatile compounds, cold-trapping at solid carbon dioxide or liquid nitrogen temperature is a common procedure. However, under these conditions, it is difficult to avoid contamination from environmental water, particularly after extended collection periods. Moreover, significant losses can occur when the traps are brought to room temperature during sample transfer⁵.

Other trapping procedures involve the use of adsorbents⁶. This leads to an efficient collection, but it is notoriously difficult to accomplish a quantitative desorption. Another alternative is to use a trap, coated with a film of stationary phase. Sandra *et al.*⁷ used this approach; the trapped material was washed out together with the stationary phase, and the material was reinjected on a GC column. However, to obtain pure fractions for spectroscopic work, an additional liquid chromatographic (LC) work-up would be necessary, involving a serious risk of sample losses.

An attractive idea is to collect fractions on an immobilized stationary phase. Apart from thermal desorption, as is common in cold-trapping/reinjection techniques^{5,8}, the use of a pre-extracted immobilized phase would allow a recovery of the fractions by liquid desorption with a minimum risk of contamination from the stationary phase. For an efficient collection of volatile compounds over an extended period, a high retention power is required. Apart from cold-trapping, this can be achieved by a large reduction of the phase ratio. However, with present-day coating techniques, the preparation of films thicker than about 10 μm is not feasible.

In this work, we have studied fraction collection on open-tubular traps, having films of an immobilized silicone polymer of up to 80 μm in thickness. A new coating technique was employed to obtain such thick films. The retention characteristics in terms of capacity factors and breakthrough volumes for compounds of different volatilities were measured, and the recoveries after thermal as well as liquid desorption are reported.

EXPERIMENTAL

Capillary traps

Pyrex capillaries (2 m \times 0.7 mm I.D.) were coated with a methyl-silicone polymer (Sylgard-184, Dow-Corning) by the mercury-plug method with an immediate film fixation at 200°C⁹. The phase ratio and film thickness were calculated from the weight and the density of the cross-linked polymer. Trapping experiments were carried out on a 80- μm thick-film capillary. Capillaries having a film thickness of 20 μm were prepared for the determination of capacity factors. In order to compare the retention behaviour of the Sylgard polymer with that of a known stationary phase, a capillary was coated with PS-255 (Petrarch-Systems), by the static method ($d_t = 14 \mu\text{m}$) and the stationary phase was cross-linked with dicumyl peroxide.

Retention properties of the coated traps

The retention properties of the traps were evaluated for a number of volatile hydrocarbons (Figs. 2 and 3). For this purpose, the traps were operated as normal GC columns (carrier gas, helium; flow velocity, 15 cm/s). The capacity factors were determined at different temperatures, utilizing methane for t_M measurements. Extrapolations of plots of $\ln k'$ as a function of $1/T$ were made to estimate k' values at room temperature. The breakthrough volumes were calculated as the volume of gas necessary to elute 2.3% of the compounds (equivalent to the retention volume $- 2\sigma$).

Fraction collection

First an experiment was carried out to verify that quantitative trapping occurred within the calculated breakthrough volume. Thus, injections of a seven-com-

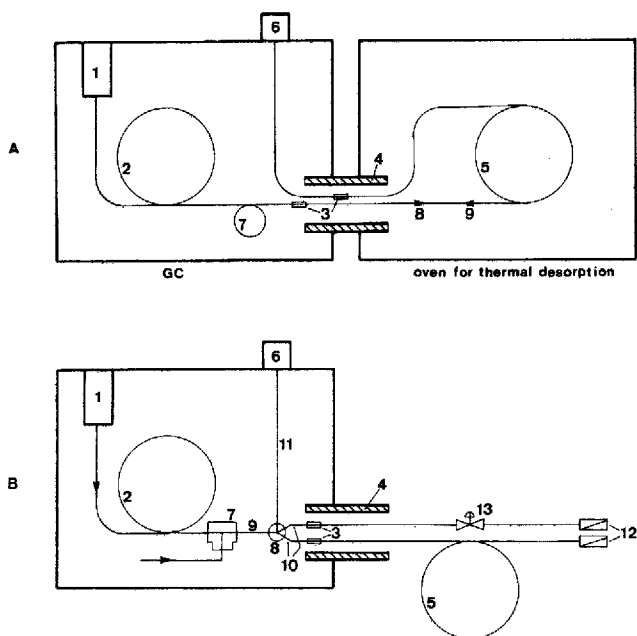


Fig. 1. (A) Experimental set-up where the trap is connected directly to the column for total collection and subsequent thermal desorption of the sample. 1 = On-column injector; 2 = capillary column; 3 = miniature connectors¹³; 4 = heated copper tube; 5 = capillary trap; 6 = detector; 7 = cold-trap for reconcentration during thermal desorption; 8 = direction of the gas flow during collection; 9 = direction of the gas flow during thermal desorption. (B) Apparatus used for repetitive fraction collection. 1–6 as in A; 7 = make-up Tee; 8 = polyimide splitter; 9 = splitter inlet line (fused silica, 0.5 mm I.D.); 10 = outlets to the trap and to waste (fused silica, 0.32 mm I.D.); 11 = outlet line to detector (fused silica, 0.1 mm I.D.); 12 = computer-controlled micro-valves; 13 = gas flow restrictor (Nupro valve).

ponent mixture were made, where the trap was connected in series within the analytical column (Fig. 1A). The outlet of the trap was connected to the detector, in order to reveal a possible breakthrough during the trapping procedure.

In subsequent studies, a repetitive fraction collection was performed, where the trap was connected to the column via a make-up gas Tee and a polyimide splitter manifold (Fig. 1B). A restrictor was inserted in the waste line in order to obtain the same flow resistance as the trap. Both outlets were connected to microvalves (Brunswick Scientific). The splitting ratio between the detector and the trap was determined to be 1:39. The fraction collection process was computer controlled as previously reported⁴.

A total of 70 fractions were collected from ten injections of the seven-component mixture. All fractions were collected in the same trap. The average collection time per fraction was 19.4 s, which corresponded to 1.62 ml of carrier gas. Thus, the total gas volume that passed the trap was *ca.* 110 ml.

Recovery of the trapped material

(a) *Thermal desorption.* In experiments where the trap was connected directly to the column, the gas flow was simply reversed after completion of the trapping by

shifting the in- and outlet of the column/trap assembly. The trap was heated to 140°C in a separate oven, while a section (60–70 cm) of the analytical column was cooled in liquid nitrogen (Fig. 1A), in order to refocus the released compounds. After a transfer period of 20 min, the column temperature programme was started. In the studies of repetitive trapping, the splitter manifold and make-up Tee were removed and the trap was connected directly to the column. Thermal desorption was then performed as described above.

(b) *Liquid extraction.* The trap was slowly flushed with pentane (5–6 $\mu\text{l}/\text{min}$) using a dispenser pump (Perfusor E; Braun/Melsungen AG, F.R.G.) equipped with a 500- μl syringe. The outlet of the trap, which was coupled to a fused-silica line, was guided into a conical micro vial, closed by a PTFE-faced silicone rubber membrane. The vial was cooled with solid carbon dioxide during the extraction period.

Apparatus and chromatographic conditions

Gas chromatograph: Varian Model 6000 equipped with a flame ionization detector and an on-column injector (SGE OCI-3). Analytical column: SE-54, cross-linked, $d_f = 0.6 \mu\text{m}$, 50 m \times 0.31 mm I.D. fused silica. Carrier gas: helium, 40 cm/s. Temperature programme: from 30 to 160°C at 8°C/min.

RESULTS AND DISCUSSION

Evaluation of the retention properties of the trap

Under normal chromatographic conditions, the retention volume, V_R , for a compound is given by

$$V_R = V_g(1 + k') \quad (1)$$

where V_g is the hold-up volume of the column and k' is the capacity factor. The collection of a compound on a trap coated with a stationary phase can be regarded as a very slow chromatographic process, and therefore the retention volume of the component can be approximated as proportional to the capacity factor. However, the total volume of gas that can be passed through the trap before a breakthrough occurs, V_b , is also dependent on the band broadening, as reported by Raymond and Guiochon¹⁰

$$V_b = V_R - 2\sigma \quad (2)$$

where σ is related to the number of theoretical plates, n , according to the equation:

$$n = \left(\frac{V_R}{\sigma} \right)^2 \quad (3)$$

combining eqns. 2 and 3 leads to:

$$V_b = V_R \left(1 - \frac{2}{\sqrt{n}} \right) \quad (4)$$

Thus, a breakthrough factor, f_b , defined as the breakthrough volume relative to the void volume, can be expressed as:

$$f_b = \frac{V_b}{V_g} = (1 + k') \left(1 - \frac{2}{\sqrt{n}}\right) \quad (5)$$

In a trapping process where k' is very large, f_b can be approximated to

$$f_b = k' \left(1 - \frac{2}{\sqrt{n}}\right) \quad (6)$$

i.e., it is dependent on the capacity factor and the chromatographic efficiency of the trap. The capacity factor can be increased by lowering the phase ratio. An obvious approach would therefore be to use a packed bed, as was employed in early work^{11,12}. However, open-tubular traps have a much lower pressure drop and a superior compatibility with capillary columns is obtained. Moreover, they are unequalled in terms of inertness.

For the present work, we were able to prepare an open-tubular trap with a phase ratio of 1.44. This is 20–100 times lower than reported by previous workers.

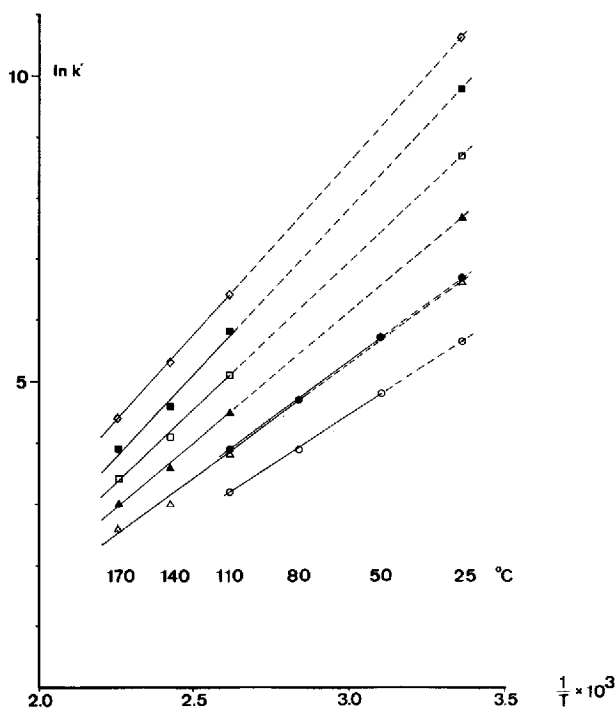


Fig. 2. Plots of $\ln k'$ for a number of hydrocarbons on the 80- μm trap as a function of the reciprocal of the absolute temperature. Capacity factors at room temperature were calculated by extrapolation (as indicated by the dashed parts of the lines) from retention data obtained at higher temperatures. Samples: benzene (O); toluene (●); octane (Δ); nonane (\blacktriangle); decane (\square); undecane (\blacksquare) and dodecane (\diamond).

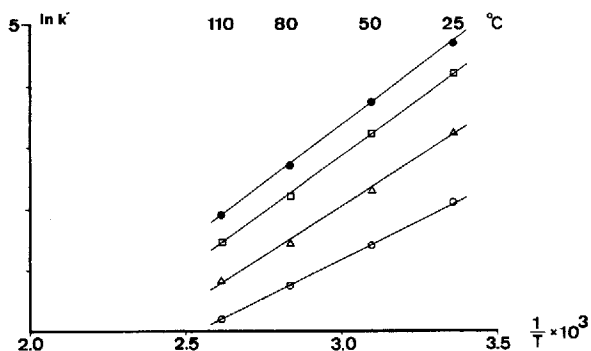


Fig. 3. Plots of $\ln k'$ for pentane (○), hexane (△), heptane (□) and toluene (●) on the 20- μm trap as a function of the reciprocal of the absolute temperature.

Although the very thick film will lead to a poor chromatographic efficiency, a large breakthrough factor is expected. This should allow the collection of volatile compounds without having to cool the trap.

In practice it is difficult to measure the capacity factor for strongly retained compounds, due to excessive peak broadening and associated detection problems. It is more convenient to calculate breakthrough factors from retention data, obtained at elevated temperatures. This method was applied for the 80- μm trap. In Fig. 2, $\ln k'$ is plotted as a function of $1/T$ for a number of volatile hydrocarbons.

Capacity factors at room temperature were estimated by linear extrapolation. This was considered to provide an adequate approximation, which is supported by the results from complementary measurements on a trap coated with a 20- μm film. As is seen in Fig. 3, virtually linear plots were obtained.

In terms of its retention properties, Sylgard-184 resembles the cross-linked methylpolysiloxane PS-255, for the compounds tested. A more complete characterization (determination of McReynolds constants) is in progress.

Breakthrough factors on the 80- μm trap were calculated according to eqn. 6. The results are summarized in Table I.

TABLE I

CAPACITY FACTORS, k' , BREAKTHROUGH FACTORS, f_b , AND BREAKTHROUGH VOLUMES, V_b , AT ROOM TEMPERATURE FOR THE 80- μm TRAP ($n = 16$)

Compound	k'	f_b	V_b (ml)	Compound	k'	f_b	V_b (ml)
Pentane	48	24	13	Toluene	779	389	214
Methylene chloride	65	32	18	Nonane	2078	1039	571
Ethyl formate	72	36	20	Decane	5779	2889	1589
Acetone	77	39	21	Undecane	17 395	8697	4784
Diethyl ether	78	39	21	Dodecane	40 389	20 194	11 107
Hexane	160	80	44				
Ethyl methyl ketone	231	116	64				
Benzene	285	142	78				
Heptane	442	221	121				
Octane	732	366	201				

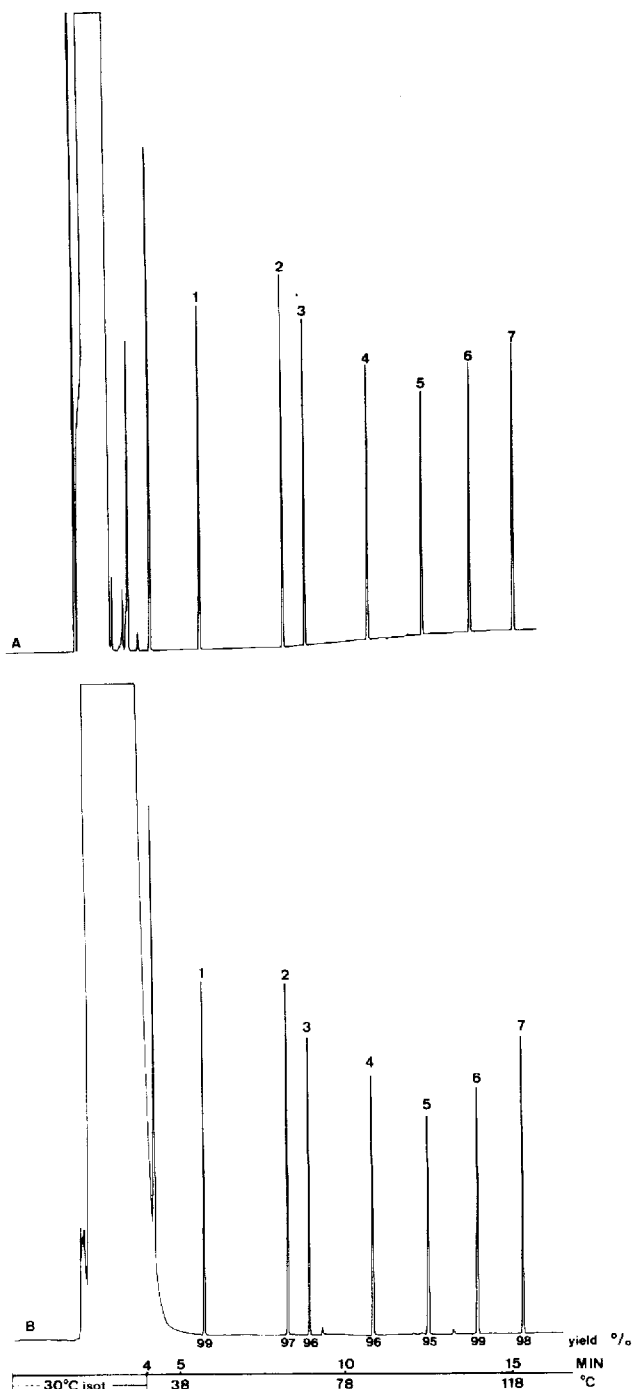


Fig. 4. (A) Chromatogram of a seven-component mixture containing 14 ng each of benzene (1), toluene (2), octane (3), nonane (4), decane (5), undecane (6) and dodecane (7). The same sample was injected when the thick-film trap was connected in series with the column. (B) Chromatogram obtained after thermal desorption/reinjection of the collected material. The percentage recoveries are given in the lower chromatogram below the peaks.

The thick-film trap will retain volatile solvents such as diethyl ether at room temperature, even when purged with an equivalent of 40 trap volumes. Although higher efficiency ($n = 64$) was obtained with the 20- μm trap, the breakthrough factors were 3.6 times lower than for the 80- μm trap. It is evident from eqn. 6 that there exists an optimum between the film thickness and the breakthrough factor. This point is reached when the number of theoretical plates of the trap becomes so small that the effect of the increase in capacity factor is nullified. For a given temperature and tube diameter, the optimum for d_f is dependent on parameters like the length of the trap, the diffusion coefficient in the polymer and the gas velocity. In a forthcoming paper on the sample capacity of the thick-film trap, this optimization will be treated in more detail.

Trapping studies

The powerful retention of the thick-film trap was confirmed in the initial experiment, where the trap was directly connected to the column and kept at room temperature. A complete recovery was obtained for all components except for the solvent (Fig. 4). The presence of some small additional peaks can also be noted. This underlines the importance of clean systems and carefully preconditioned traps. Pentane was only partially retained, since the purge volume during the continuous trapping exceeded the breakthrough volume.

In order to compare the thick-film concept with conventional cryogenic procedures, the same experiment was carried out on an empty trap, cooled to different temperatures. The solvent was allowed to elute from the trap, before cooling was applied, to prevent a blockage or flow restrictions. The results are shown in Table II. Full recovery was obtained when the tube was cooled by liquid nitrogen or solid carbon dioxide-ice, whereas gradually increased losses were encountered at higher temperatures. The results indicate that the retention provided by the thick film corresponds roughly to the effect of an 80–90°C temperature decrease when an empty

TABLE II

COMPARISON OF TRAPPING EFFICIENCIES ON THE THICK-FILM TRAP AND ON AN EMPTY TUBE OF SIMILAR DIMENSIONS

Compound	Recoveries (%)						
	Thick-film (25°C)	Empty tube*				Empty tube + solvent**	
		-196°C	-78°C	-45°C	-20°C	-45°C	-20°C
Benzene	99	103	94	—	—	—	—
Toluene	97	103	94	—	—	2	—
Octane	96	102	93	—	—	44	—
Nonane	96	102	93	19	—	96	—
Decane	95	103	95	101	11	95	6
Undecane	99	103	97	95	100	96	90
Dodecane	98	101	98	91	96	94	90

* The cooling was applied after the solvent had been eluted from the trap.

** The cooling was applied before the solvent entered the trap.

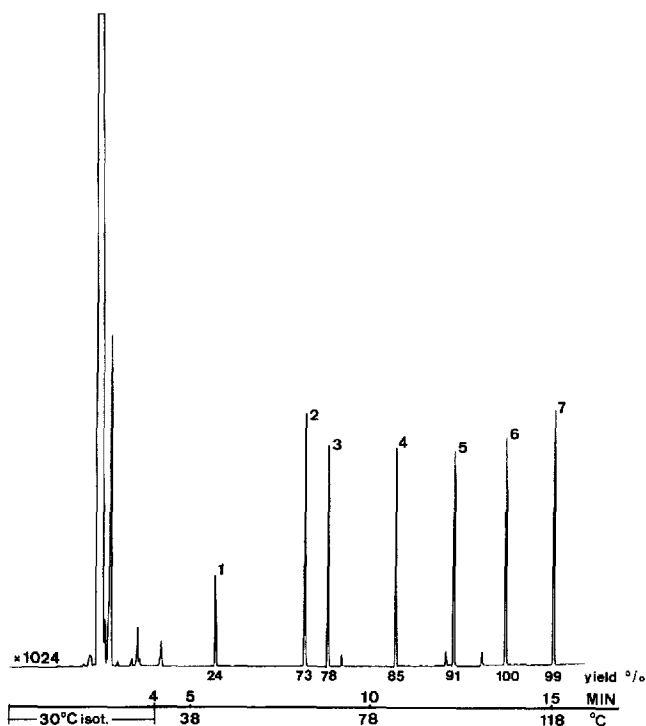


Fig. 5. Recovery after repetitive fraction collection and thermal desorption/reinjection of the seven-component mixture containing a total of 140 ng per compound. The yields of the individual substances are shown below the peaks.

tube is employed. In an attempt to increase the trapping efficiency, the cooling was applied before the solvent was eluted from the column. The condensed solvent enhanced the recovery at -45°C , whereas no significant improvement could be noticed at -20°C . Apparently, this temperature was not sufficiently low to retain the solvent barrier.

For preparative capillary GC, a particularly effective trapping is necessary, since repeated fraction collection is usually carried out over an extended period⁴. In the present evaluation, a cyclic fractionation was performed during 4.5 h. The yields and the chromatogram of the material obtained after thermal desorption are shown in Fig. 5.

Very high recoveries were obtained, except for benzene, where only 25% was recovered. The latter result is partly due to the fact that the breakthrough volume for benzene was exceeded. Additional losses might be caused by back-diffusion in the actual splitter arrangement. The presence of traces of solvent in the collected material indicates the occurrence of some diffusion. An improved splitter design where all gas passages are scavenged with carrier gas is presently under evaluation.

Recovery by liquid extraction

Thermal desorption is an attractive procedure in trapping/reinjection appli-

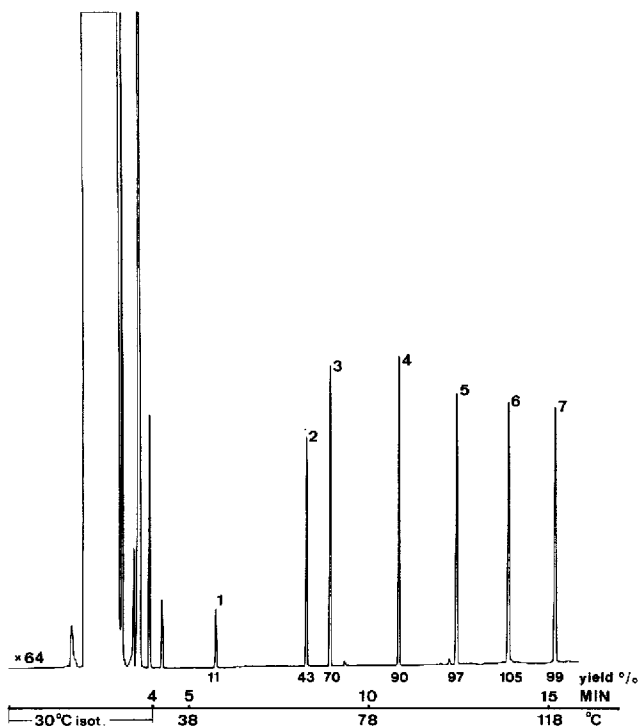


Fig. 6. A chromatogram of the pentane extract of the trapped test mixture containing a total of 700 ng of each component. Recoveries are indicated below the peaks.

cations, *e.g.*, trace enrichment for subsequent GC of mass spectrometric analyses. Solvent-free injections are obtained and a low-temperature thermal refocusing is easily accomplished. The desorption from a liquid stationary phase can take place under much milder conditions than for adsorbents. Yet, high temperatures may still be needed to release the trapped material, which may lead to a breakdown of heat-sensitive compounds or the stationary phase itself. Often, liquid extraction is therefore preferred. Also the presence of a solvent simplifies handling of the collected material.

The advantages of the cross-linked silicone are obvious in this context. The trap can be pre-extracted to remove contaminants and the release of trace components should be easier than from adsorbents such as charcoal or Tenax. The results from a cyclic fractionation, where the collected material was extracted with pentane instead of thermally desorbed, are shown in Fig. 6. The recoveries were similar to those obtained after thermal desorption. Slightly lower yields were observed for the most volatile compounds. We do not know whether these differences are significant. It is unlikely that the material has been retained on the stationary phase. The extraction with pentane was very efficient, and only a very small part of the missing material (2%) was found in a second fraction of 100 μ l of solvent.

A slow rinsing of the trap is recommended. During the extraction the phase swells considerably. This is likely to enhance the extraction process, and therefore the flow-rate of the eluent should be kept in balance with the swelling rate.

CONCLUSIONS

Capillary tubes coated with a very thick film of immobilized stationary phase exhibit high retention power as predictable from their low β -values. Such traps are suitable for repetitive collection of volatile organic compounds at room temperature. This greatly simplifies preparative capillary GC and associated handling of the collected material. The conditions for a quantitative trapping can be derived from the breakthrough volumes, which are easily determined by chromatographic measurements. A complete recovery of the collected material can be obtained either by thermal desorption or liquid extraction. Some losses may be encountered for very volatile compounds.

We believe that there are several further applications for the very thick-film traps. Due to the reduced need for cooling, their use could simplify techniques such as headspace concentration, purge and trap methods and other enrichment procedures where cryotrapping is presently employed.

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REFERENCES

- 1 D. A. Cronin, *J. Chromatogr.*, 52 (1970) 375.
- 2 I. Klimes, W. Stünzi and D. Lamparsky, *J. Chromatogr.*, 136 (1977) 23.
- 3 J. Roeraade and C. R. Enzell, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 123.
- 4 J. Roeraade, S. Blomberg and H. D. J. Pietersma, *J. Chromatogr.*, 356 (1986) 271.
- 5 J. Jetten, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 696.
- 6 K. Grob and A. Habich, *J. Chromatogr.*, 321 (1985) 45.
- 7 P. Sandra, T. Saeed, G. Redant, M. Godefroot, M. Verstaeppe and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 107.
- 8 J. A. Rijks, J. Drozd and J. Novák, *J. Chromatogr.*, 186 (1979) 167.
- 9 J. Roeraade and S. Blomberg, in preparation.
- 10 A. Raymond and G. Guiochon, *J. Chromatogr. Sci.*, 13 (1975) 173.
- 11 D. D. Howlett and D. Welti, *Analyst (London)*, 91 (1966) 291.
- 12 W. A. Aue and P. M. Teli, *J. Chromatogr.*, 62 (1971) 15.
- 13 J. Roeraade, S. Blomberg and G. Flodberg, *J. Chromatogr.*, 301 (1984) 454.