Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sommer, C. C. , Koenigbauer, M. J. , Men, L. C. and Rogers, L. B.(1985) 'Recycle Gas Chromatography Using Coarse Packings', Separation Science and Technology, 20: 7, 523 — 540

To link to this Article: DOI: 10.1080/01496398508068235

URL: http://dx.doi.org/10.1080/01496398508068235

SEPARATION SCIENCE AND TECHNOLOGY, **20**(7 & 8), pp. 523–540, 1985

Recycle Gas Chromatography Using Coarse Packings

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Abstract

The use of coated 1 mm glass beads is shown to be promising for recycle gas chromatography. In the case of an SE-30 column, the glass beads generate plates faster than porous packings as fine as 48/60 mesh. Although packings coated with SE-30 produce nearly 400,000 plates, they are unable to fractionate a mixture of benzene and perdeuterobenzene. However, a much less efficient squalane column successfully fractionates that mixture after approximately 60,000 plates, confirming earlier work in which squalane was used. Coated beads appear to be especially useful when large numbers of plates are required and milligram amounts of product are needed.

INTRODUCTION

Recycle or circulation chromatography was first suggested by Martin (*1*) as a means of resolving difficult-to-separate species on the equivalent of a very long column. Porter and Johnson (*2–4*) first applied Martin's circulation concept to gas chromatography, using two packed columns connected head-to-tail and a circulation pump to maintain the flow of

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0149-6395/85/2007-0523$3.50/0

carrier gas within the loop. Later, Maxwell (*5*) and Golay (*6*) utilized a switching valve and a carrier gas from a source external to the loop to move solutes from column to column. This design removed the dead-volume inherent in the circulation pump design, thereby increasing the efficiency of the system.

Several otherwise difficult separations for packed columns have been accomplished by recycle chromatography. In 1964, Root, Lee, and Rowland (*7*) used a system similar to that of Maxwell to separate mixtures of butane–deuterobutane and methane–deuteromethane. Chizhkov and co-workers (*8*), using again a variation of the Maxwell design, separated benzene–perdeuterobenzene and acetone–perdeuteroacetone. They also separated the structural isomers durene–isodurene on a small preparatory scale with 99% recovery of the isomer of interest (*9*).

Chizhkov et al. (*10–12*) examined the theoretical aspects of circulation chromatography and found that, under proper experimental conditions, the number of theoretical plates increased linearly with the cycle number. They also showed that broadening was a function of the ratio of the carrier gas velocities in the different columns which, in turn, was related to the compressibility of the carrier gas. The latter was the major factor that limited the maximum number of cycles and, therefore, the maximum number of theoretical plates attainable.

Studies on the operational parameters of recycle gas chromatography were also done by Pauls and co-workers (*13*). They independently confirmed the major finding of Chizhkov et al. that an elevated outlet pressure and a coarser packing increased the maximum number of cycles and of plates attainable. Otherwise, at an outlet pressure of 1 atm, the number of plates reached a maximum after a few cycles and then decreased.

In the present study, the effects of going to yet larger particle diameters, to a larger column diameter, and to higher outlet pressures (up to 1342 kPA, 180 psig) were investigated. Optimum conditions for a single pass were found to be somewhat different from those for recycling, so column efficiencies were estimated from Van Deemter curves obtained in separate experiments using a few recycles. Those data were later used to select initial parameters for longer recycle runs. Some comparisons of columns were made in terms of both absolute and reduced plate heights as well as in terms of the theoretical predictions of Chizhkov. Separations of benzene–perdeuterobenzene were then done for the purpose of comparison with those of Chizhkov et al. (*8*).

EXPERIMENTAL

Chemicals

The solutes used in this study were *n*-hexane (99 mol%, Fisher Scientific Co., Fair Lawn, New Jersey) benzene (reagent grade, Fisher), and benzene-d_6 (99.9%, Aldrich Chemical Co., Milwaukee, Wisconsin).

The stationary phase used in all hexane experiments was GE SE-30 (Alltech Associates, Deerfield, Illinois) while squalane (Eastman Kodak, Rochester, New York) was also used in some of the benzene experiments. Chromosorb A (20/30 and 40/60 mesh, Johns Manville, Denver, Colorado) and 1 mm diameter solid glass beads (Sargent Welch, Skokie, Illinois) were used as solid supports. The surfaces of all solid supports were deactivated by a double silanization procedure (*14*) using dimethyldichlorosilane and hexamethyldisilazane (both from PCR Research Chemicals, Inc., Gainesville, Florida).

Nitrogen, the nonretained species, and helium, the carrier gas (Selox, Gainesville, Georgia), were used as received.

Apparatus

Columns were prepared from stainless steel tubing of either 3.2 or 6.3 mm outer diameter. Funnel fittings of the Hargrove and Sawyer (*15*) design were made from 6.3 to 3.2 mm o.d. reducing unions (Swagelok, Georgia Valve and Fitting Company, Atlanta, Georgia). All connecting tubing was 3.2 mm o.d., 0.8 mm i.d. stainless steel so as to reduce extra column dead volume.

The large partitioned oven was modified from its previous conformation (*16*) by the removal of one of the interior walls so as to allow the installation of longer columns. The oven temperature was controlled by a Thermotrol proportional controller (Hallikainen Instrument, Richmond, California). A platinum Stikon resistance element (RdF Corporation, Hudson, New Hampshire) was used as the temperature sensor. The oven temperature was measured using a thermistor bead sensor (GA-62P22, Fenwall Electronics, Inc., Framingham, Massachusetts) which was set in one arm of a Wheatstone bridge. The output of the bridge was read using either a multimeter (Model 3500, Data Precision Corporation, Danvers, Massachusetts) or a multichannel analog-to-digital converter (Anscan model 3700, Beckman Instruments, Fullerton, California). The bridge output was calibrated against a platinum resistance thermometer (Omega Engineering Inc., Stamford, Connecticut).

The column head pressure was controlled by a Milliflow pressure regulator (Veriflow Corporation, Richmond, California), and the column outlet pressure was regulated by a micrometering valve (Nupro Model SS-256, Georgia Valve and Fitting). By using an air-actuated six-port valve (Valco Instrument Company Inc., Houston, Texas), either the inlet or outlet pressure could be measured using an Alphaline transducer (Model 115, Rosemount Inc., Minneapolis, Minnesota). The pressure signal was amplified to yield a 0–10 V output over a range of 0 to 1379 kPa (200 psig) above atmospheric pressure. It was read either by the multimeter or the Anscan. The transducer was calibrated against a Heise pressure gauge. The mass flow rate of the carrier gas was measured using a mass flowmeter (Model LF-50, Hastings Raydist, Hampton, Virginia). All transducers and other electronics were kept in a thermostated enclosure to improve stability.

A Valco six-port switching valve, having either a 150- or a 300-μL sample loop, was used to inject 1.0 or 2.0 mg of sample, respectively. The sample loop was automatically filled by passing nitrogen gas through the pure liquid solute and into the sample loop. A Valco low-dead-volume six-port switching valve was used to circulate the solute through the columns. All valving was under computer control (*17*). Computer-generated signals were used to activate two-way solenoid valves (Model 3C301, Airswitch, Mosier Industries Inc., Dayton, Ohio) by means of zero-crossing relays, which actuated the switching valves pneumatically.

A Gow Mac Model 10-470 microcell with thermistor sensors (Gow Mac Instrument Co., Madison, New Jersey) was used as the detector. The cell was connected to a Model 100 microdetector bridge and power supply (Carle Instruments Inc., Fullerton, California). The output of the bridge was amplified and fed to a digital electrometer (Model 615, Keithly Instruments, Cleveland, Ohio) for analog-to-digital conversion.

On-line data acquisition and analysis were performed using a PDP 11/20 computer system (Digital Equipment Corporation, Maynard, Massachusetts) programmed in 1-8 user real-time BASIC.

Procedures

All stainless steel tubing was cleaned using 8 *N* nitric acid and then rinsed successively with distilled water, methanol, methylene chloride, and acetone before being dried by a stream of nitrogen. The tubing was then capped until used.

Chromosorb A was sieved to size, acid washed, and silanized using dimethyldichlorosilane following the procedure of Pesek and Graham (*18*). The two Chromosorb A packings were coated (3% SE-30 and 12% SE-30) using a rotary evaporator method.

Approximately 0.06% w/w SE-30 or squalane on 1 mm glass beads was prepared by the following method. The beads were etched using 3.7 *N* sodium hydroxide for 18 h at 40°C to produce a finely roughened surface. The beads were then rinsed successively with dilute nitric acid, distilled water, and methanol. A two-step reaction was used to render the beads inert. Initially, the beads were reacted with dimethyldichlorosilane. Hexamethyldisilazane was then added to scavenge any residual active sites. The deactivated beads were then pan-coated with SE-30 or squalane to yield a 0.06% loading.

All columns were packed by adding material while tapping. The columns were pressurized to 148 kPa (20 psig) and again tapped to settle the bed. Material was added as necessary to fill any void caused by pressurization of the column. All columns were conditioned at 100°C with zero flow for 4 h, except fo rthe squalane-coated columns which were conditioned at 65°C with zero flow for 12 h. Separation behavior was examined at 80 and 65°C for the SE-30 and squalane columns, respectively.

The recycle system consisted of two chromatographic columns joined by a six-port valve in a head-to-tail manner. The outlet of each column was fed into one side of the thermal conductivity detector and then passed to the head of the next column through the six-port valve. The outlet pressure was monitored by the pressure transducer and controlled by a metering valve. All connecting tubing had the minimum internal diameter available so as to minimize dead volume.

The recycle instrument was operated in either of two modes: a single pass through both columns or in a recycle fashion. Both modes used computer automation to fill the sample loop, inject the sample, gather data, and store it. Only manual settings of the flow rate and the final outlet pressure were required. The rate of data acquisition was chosen by the operator at the beginning of each experiment.

For the single-pass mode, the program stopped the data acquisition after four peaks had been detected above a preset threshold. Two peaks (one positive and one negative) represented the nonretained nitrogen in each of the two columns. The other two peaks, again one for each column, were those for the solute. The program then stored the data on a floppy disk before starting the calculation of various peak parameters such as retention time, height equivalent to a theoretical plate, *H*, and peak area. Finally, the results were printed.

In the recycle mode, after an initial single pass to locate the retention times of nitrogen by passing the sample through the first column, its detector, and onto the second column, the column connections were changed by actuating the switching valve. After the sample had eluted from the second column and its detector, and back onto the first column, the valve was switched back to its original position, thus completing one cycle. This process was repeated until either the peak(s) of interest had broadened to the point of overflowing one column volume or the desired number of cycles had been achieved.

The switching operation could be done at any given fraction of the time for a single pass. For a single solute, switching when the solute peak was in the center of a column produced the maximum number of cycles. Data were recorded only for alternate half cycles so as to reduce the total number of points stored.

Peaks were located using a slope-sensing routine. The peak height and the width at half the maximum height were determined so as to calculate both the number of theoretical plates and the height equivalent to a theoretical plate, HETP.

When using 12% loadings of the stationary phase, the detector cell was fouled repeatedly by column bleed. This required cleaning of the thermistors and the cell block in a stirred chloroform bath after the cell had been disassembled. The parts were dried under a stream of dry nitrogen before the cell was reassembled.

A brief study of the effect of sample size on column efficiency was made using Column G in Table 1, using 3-cycle experiments run at a

TABLE 1
Columns Used in This Study

				Column	
Column	Material	Mesh size	SE-30 (w/w %)	i.d. (mm)	Length (m)
A	Chromosorb A	48/60	12	2.1	1.5
B	Chromosorb A	20/30	12	5.3	1.5
C	Chromosorb A	48/60	3	5.3	1.5
D	Chromosorb A	20/30	3	5.3	1.5
E	Glass beads	18	0.06	5.3	1.5
F	Glass beads	18	0.06	5.3	7.5
G	Glass beads	18	0.06[a]	5.3	7.5

[a] Squalane substituted for SE-30

linear velocity of 0.58 cm/s and an outlet pressure, P_o of 1342 kPa. The H values for 0.7, 1.4, and 2.0 mg samples of benzene were almost the same. However, on going to 3.6 mg, the H value increased by approximately 53%. Hence, 2.0 mg was the maximum size used.

Calculations

The height equivalent to a theoretical plate, H, was calculated by

$$H = L/N \tag{1}$$

where L is the total column length and N is the number of theoretical plates calculated by

$$N = 5.54(t_R/W_{1/2})^2 \tag{2}$$

where t_R is the retention time and $W_{1/2}$ is the width at half the peak height (both in seconds).

Reduced chromatographic parameters were used to compare the efficiencies of different sizes of packings. The reduced plate height, h, was calculated using

$$h = H/d_p \tag{3}$$

where d_p is the particle diameter in centimeters. The reduced velocity, v, was calculated by

$$v = d_p\mu/D_m \tag{4}$$

where μ is the linear velocity in cm/s and D_m is diffusion coefficient of the solute in the mobile phase.

D_m was estimated by the Chen-Othmer equation (*19*):

$$D_m = \frac{0.43(T/100)^{1.81}(1/m_1 + 1/m_2)^{1/2}}{p(T_{c1}T_{c2}/10^4)^{0.1405}[(V_{c1}/100)^{0.4} + (V_{c2}/100)^{0.4}]^2} \tag{5}$$

where T is the absolute temperature; T_c, V_c, and m are the critical temperature, colume, and molecular weight with the subscripts *1* and *2* added to indicate solute and carrier gas, respectively; and p is the outlet pressure in atmospheres.

Chizhkov (*12*) derived the following expression to calculate band spreading as a function of cycle number:

$$W_m = W_l \left[\frac{b^{2m} - 1}{b^2 - 1} \right]^{1/2} \tag{6}$$

where W_m is the peak width after the *m*th half cycle, W_l is the peak width after the first column, and *b* is given by

$$b = \mu_2/\mu_1 \tag{7}$$

where μ_2 and μ_1 are the average linear carrier gas velocities in the first and second columns. These are calculated by

$$\mu_1 = \frac{(\mu_0/C) + \mu_{1/2}}{2} \tag{8}$$

where *C* is the ratio of inlet to outlet pressure and $\mu_{1/2}$ and μ_0 are the linear velocities at the exit of the first and second column, respectively.

RESULTS

Comparison with an Earlier Study

Recycle columns similar to those found to be most efficient (Column A of Table 1) were used under conditions close to those of the earlier study (*13*) so as to check the reproducibility of the results. The present study then extended those experiments to higher outlet pressures. The results of a series of single-pass experiments were used to plot van Deemter curves for each of the outlet pressures.

The values of H_{min} at 412 kPa (45 psig) and at 722 kPa (90 psig) outlet pressures were found to be in relatively close agreement (Table 2). When extended to pressures above 722 kPa (90 psig), the data confirmed the trend of a higher outlet pressure yielding a smaller H_{min} value. In addition, the Van Deemter curve flattened into a very broad region for H_{min}. However, the H_{min} values at still higher outlet pressures, 1032 kPa (135 psig) and 1342 kPa (180 psig), were greater than those at 722 kPa (90 psig), a reversal of the previously observed behavior (*13*). Since all of the other

TABLE 2
Optimal Values for Plate Height and Flow Rate for 1.5 m Columns of 48/60 Mesh Chromosorb A Coated with 12% SE-30 (Column A)

	H_{min} (mm)		μ_{min} (cm/s)	
Pressure (kPa)	Pauls	Present	Pauls	Present
412	0.89	0.98	2.30	1.82
722	0.92	0.92	1.80	1.33
1032	[a]	0.93	[a]	1.27
1342	[a]	1.06	[a]	0.97

[a] Not done in the earlier study.

characteristics of the two columns are very similar, the source of this difference is unknown. The fact that the μ_{min} values continued to decrease at higher outlet pressures means that the cycle times increased with pressure when operated at the μ_{min}.

Recycle experiments were then done at 722 kPa (90 psig) where the greatest number of theoretical plates had been obtained during the single-pass experiments. The flow rate was set to give an average linear velocity slightly lower than the value at the minimum of the Van Deemter curve. The experiment was continued until the solute peak no longer broke the preset threshold. Operating in the recycle mode, the system generated 39,135 theoretical plates in 17 cycles for an average of 2300 plates per cycle. After 3.00 h, when the experiment was stopped, the solute filled 67% of the available column volume. *H* values were calculated for each pass of the solute through the detector. Those values increased with cycle number, from an initial value of 0.77 mm to a final value of 1.26 mm. These results agree with both the theoretical predictions of Chizhkov (*12*) and qualitatively with the experimental results of Pauls et al. (*13*) who found that the *H* values at 722 kPa increased from 0.87 to 2.70 mm over the course of a 50-cycle experiment. Using experimental parameters in Chizhkov's equation for the expansion of peak width with cycle number, an estimate of 128 s was calculated for a 17-cycle experiment, a difference of only 1.5% from the experimental value of 126 s. The plate growth rate, the number of plates generated per minute, was greater than that found in Pauls' study, i.e., 217 plates per minute compared to 141 plates per minute. Altogether, these columns were close in performance to those used in previous studies.

TABLE 3
Optimal Values of Reduced Plate Height and Flow Rate for Columns Operated for Five Cycles

		v_{min}				h_{min}			
Column	P_0 (kPa):	412	722	1032	1342	412	722	1032	1342
A		0.44	0.56	0.77	0.76	3.59	3.37	3.41	3.88
B		0.98	0.64	0.56	—	2.77	2.31	2.15	—
C		0.42	0.49	0.69	—	3.48	2.64	2.71	2.67
D		0.96	1.04	0.88	0.54	2.24	2.27	2.04	2.00
E		1.40	1.31	1.20	1.25	1.54	1.74	1.55	1.34
F		—	1.50	2.05	2.54	—	1.78	1.53	1.18
G		—	1.40	1.22	1.21	—	2.60	1.90	1.80

Larger Diameter Packings

Larger particles result in a smaller pressure drop per unit length which, when inserted into Chizhkov's equation, give a slower rate of peak broadening. As a result, both the maximum number of cycles and the maximum number of theoretical plates should increase. Larger porous particles were examined briefly in single-pass and recycle experiments using the same liquid loading (12%) as for the earlier experiments with finer particles. However, it was recognized that lighter loadings would be desirable for later runs so as to have the same amount of liquid in all of the 1.5-m columns. Hence, a percentage was chosen that provided an amount equal to the maximum held by the beads.

When a series of single-pass experiments similar to those for Column A were run at equivalent linear velocities using the 1-mm Chromosorb A, the pressure drop across the column was found to be only one-fourth of that across Column A. The same was also observed at higher outlet pressures. For example, at 1032 kPa (135 psig), Column B had a pressure drop of 5.6 kPa (0.81 psi) compared to Column A of 20.8 kPa (3.01 psi).

The H_{min} values for these coarse particles decreased with increasing pressure. As pressure increased from 412 to 722 to 1032 kPa (45 to 90 to 135 psig), the H_{min} continued to decrease from 1.98 to 1.65 to 1.54 mm, respectively, as expected from the earlier study (*13*), rather than going through a minimum as seen with Column A. The μ_{min} values also decreased with increasing pressure, from 1.55 to 0.58 to 0.35 cm/s.

To allow another comparison of the two sets of results, reduced plate heights and velocities are reported in Table 3. Note the lower reduced plate height of Column B; in contrast, the conventional plate height of

Column A at 412 kPa was clearly lower (0.98 mm compared to 1.98 mm).

Recycle experiments at 722 kPa outlet pressure using Column B produced 44,077 theoretical plates in 14 cycles for an average of 3148 plates per cycle. The solute occupied 52% of the available column volume when the experiment was stopped, somewhat less than in the previous recycle experiment. The experiment took 5.00 h so that the rate of plate generation was only 147 plates per minute, a rate that was only half of that for the smaller diameter particles (Column A). Another major difference was found in the change of *H* during a run. Instead of increasing with cycle number, the *H* values decreased from an initial value of 1.99 mm to a final value of 0.95 mm. Part of the reason for this difference was the smaller increase in peak width with cycle number. This was checked by comparing the experimentally determined values with those predicted by Chizhkov's equation. The equation predicted a final peak width of 306 s after 14 cycles, whereas the actual value was 199 s, a difference of over 100 s (30%). Similarly, when the theoretical value was substituted for the actual in the plate equation and *H* was calculated from the plate count, the final *H* value was 2.24 mm, more than twice the experimental result. Hence, Chizhkov's equations failed to hold for the coarsest particles. Fortunately, the failure was in the favorable direction for the present study.

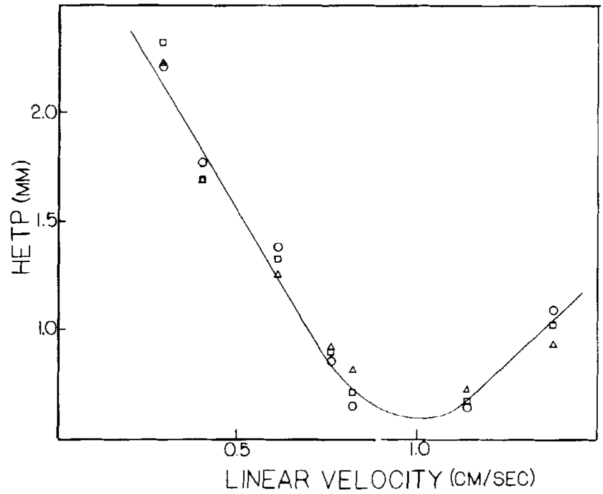

FIG. 1. Plot of HETP vs linear velocity for cycles 1 (□), 3 (△), and 5 (○) on Column C at 722 kPa.

Though the recycle results for peak spreading were promising, the efficiencies of the coarse porous particles left much to be desired. For example, at 722 kPa the H_{min} of Column B was 80% larger than the value for Column A while its minimum occurred at a linear velocity one-half that of Column A. At 1032 kPa, the value for Column B was 66% larger than that for Column A. Even taking into account the gains in efficiency with cycle number for coarse particle columns, those columns needed many more cycles to produce an equal number of theoretical plates. Taking 722 kPa outlet pressure as an example, after 10 cycles the H value for Column B was 1.30 mm compared to 1.06 mm for Column A. Nevertheless, when viewed in terms of reduced parameters, the coarse particle columns were closer to the theoretical minimum of 2 for packed columns (*20*). The minima in the reduced plate height and the corresponding reduced velocity for Column B followed the same trends as those for the absolute parameters. This was not the case with Column A for which the reduced plate height increased with outlet pressure.

The observed increase in H_{min} at 1342 kPa using Column B might have been due to diffusion through the particles, thereby leading to wider peaks. To eliminate that possibility, solid glass beads were tested as a support. When it was found that 0.06% w/w was close to the useful maximum for the glass beads, the decision was made to repeat the studies for Chromosorb A using 3% w/w, a value that led to approximately equal volumes of liquid in columns using both types of supports. In that way, a better comparison between the Chromosorb A packings and the glass beads might be made.

Lightly Loaded Columns

Porous Particles, 48/60. Because sample size might be reducing the efficiency, especially for the first cycle, when using the lower level of liquid loading, five-cycle experiments rather than single-pass experiments were used to estimate the optimum operating conditions for recycling. Whether 150 or 300 μL was injected, the first cycle always gave H_{min} values somewhat larger than the values observed in later cycles. (See Fig. 1.) However, values for later cycles for both sample sizes were nearly the same and nearly constant; they were also consistent with values obtained during longer recycling experiments. Hence, five-cycle experiments were used in all further studies of optimization.

First, a series of five-cycle experiments was done on 48/60 mesh Chromosorb A in Column C. At the four pressures previously investigated, minimum H values followed the trend observed with the more heavily loaded Column A shown in Table 2. However, the H_{min} values started at from 1.12 mm at 412 kPa and decreased to a minimum of 0.64 mm at 722 kPa before increasing to a final value of 0.71 mm at 1342 kPa outlet pressure. Note, however, that the new values at the three higher pressures were smaller, as one would expect for a lighter loading. The μ_{min} also followed the previously observed trend, decreasing with increasing outlet pressure from 1.73 cm/s for 412 kPa to 0.92 cm/s for 1342 kPa.

Table 3 permits a direct comparison of Columns A and C to be made using reduced parameters. Note that the v_{min} and h_{min} values agreed rather well between the columns. However, the values for Column C at the higher pressures were smaller than their counterparts for Column A, indicating that Column C was more efficient.

Porous Particles, 20/30. The lighter loading on Column D relative to Column B shows that h_{min} was marginally better whereas v_{min} was significantly better at higher pressures. Therefore, the lower loading gave better performance. The advantage for lighter loading is confirmed in Table 4 at a pressure of 722 kPa but not at 1342 kPa. However, some data are missing in Table 3 for Column B so one cannot be sure that the data in Table 4 are representative.

Solid Beads, 1 mm (18 mesh). Diffusion within the particles had to be a major contributor to band spreading for the large porous packings. Hence, solid glass beads were selected because they were very close to the average diameter of the porous particles. Comparing in Table 3 the beads, Column E, with Column D, shows that both the h_{min} and v_{min} were favorable for Column E. Table 4 confirmed the advantage of the beads with respect to the rate of generating plates. However, from a practical standpoint, these columns were not useful for recycle because of the very short times for each half cycle. Hence, it was desirable to increase the time-window by lengthening the columns. To that end, two 7.5-m columns having "funnel" end-fittings (*15*) were prepared using the 1-mm diameter glass beads (Column F). A typical set of Van Deemter curves is shown in Fig. 2.

Table 4 shows that Column F had the highest rate of plate generation of any of the columns. The table also shows that a smaller fraction of the column was occupied by the peak at the conclusion of each run than for the corresponding run for porous particles. When the equation of Chizhkov et al. (*9*), which was derived from calculating peak widths for porous particles, was used to calculate the peak width, those calculated Chizhkov values were much larger than the observed values for the beads. This suggests that the relationship derived by Chizhkov et al. (*9*) is not as general as one might have inferred.

TABLE 4
Theoretical Plates Generated Using Columns at the Minimum of the Van Deemter Curve

Column	P_o (kPa)	Cycles	Plates × 10^{-3}	Time (h)	Plates/min	% Column filled
A	722	17	39.1	3.00	217.0	67
B	722	14	44.1	5.00	147.0	52
C	722	20	52.9	3.00	294.0	70
	1342	20	43.7	1.90	384.0	60
D	722	15	36.0	2.50	240.0	64
	1342	12	37.7	7.20	87.2	49
E	722	10	17.5	1.00	291.0	60
	1342	10	28.2	2.00	235.0	53
F	412	5	53.3	1.90	468.0	10
	722	5	88.9	2.72	545.0	17
G	722	10	38.2	6.48	98.3	50
	1032	10	53.6	12.00	74.5	39
	1342	10	193.0	15.00	215.0	40

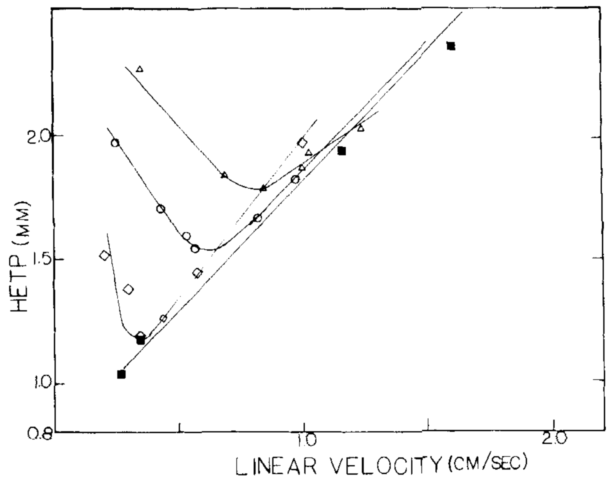

FIG. 2. Plot of HETP vs linear velocity at various pressures for a three-cycle experiment on Column F (open symbols) and Column D (closed symbols): 722 kPa (△), 1032 kPa (○), 1342 kPa (◇), and 1342 kPa (■).

Mixture of Benzene-Perdeuterobenzene

SE-30. Because the number of plates obtained at 722 kPa appeared to be more than enough to fractionate a mixture of benzene-perdeuterobenzene (*8*), the decision was made to examine that fractionation before obtaining Van Deemter data on benzene alone at higher pressures. Using Column F at 722 kPa, more than 200,000 plates were generated without any hint of additional peak broadening (compared to benzene alone) or of a shoulder attributable to a second component. This experiment was

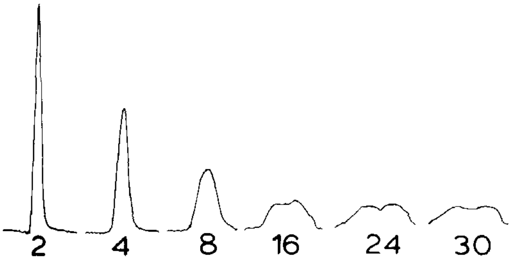

FIG. 3. Separations at various cycle numbers of benzene and deuterobenzene on Column G at 722 kPa, 65°C, and a flow rate of 25 mL/min.

repeated five times, including some runs at 1342 kPa, all of which gave similar results. Hence, the decision was made to change the stationary phase to squalane which Chizhkov et al. (*8*) had used on a porous support to obtain a very satisfactory fractionation.

Squalane. Table 4 shows that the squalane, Column G, generated plates at only approximately 20% of the rate for the comparable SE-30 column. Nevertheless, as shown in Fig. 3, noticeable fractionation of the isotopic benzenes had occurred after 16 cycles at a pressure of 722 kPa. Approximately 60,000 plates had been generated at that point. The advantage of operating at a higher pressure, which required a longer time for a given number of cycles, is clearly shown in Fig. 4 as well as in the rate of generating plates (Table 4). However, because the Van Deemter plots had relative sharp minima (Fig. 2), one was forced to work at very low linear flows; there was virtually no opportunity to trade a small loss in efficiency for a large decrease in cycle time. Hence, although the h_{min} values, were very favorable, being less in some cases than the theoretical minimum of 2 (a phenomenon reported by others) (*21*, *22*), the rate of plate generation was low as indicated by the very small v_{min} values.

In the study by Pauls et al. (*13*), the rate of generating plates was linear at first, then fell off so that the total number of plates as a function of time actually passed through a maximum and later decreased. Figure 5 shows that the rate of plate generation at 1342 kPa was constant for nearly 33 h,

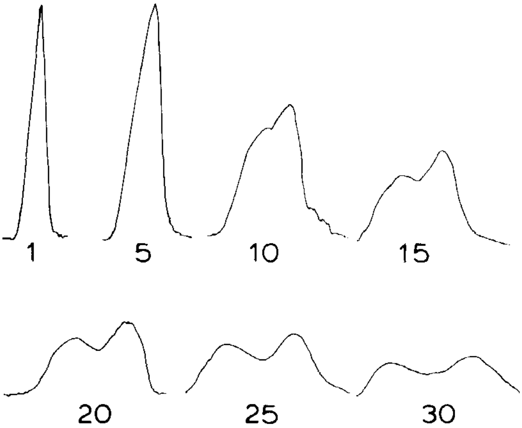

FIG. 4. Separations at various cycle numbers of benzene and deuterobenzene on Column G at 1342 kPa, 65°C, and a flow rate of 21 mL/min. The first peak shown was recorded at half the sensitivity of the succeeding peaks.

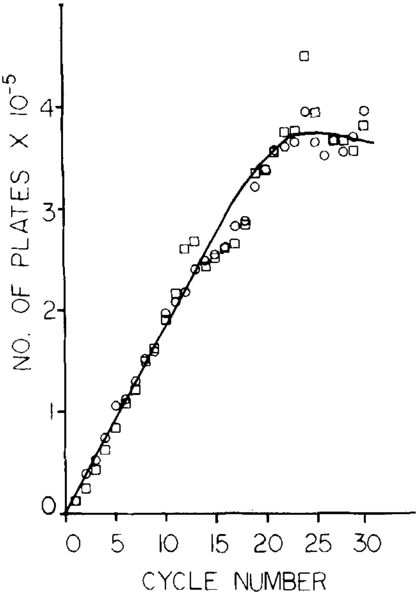

FIG. 5. Plot of number of plates vs cycle number on Column G at 1342 kPa and 65°C. Symbols represent each of the two 7.5 m columns used.

after which the total remained relatively constant for the next 12 h. Note that nearly 400,000 plates were generated. At lower pressures the plateau values as well as the generation rates were lower. For example, at 1032 kPa the total plates leveled off at 75,000 after only 18 h. This trend was consistent with the earlier work in which packed columns were used (*13*).

CONCLUSIONS

Beads, as expected, exhibited smaller pressure drops than corresponding sizes of porous particles. They appeared to be promising on the milligrams scale for fractionations that require large numbers of plates, like those for which long open tubular capillary columns are used in analytical separations. Although the fractionation of benzene and perdeuterobenzene was attained by the squalane column, it was a very inefficient column (when measured using *n*-hexane) relative to the corresponding one coated with SE-30. If further work were to be done with squalane, the preparation of a suitable coating should be the first priority. The coating procedures which have been used successfully for open tubular capillary columns represent an obvious starting point.

The successful use of squalane for the benzene species confirmed the earlier report by Chizhkov et al. (*8*). In addition, it served to emphasize the differences in solute–solvent interactions in that another nonpolar phase, SE-30 failed completely in spite of the fact that many more plates were generated.

Acknowledgments

The authors gratefully acknowledge support of this work by the Department of Basic Energy Sciences, Department of Energy, Contract No. DE-AS09-76ER00854. We would like to thank William A. Howard for his help with some of the experiments.

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Received by editor January 30, 1985