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PREPARATION OF SMALL-DIAMETER CAPILLARY COLUMNS FOR GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

Small diameter (25–100 μm I.D.) fused-silica capillary columns with non-extractable SE-33, SE-54 and 50% phenyl polysiloxane stationary phases were prepared. Elevated coating temperatures and mixed solvent coating solutions facilitated the static coating of these small-diameter columns. Azo-*tert.*-butane was used as the free-radical initiator for crosslinking. Stationary phase film thicknesses of up to 1 μm were successfully immobilized. Coating efficiencies were above 70% (SE-33), 50–80% (SE-54), and 20–40% (50% phenyl polysiloxane). Nearly 700,000 theoretical plates (gas chromatography) were generated by a 46 m \times 50 μm I.D. column coated with a 0.25- μm film of SE-54. In general, supercritical fluid chromatography efficiencies at practical mobile phase velocities were approximately one-fifth of those produced by gas chromatography at optimum mobile phase velocities from the same columns. Experimental determinations of column performance agreed well with theoretical predictions.

INTRODUCTION

Recent developments in high-speed gas chromatography (GC) and capillary column supercritical fluid chromatography (SFC) require small diameter ($< 100 \mu\text{m}$ I.D.) capillary columns properly coated with stationary phases^{1–4}. For good performance, the small-diameter columns should possess the usual qualities of high efficiency, excellent deactivation, and lasting stability as are desired for regular-bore capillary columns. However, the preparation of small-diameter columns is technically not as straightforward as for regular-bore columns because of their small diameters; plugging during pretreatment, coating, and conditioning is a continual problem. Therefore, modification of the established procedures for the preparation of regular-bore capillary columns is necessary.

A necessary requirement for high efficiency is a homogeneous stationary phase film along the length of the column. To achieve a homogeneous coating, the inner wall of the column must be wettable by the stationary phase. Contact angle measurements⁵ have shown that the untreated fused-silica capillaries are wettable by most apolar and polar stationary phases. However, the coating efficiencies of polar phases on untreated fused silica are usually poor. Various surface treatments or modifications^{6,7} have improved the coating efficiencies of capillary columns coated with moderately polar to polar phases.

Recently, stationary phase viscosity has been shown to affect film formation as well as film stability⁸. Polysiloxane gum phases with long polymer chains and high viscosities have been synthesized in order to improve coating efficiencies on both treated^{6,7} and untreated^{9,10} fused-silica capillaries. Vinyl or tolyl functional groups were incorporated in the polysiloxane backbone to facilitate the free-radical crosslinking of polysiloxane gums into rubbers, which exhibit high film stabilities to both high temperature heating and solvent extraction. Peroxides were originally used as free-radical crosslinking reagents^{9,11-13}, however, peroxide crosslinking tends to produce active columns. Recently, azo compounds^{10,14,15}, such as azo-*tert.*-butane, azo-*tert.*-octane, and azo-*tert.*-dodecane, have been favorably employed for free-radical crosslinking to produce less active columns. Resultant nonextractable phases exhibit long column lifetimes under gas chromatographic conditions, and can be used in supercritical fluid chromatography.

The static coating method¹⁶ is generally superior to the dynamic coating method¹⁷⁻²⁰. However, the coating of long and/or small-diameter columns has not been an easy task. Recently, elevated temperatures²¹ were employed for static coating of small-diameter columns. The use of mixed solvents in coating solutions²² also facilitated the static coating of moderately polar phases such as Superox 20M and phenyl polysiloxanes.

In this study, the preparation of small-diameter (25–100 μm I.D.) untreated fused-silica capillary columns coated with non-extractable stationary phases is described. Their chromatographic performance for both GC and SFC is discussed.

EXPERIMENTAL

Fused-silica capillary tubing (100 to 50 μm I.D., from Hewlett-Packard, Avondale, PA, U.S.A.; and 25 μm I.D. from Scientific Glass Engineering, Austin, TX, U.S.A.) was coated without prior surface modification or deactivation.

The three stationary phases used in this study were SE-33 (Applied Science, State College, PA, U.S.A.), SE-54 (Applied Science) and a 50% phenyl, 49% methyl, 1% vinyl polysiloxane which was synthesized in this laboratory⁹. The solvents used to prepare the coating solutions were *n*-pentane for SE-33 and SE-54 and 2:1 (v/v) ratio of *n*-pentane–methylene chloride for the 50% phenyl phase. Appropriate amounts of the stationary phases were dissolved in their respective coating solvents to give desired film thicknesses.

The capillary columns were coated statically¹⁶ at different elevated temperatures ranging from 30°C to 80°C depending on the diameters and lengths of the columns. In addition to coating at elevated temperatures, an *n*-pentane–methylene chloride mixed solvent for the 50% phenyl polysiloxane greatly reduced the coating time. After coating, the columns were purged with nitrogen gas for 30 min at room temperature.

For crosslinking, azo-*tert.*-butane was purged through the column at room temperature for a certain period of time (see Tables I and II) depending on the column diameter and length. To facilitate the purging of azo-*tert.*-butane through the small diameter columns, a device depicted in Fig. 1 was employed. After azo-*tert.*-butane purging, the columns were sealed and temperature programmed from 40°C to 220°C at 4°C min⁻¹ and held at 220°C for 1 h for crosslinking. The columns

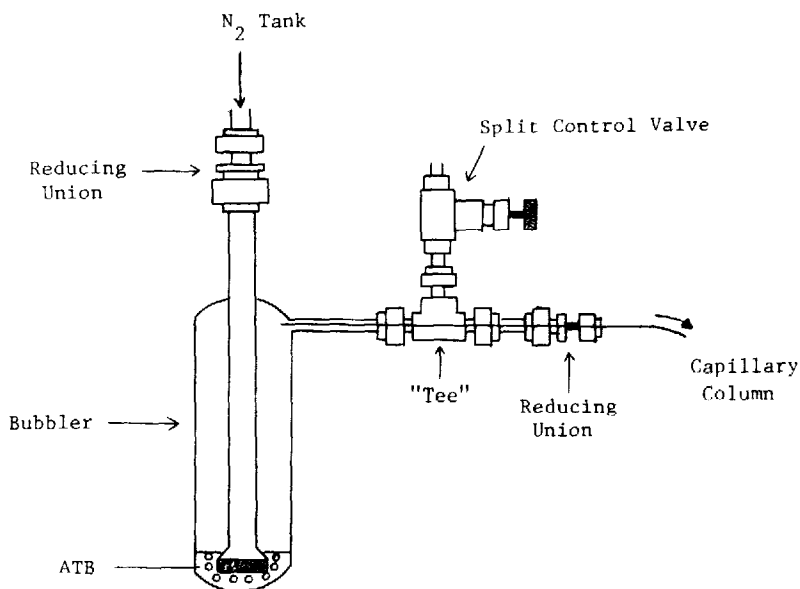


Fig. 1. Azo-*tert.*-butane purging device.

were then normally temperature programmed from 40°C to 250°C at 0.5°C min⁻¹ under a gas stream (nitrogen or helium) and held at 250°C overnight.

The finished columns were subsequently evaluated with a HP 5790 gas chromatograph equipped with a flame ionization detector. Because a high head pressure was required to obtain the appropriate flow of carrier gas (helium), a high pressure regulator and a needle valve were used for pressure control and split adjustment²¹. A standard solution containing *n*-decane, *n*-undecane, and *n*-dodecane in methylene chloride at a concentration of 0.1 mg ml⁻¹ each was prepared for the evaluation of column efficiency. With a split ratio of greater than 100:1, less than 1 ng per component was injected.

After gas chromatographic evaluation, the columns were washed with 50 to 100 ml of methylene chloride using a Varian Model 8500 LC pump. Washout data were obtained based on the change of *k'* values before and after washing. Further washout was also checked after the columns were used in supercritical fluid chromatography.

Two home-built supercritical fluid chromatographs equipped with flame ionization²³ and on-column UV²⁴ detectors were used in this study. Both chromatographs were equipped with splitter injectors for sampling. The standard solution containing 0.1 mg ml⁻¹ of *n*-decane, *n*-undecane, and *n*-dodecane was used for CO₂-SFC, while a standard solution containing 0.1 mg ml⁻¹ each of phenanthrene and pyrene in methylene chloride was prepared for column evaluation for *n*-pentane-SFC. A carbon black extract was analyzed to demonstrate the performance of a column coated with the 50% phenyl polysiloxane stationary phase.

Theoretical SFC $H-\bar{u}$ curves were constructed using an Apple II+ micro-computer from the Golay equation²⁵ for capillary columns:

$$H = \frac{2 D_m}{\bar{u}} + \frac{(1 + 6 k' + 11 k'^2) d_c^2 \bar{u}}{96 D_m (1 + k')^2} + \frac{2 k' d_f^2 \bar{u}}{3 (1 + k')^2 D_s} \quad (1)$$

where $D_m = 2 \cdot 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ and $D_s = 1 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$.

Theoretical GC $H-\bar{u}$ curves were constructed from the Golay equation as modified by Giddings²⁶:

$$H = \frac{2 D_m f_2}{\bar{u}} + \frac{(1 + 6 k' + 11 k'^2) f_1 d_c^2 \bar{u}}{96 (1 + k')^2 D_m f_2} + \frac{2 k' d_f^2 \bar{u}}{3 (1 + k')^2 D_s} \quad (2)$$

where f_1 and f_2 are pressure drop correction factors:

$$f_1 = \frac{9 (P^4 - 1) (P^2 - 1)}{8 (P^3 - 1)^2} \quad (3)$$

$$f_2 = \frac{3 (P^2 - 1)}{2 (P^3 - 1)} \quad (4)$$

and

$$P = \frac{P_{\text{in}}}{P_{\text{out}}} \quad (5)$$

where P_{in} and P_{out} are the column inlet and outlet pressures, respectively. For GC, $D_m = 0.27 \text{ cm}^2 \text{ sec}^{-1}$ and $D_s = 6 \cdot 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. Values of \bar{u} were determined following the method of Cramers *et al.*²⁷:

$$\bar{u} = \frac{3 d_c^2 P_0 (P^2 - 1)^2}{128 \eta L (P^3 - 1)} \quad (6)$$

where η is the viscosity and L is the column length.

RESULTS AND DISCUSSION

One of the advantages of static coating is that the film thickness can be calculated from the concentration of the coating solution. The necessary concentration and, hence, viscosity of the coating solution increase as the column diameter decreases, which makes the filling of columns and the evacuation of solvent from the columns very difficult. For example, a 7.7% (w/v) SE-54 coating solution is required for the coating of a 50- μm I.D. column with a 1- μm film thickness. In this work, high nitrogen gas pressures of up to 1200 p.s.i. were used to fill long and/or small diameter columns with the coating solutions. The use of mixed solvents for coating solutions of 50% phenyl polysiloxane greatly reduced the viscosity and, therefore, facilitated the filling and evacuation of the column. The choice of coating temperature depended

on the diameter and length of the column. With these modifications in the static coating method, a $50 \text{ m} \times 50 \mu\text{m}$ I.D. column could be coated at 60°C within 10 h. Temperatures between 70 and 80°C were employed to coat the $25\text{-}\mu\text{m}$ I.D. columns.

Azo-*tert.*-butane was chosen as the free-radical initiator for crosslinking because (a) it does not affect the polarity or activity of the column¹⁵ and (b) it can be purged as a vapor through the column, thus avoiding plugging problems. The purging device described in the experimental section was employed for saturating the stationary phase with azo-*tert.*-butane. By adjusting the bypass opening, the bubbling of nitrogen through the liquid azo-*tert.*-butane in the bubbler was maintained, and the flow of nitrogen and azo-*tert.*-butane through the column remained constant. Otherwise, purging often stopped when the column diameter was small because the gas pressure regulator used was not sensitive enough to handle small changes in pressure. Longer azo-*tert.*-butane purging times were employed for longer columns. As a rule of thumb, an additional 10 m of column required an additional hour of purging to saturate the column with azo-*tert.*-butane and to effect acceptable crosslinking. Crosslinking twice, each time after purging azo-*tert.*-butane from opposite ends of the column, increased the successful crosslinking rate. It was found that SE-33 and SE-54 were not over-crosslinked even after crosslinking 5 times. However, detectable hardening of the 50% phenyl polysiloxane was obtained after 4 crosslinking steps.

Tables I and II list coating conditions, gas chromatographic efficiencies, and washout data of columns coated with SE-54, SE-33, and 50% phenyl polysiloxane. Even though these columns were not operated at optimum linear velocities, some of the long columns showed very high efficiencies. For example, the $46 \text{ m} \times 50 \mu\text{m}$ I.D. column coated with SE-54 produced 684,480 total plates, and the $12.5 \text{ m} \times 25 \mu\text{m}$ I.D. column exhibited over 400,000 total plates.

TABLE I

PREPARATION CONDITIONS AND GAS CHROMATOGRAPHIC EFFICIENCIES OF NON-EXTRACTABLE SE-54 COLUMNS WITH DIFFERENT DIMENSIONS

All columns had $0.25\text{-}\mu\text{m}$ film thickness.

Column I.D. (μm)	Column length (m)	Coating temperature ($^\circ\text{C}$)	ATB purging time* (h)	T ($^\circ\text{C}$)	\bar{u}_{He} (cm sec^{-1})	k'	N:L (plates m^{-1})	N	Washout** (%)
100	15	38	2,2	100	50	10.3	5234	78,510	0.0
	30	44	3,3	150	10	2.1	4333	129,990	5.0
	50	50	4,4	100	30	9.6	7103	355,150	4.2
75	15	38	2,2	150	16	3.5	3258	48,870	—
	29	38	4,4	100	29	12.3	11,519	334,051	0.8
50	23	38	4,4	100	20	17.8	14,592	335,616	8.4
	46	60	5,5	150	18	6.7	14,888	684,480	—
25	7	70	4,4	100	25	5.5	27,966	195,762	—
	12.5	70	5,5	100	24	35.0	32,694	408,675	—

* Crosslinking twice; azo-*tert.*-butane was purged from opposite ends.

** Washout data were obtained from the difference in k' before and after washing with 100 ml of methylene chloride.

TABLE II
 PREPARATION CONDITIONS AND GAS CHROMATOGRAPHIC EFFICIENCIES OF COLUMNS COATED WITH NON-EXTRACTABLE SE-33
 AND 50% PHENYL POLYSILOXANE

All columns had 0.25- μm film thickness.

Stationary phase	Column I.D. (μm)	Column length (m)	Coating temperature ($^{\circ}\text{C}$)	ATB purging time* (h)	T ($^{\circ}\text{C}$)	\bar{u}_{He} (cm sec $^{-1}$)	k'	N/L (plates m $^{-1}$)	N (plates)	Washout** (%)
SE-33	50	10.5	35	3	70	24	82	17,110	179,660	4.1
	50	20	35	5	100	20	21	12,097	241,940	—
50% Phenyl	100	15	28	2,2	100	36	19	5849	87,735	0.0
	50	28	60	5,5	60	18	14	6348	177,744	—
	50	40	55	5,5	100	15	7.4	5343	213,720	—

* Crosslinking once (SE-33) or twice (50% phenyl).

** Washout data were obtained from the difference in k' before and after washing with 100 ml of methylene chloride.

From experimental $H-\bar{u}$ plots (GC) it was found that the coating efficiency ($k' > 10$) was usually over 90% for SE-33, 50–80% for SE-54, but only 20–40% for 50% phenyl polysiloxane coated on $\leq 100 \mu\text{m}$ I.D. untreated fused silica columns. In contrast, the coating efficiencies of fused-silica columns with I.D.s over $200 \mu\text{m}$ are usually above 70%^{6,9}. Surface modification of the column^{6,7} should improve the coating efficiency.

Typically, the efficiencies of columns coated with a $0.25\text{-}\mu\text{m}$ film of SE-54 were 7000, 11,000 and 14,000 plates m^{-1} for 100-, 75- and $50\text{-}\mu\text{m}$ I.D. columns, respectively, while approximately 10,000 and 17,000 plates m^{-1} were obtained for 100- and $50\text{-}\mu\text{m}$ I.D. columns, respectively, coated with SE-33. Only 5500 and 6500 plates m^{-1} were obtained for 100- and $50\text{-}\mu\text{m}$ I.D. columns, respectively, coated with 50% phenyl polysiloxane.

Fig. 2 shows $H-\bar{u}$ plots for 50- and $25\text{-}\mu\text{m}$ I.D. columns under GC conditions. The dotted lines represent theoretical curves, while the experimental results are plotted for comparison. Measurements at the required column head pressures (400–500 p.s.i.) were rather tedious to obtain, and account for some of the scatter in the experimental data. Nevertheless, it can be seen that small diameter columns possessing efficiencies that approach those theoretically predicted can be prepared.

The washout data listed in Tables I and II show that over 90% non-extractability was reached with azo-*tert.*-butane crosslinking. A long column could be plugged during washing when the dissolved stationary phase accumulated enough to make a concentrated and very viscous solution at the solvent front. Gradient solvent

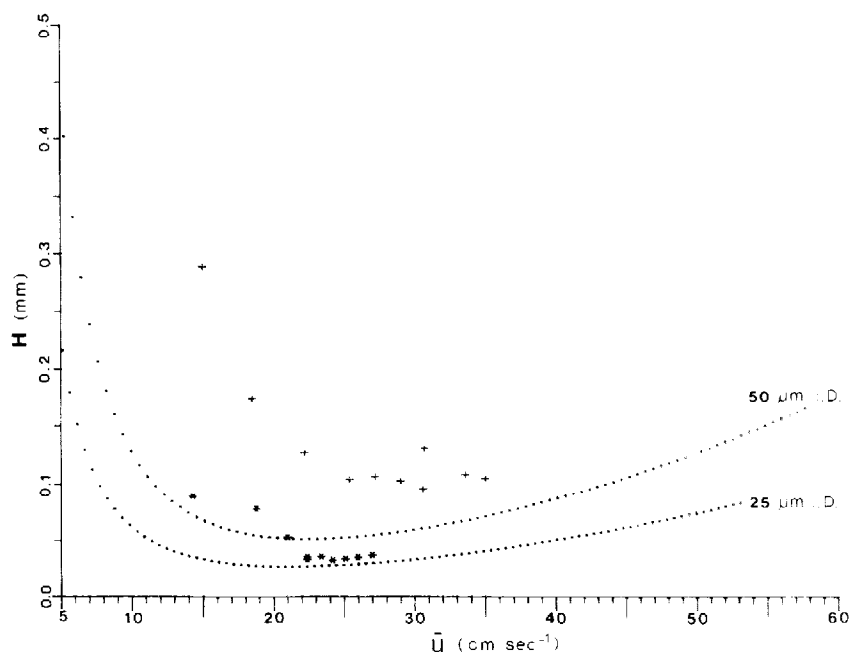


Fig. 2. Gas chromatographic $H-\bar{u}$ curves of a $23\text{ m} \times 50 \mu\text{m}$ I.D. column and a $12.5\text{ m} \times 25 \mu\text{m}$ I.D. column coated with SE-54 ($0.25 \mu\text{m}$ film thickness). Column conditions: helium carrier gas at 100°C isothermal; $k' = 6.2$ and 9.3 for *n*-decane on the $50\text{-}\mu\text{m}$ and $25\text{-}\mu\text{m}$ I.D. columns, respectively.

TABLE III

GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHIC PERFORMANCE OF NON-EXTRACTABLE SE-54 AND 50% PHENYL POLYSILOXANE

Columns: SE-54, 23 m × 50 μm I.D., 0.25 μm film thickness; 50% phenyl, 27 m × 50 μm I.D., 0.25 μm film thickness.

Stationary phase	GC*				SFC**			
	<i>k'</i>	<i>N/L</i> (plates m ⁻¹)	<i>H</i> _{min} (mm)	<i>ū</i> _{opt} (cm sec ⁻¹)	<i>k'</i>	<i>N/L</i> (plates m ⁻¹)	<i>H</i> (mm)	<i>ū</i> (cm sec ⁻¹)
SE-54	23	16,666	0.060	27	1.5	4240	0.236	3.0
					2.4	3050	0.328	3.0
					3.9	3000	0.333	3.0
50% Phenyl	14	6654	0.150	18	1.5	1390	0.719	4.7
					2.6	1707	0.586	4.7

* GC conditions: helium carrier gas at 27 cm sec⁻¹ (SE-54) and 15 cm sec⁻¹ (50% phenyl); isothermal temperature at 100°C (SE-54) and 60°C (50% phenyl).

** SFC conditions: carbon dioxide mobile phase for SE-54 at 40°C and 72 atm; *n*-pentane mobile phase for 50% phenyl at 210°C and 26.7 atm.

washing (increasing methylene chloride in *n*-pentane) was found to be essential for rinsing of the 50% phenyl polysiloxane columns.

Conditioning of the columns after coating and before crosslinking may be detrimental because of efficiency losses⁸ resulting from a decrease in viscosity with temperature. However, columns were usually conditioned by temperature programming up to high temperatures (*ca.* 280°C) under a nitrogen or helium stream immediately after the crosslinking step. The columns were also conditioned with supercritical fluids if they were to be used for SFC.

Table III compares the GC and SFC performance of SE-54 and 50% phenyl polysiloxane. Because the optimum average linear velocity of the mobile phase in

TABLE IV

GC AND SUPERCRITICAL FLUID CHROMATOGRAPHIC PERFORMANCE OF NON-EXTRACTABLE SE-54 COLUMNS WITH DIFFERENT DIAMETERS

All columns had 0.25-μm film thickness.

Column diameter (μm)	Column length (m)	GC*				SFC**			
		<i>k'</i>	<i>N/L</i> (plates m ⁻¹)	<i>H</i> _{min} (mm)	<i>ū</i> _{opt} (cm sec ⁻¹)	<i>k'</i>	<i>N/L</i> (plates m ⁻¹)	<i>H</i> (mm)	<i>ū</i> (cm sec ⁻¹)
100	24	14	7692	0.130	28	2.02	2874	0.348	0.9
						2.22	1513	0.661	1.9
75	24	17	9091	0.110	20	2.57	2890	0.346	1.3
						2.72	2342	0.427	1.8
50	23	23	16,666	0.060	27	3.39	3480	0.287	2.0
						3.86	3000	0.333	3.0

* GC conditions: helium carrier gas; 100°C isothermal.

** SFC conditions: carbon dioxide mobile phase; 72 atm isobaric.

SFC is too low for practical use (*ca.* 0.2 cm sec^{-1}), an average linear velocity of over $10 \bar{u}_{\text{opt}}$ was usually employed. Therefore, column performance in SFC was evaluated at these higher velocities.

The SFC efficiencies were higher at lower k' values which is consistent with theoretical predictions. The GC efficiencies at \bar{u}_{opt} were about five times those of SFC at $\bar{u} \approx 10 \bar{u}_{\text{opt}}$ with the same columns. In SFC, the SE-54 column (23 m) generated about 78,000 plates, while the 50% phenyl polysiloxane (27 m) produced only about 40,000 plates.

Table IV compares the performance of different diameter columns coated with SE-54 ($0.25 \mu\text{m}$ film thickness) for both GC and SFC. As expected, GC efficiency increases as column diameter decreases. The k' values increase as the diameter decreases as a result of the decrease in the phase ratio (constant film thickness). Again, the GC efficiencies at \bar{u}_{opt} are about five times those of SFC obtained at velocities 10–20 times \bar{u}_{opt} . The total SFC plate numbers for 100-, 75- and $50\text{-}\mu\text{m}$ I.D. columns are about 36,000, 55,000 and 78,000, respectively, which is comparable with the performance of a typical $20 \text{ m} \times 300 \mu\text{m}$ I.D. column in GC.

Fig. 3 shows representative $H\text{-}\bar{u}$ plots for 75- and $50\text{-}\mu\text{m}$ I.D. columns under carbon dioxide supercritical fluid chromatographic conditions. The solid lines represent theoretical curves, and the experimental measurements are again plotted for comparison. In this example, and in most cases for SFC, the experimental data agreed remarkably well with theory.

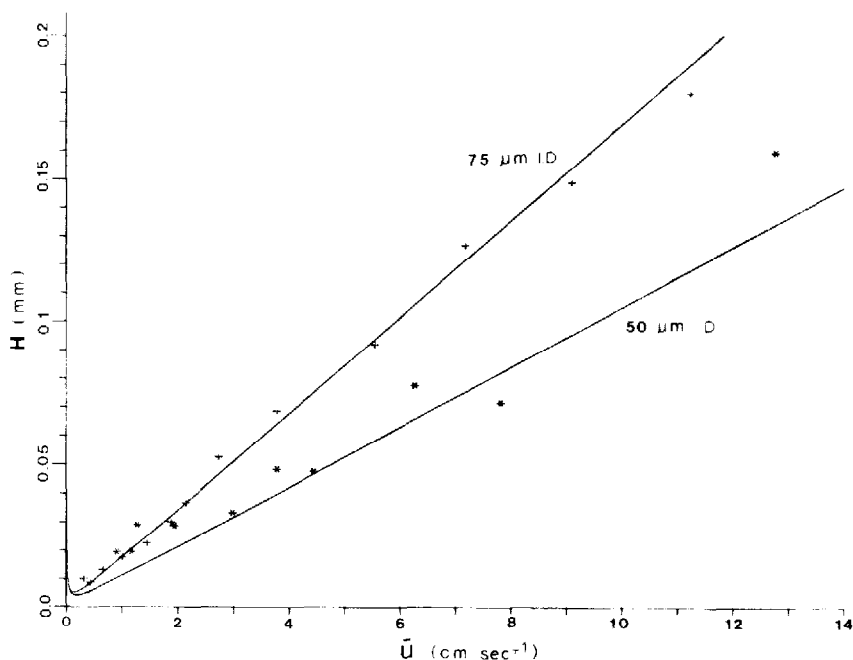


Fig. 3. Supercritical fluid chromatographic $H\text{-}\bar{u}$ curves of a $10 \text{ m} \times 75 \mu\text{m}$ I.D. column ($0.19\text{-}\mu\text{m}$ film thickness) and a $23 \text{ m} \times 50 \mu\text{m}$ I.D. column ($0.25\text{-}\mu\text{m}$ film thickness) coated with SE-54. Column conditions: carbon dioxide mobile phase at 40°C and 72 atm ; $k' = 1.6$ and 3.9 for *n*-dodecane on the 75- and $50\text{-}\mu\text{m}$ I.D. columns, respectively.

TABLE V

GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHIC PERFORMANCE OF NON-EXTRACTABLE SE-54 COLUMNS WITH DIFFERENT FILM THICKNESS

All columns were 11 m except the 0.25- μm I.D. column which was 23 m.

Film thickness (μm)	GC*				SFC**			
	k'	N/L (plates m^{-1})	H_{min} (mm)	\bar{u}_{opt} (cm sec^{-1})	k'	N/L (plates m^{-1})	H (mm)	\bar{u} (cm sec^{-1})
0.25	23	16,666	0.060	27	3.4	3480	0.287	2.0
					3.7	3000	0.333	3.0
0.50	46	13,425	0.074	33	5.7	2519	0.397	2.3
					5.8	2415	0.414	1.9
0.75	70	18,559	0.054	32	9.7	3534	0.283	2.0
					10.2	2457	0.407	3.0
1.00	97	19,300	0.052	30	13.7	3058	0.327	1.8
					13.9	2326	0.430	2.3

* GC conditions: helium carrier gas; 100°C isothermal.

** SFC conditions: carbon dioxide mobile phase; 72 atm isobaric.

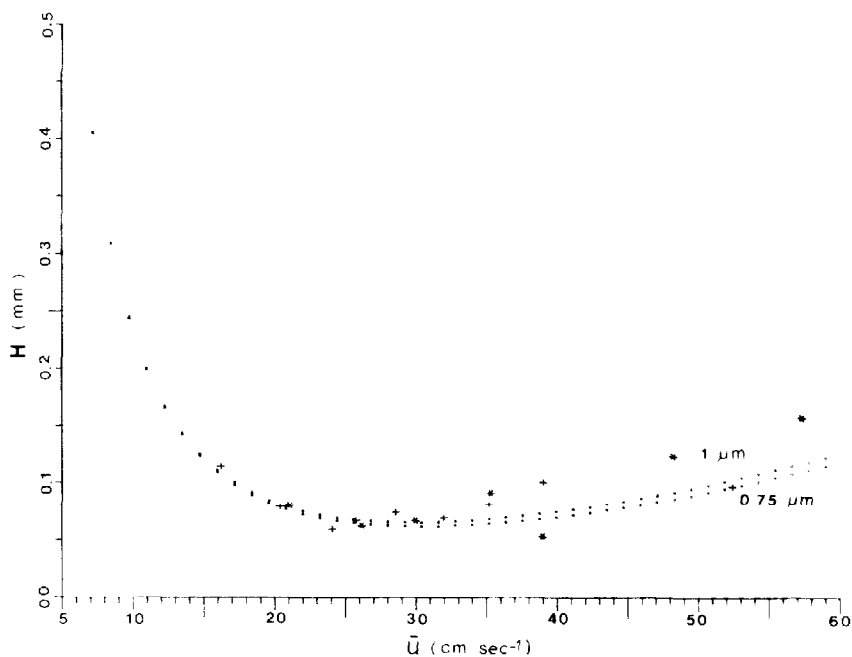


Fig. 4. Gas chromatographic H - \bar{u} curves of 11 m \times 50 μm I.D. columns coated with 0.75- μm and 1.0- μm film thicknesses of SE-54. Column conditions: helium carrier gas at 100°C isothermal; $k' = 19$ and 26 for n -decane on the 0.75- and 1.0- μm film columns, respectively.

The performance of columns with different film thicknesses is listed in Table V. Note that the GC efficiencies increase for the same standard solute as the film thickness increases, except for the column with 0.5- μm film thickness, which exhibited poor coating efficiency. The retention of a solute increases proportionally in both GC and SFC as the film thickness increases. The GC $H \bar{u}$ theoretical curves and experimental data of the 0.75- and 1.0- μm film columns (11 m \times 50 μm I.D. SE-54) are shown in Fig. 4. The experimental data here agree better with theory than was observed in Fig. 2, probably because of the larger k' values and less overloading of the column. For these large k' values, stationary phase film thicknesses of up to 1.0 μm have very little contribution to the total plate height.

Assuming that the GC efficiency is about five times the SFC efficiency (at 10 \bar{u}_{opt}), 25, 34 and 100 m are required in SFC to produce 10^5 plates for SE-33, SE-54 and 50% phenyl polysiloxane columns, respectively. Based on an analysis of an aliphatic fraction of a synfuel²³, the analysis times would be approximately 1.5, 2 and 6 h for the previous phases, respectively, in order to achieve the same efficiencies.

The SFC performance of a 27 m \times 50 μm I.D. column coated with 50% phenyl polysiloxane is shown in Fig. 5. Polycyclic aromatic compounds containing up to ten rings were found in a carbon black extract. This chromatogram illustrates good efficiency throughout the pressure program, even for relatively large molecules.

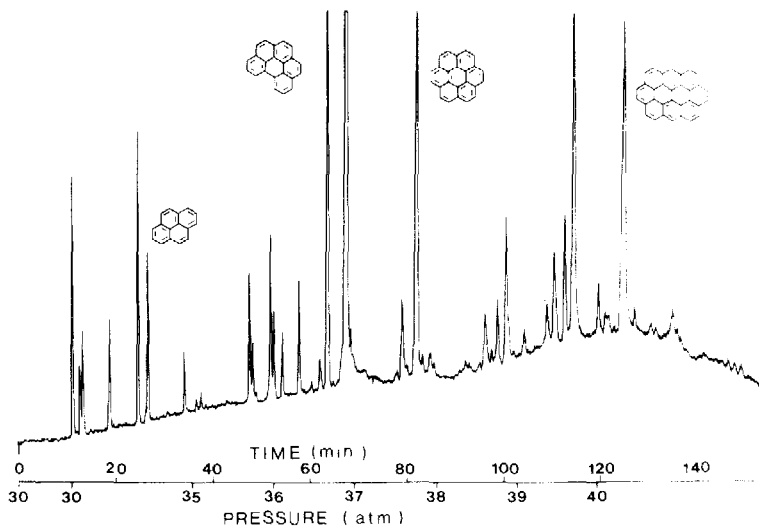


Fig. 5. Supercritical fluid chromatogram of a carbon black extract. Conditions: 27 m \times 50 μm I.D. fused silica column coated with 50% phenyl polysiloxane (0.25- μm film thickness); *n*-pentane mobile phase at 210°C, pressure programmed from 30 to 35 atm at 0.2 atm min^{-1} , then to 40 atm at 0.06 atm min^{-1} ; UV-detection at 214 nm.

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tions expressed herein are those of the authors and do not necessarily reflect the views of GRI.

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