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 Pauls, R. E. , Shepard, A. T. , Phelps, J. E. , Davis, J. E. and Rogers, L. B.(1977) 'Experimental Variables in Recycle Gas Chromatography', Separation Science and Technology, 12: 3, 289 — 306
To link to this Article: DOI: 10.1080/00372367708058078
URL: http://dx.doi.org/10.1080/00372367708058078

SEPARATION SCIENCE. 12(3), pp. 289–306, 1977

Experimental Variables in Recycle Gas Chromatography

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Abstract

Variations in experimental parameters in recycling chromatography have been investigated. The effects of column length, column outlet pressure, support mesh size, carrier gas flow rate, and capacity ratio on the maximum number of cycles have been determined for a single component. The maximum number of cycles was obtained under conditions which minimized effects of gas compressibility. These conditions also caused the number of theoretical plates to increase linearly with cycle number for a larger fraction of the time before the sample overflowed the volume of one column.

INTRODUCTION

In order to achieve a difficult chromatographic separation it is necessary to produce a large number of theoretical plates. This can be accomplished by increasing the column length, but if packed columns are used, a large pressure drop across the column will accompany the increased number of

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plates. An alternate approach is to recycle or circulate the sample through short columns.

Recycle (circulation) chromatography was first suggested by Martin (*1*) as a means to achieve very long column lengths. Porath and Bennick (*2*) utilized the recycle technique in gel permeation chromatography. They used a single column and repumped the column effluent back into the column inlet. Recently, recycling has been widely used in high-performance liquid chromatography (*3–5*) to achieve increased column length.

Porter and Johnson (*6–8*) first applied the recycling concept to gas chromatography. They used a circulation pump to recycle the carrier gas through a closed system consisting of two columns connected head-to-tail and separated by a single detector. Maxwell (*9*) proposed a recycle chromatograph which consisted of two columns and a 6-port 2-position valve to reverse the column positions as the solute passed from column-to-column. A similar approach was used by Root, Lee, and Rowland (*10*) to separate the isotopically substituted molecules CH_4 and CD_4.

Chizhkov and co-workers (*11–21*) have extensively studied the theoretical and experimental aspects of recycle chromatography. Their apparatus consisted of dual columns coupled by a 6-port valve and a flame ionization detector. A small portion of the carrier gas stream was diverted to the detector. Chizhkov and co-workers (*19*) have demonstrated the usefulness of the recycle approach in the separation of isotopic species such as C_6H_6 and C_6D_6. They have also explored the possibility of using recycle chromatography to carry out preparative-scale separations of isomeric species (*21*), and concluded that the productivity of a long packed column was 2.5 times better than if it was used in the recycle approach. They have pointed out that under the proper experimental conditions there was a linear increase in the number of theoretical plates with cycle number and that gas compressibility effects could have a large effect upon the maximum number of cycles obtained. Reid (*22*) has recently utilized the recycle concept to program column length in the separation of isomeric xylenes.

The maximum column length which can be obtained in recycle gas chromatography is limited by the band broadening. The limit is reached when the peak width is equal to the volume in a column length. Chizhkov (*20*) has developed an expression giving the peak width as a function of the cycle number

$$W_m = \frac{b^{2m} - 1}{b^2 - 1} W_1 \qquad (1)$$

where W_m is the peak width after the mth cycle, W_1 is the width after the first column, and b is given by

$$b = \mu_2/\mu_1 \tag{2}$$

where μ_2 and μ_1 are the average linear carrier gas flow rates in the first and second columns.

The values of μ_2 and μ_1 can be calculated (*20*) by

$$\mu_1 = \frac{(\mu_0/C) + \mu_{1/2}}{2} \tag{3}$$

$$\mu_2 = \frac{\mu_0 + \mu_{1/2}}{2} \tag{4}$$

where C is the ratio of the inlet and outlet pressures and μ_0 and $\mu_{1/2}$ are the linear carrier gas flow rates at the exit of the recycle apparatus and at the end of the first column, respectively.

In our study the effects of column parameters, such as the mesh size of the solid support, carrier gas flow rate, and column length, on the maximum number of cycles obtained and on the maximum number of plates were determined. These present studies were carried out independently of the work of Chizhkov et al. and are reported because they provide new and more detailed information on these effects. Our results are also compared to the theoretical predictions of Chizhkov.

EXPERIMENTAL

Reagents

The solutes used in this study were *n*-hexane, 3-methyl pentane (99 mole-% pure Phillips Petroleum Company, Bartlesville, Oklahoma), benzene (spectroquality, Matheson, Coleman, Bell, East Rutherford, New Jersey), and cyclohexane (GC-spectrophotometric grade, J. T. Baker Co., Phillipsburg, New Jersey).

The liquid phase used in all experiments was GE SE-30 (Alltech Associates, Arlington Heights, Illinois). Chromosorb W in a variety of mesh ranges from 30/45 to 100/120 mesh was obtained from Alltech Associates.

Nitrogen was used as a nonretained species and helium (Selox, Inc.) as carrier gas. Dichlorodimethylsilane (Aldrich Chemical Co., Milwaukee, Wisconsin) was used to silanize the Chromosorb W.

Apparatus

A large multioven chromatograph previously described (*23*) was used in this study. The oven temperature was controlled by a Thermotrol proportional controller (Hallikainen Instrument Co., Richmond, California). A platinum Stikon resistance element (Rdf. Corp., Hudson, New Hampshire) was used as a sensor. The oven temperature was measured with a thermistor bead sensor (GA 62P22, Fenwall Electronics Inc., Framingham, Massachusetts) which was placed in one arm of a Wheatstone bridge. The output of the bridge was read with a digital multimeter (Keithley Instruments, Cleveland, Ohio). The bridge output was calibrated against a platinum resistance thermometer (Omega Engineering Inc., Stamford, Connecticut).

The column head pressure was controlled by a Millaflow pressure regulator (Veriflow Corp., Richmond, California) and the column outlet pressure was regulated by a micrometering valve (SS-256, Nupro Co., Cleveland, Ohio). The inlet and outlet pressures were measured by electronic pressure transducers. A Model 1332-G7 pressure transducer (Rosemont Engineering Co., Minneapolis, Minnesota) which had a 0 to 5 V output over a range of 0 to 250 psi was used to measure the inlet pressure. The column outlet pressure was measured by either a Model 1331-63 transducer (Rosemont Engineering Co.), which gave a 0 to 5 V output over a 0 to 50 psi range, or a Model 540 transducer (MB Electronics) which gave a 0 to 50 mV output over a 0 to 100 psi range. The transducers were calibrated against a Heise pressure gauge. The mass flow rate of the carrier gas was measured with a Type 5810-IN3B4A sensor (Brooks Instrument Division, Emerson Electric Co., Hatfield, Pennsylvania). All transducers and other electronics were kept in a thermostated chamber to improve stability.

A Seiscor Model VIII high temperature sampling valve (Seismograph Service Co., Tulsa, Oklahoma) with a 0.5 μl internal loop was used to inject samples. A Valco low dead-volume 6-port switching valve (Valco Instruments Inc., Houston, Texas) was used to circulate the solute through the columns. Computer control of the valves was achieved through an experimental interface previously described (*24*) which was used to turn on and off the zero-crossing solid-state relays which, in turn, pneumatically actuated the valves through two-way solenoid valves (Air Switch, Model 3C301, Mosier Industries Inc., Dayton, Ohio).

The thermal conductivity block was a Gow Mac Model 10–470 Microcell with thermistor sensors (Gow Mac Instrument Co., Madison, New Jersey). This was used in conjunction with a Carle 100 Micro Detector bridge and

power supply (Carle Instruments Inc., Fullerton, California). The output signal of the detector bridge was amplified by a differential amplifier, and this output, as well as all transducer outputs, was sent to a multichannel analog-to-digital converter (Anscan Model 3700, Beckman Instruments, Fullerton, California).

On-line data acquisition and analysis were performed using a PDP 11/20 computer system.

Procedures

Chromosorb W was sieved to size, acid washed, and silanized according to the procedures of Leibrand and Dunham (*25*). The SE-30 liquid phase was pan-coated onto the Chromosorb W. A 20% loading was normally used in order to hold up the solute in the first column long enough for the nonretained peak to elute through both columns. The coated Chromosorb was packed into 2.1 mm i.d. stainless steel tubing which had previously been washed with water, methanol, acetone, and methylene chloride.

Sampling was carried out by bubbling nitrogen through a saturator containing the solute and then into the sample loop of the sample valve. The nitrogen flow was continued for 20 sec before injection. The nitrogen flow rate was controlled by a manual flow controller (Brooks Instrument Div., Emerson Electric Co., Hatfield, Pennsylvania). The saturator was heated with a heating tape for the higher boiling solutes so as to increase the vapor pressure and give larger amounts of the sample.

The recycle gas chromatograph is diagrammed in Fig. 1. The essential features include a 6-port switching valve, two columns, each followed by half of a thermal conductivity cell, and a metering valve on the column outlet to control the outlet pressure. All connecting tubing was of 1 mm i.d. so as to minimize dead volume. Total dead volume in the system was on the order of 200 μl.

The apparatus was operated in either a switching or nonswitching mode. In the nonswitching mode the sample was injected and then passed through the two columns before being exhausted as in a normal chromatograph. In the switching mode the sample was injected and passed through the first column and detector onto the second column and the valve was then switched. Later, when the peak had eluted from the second column onto the first column, the valve was again switched. The process was repeated until the peak had broadened enough to overflow the volume of one column.

The system could be switched either manually or under computer control. In the manual mode the operator observed on a strip chart

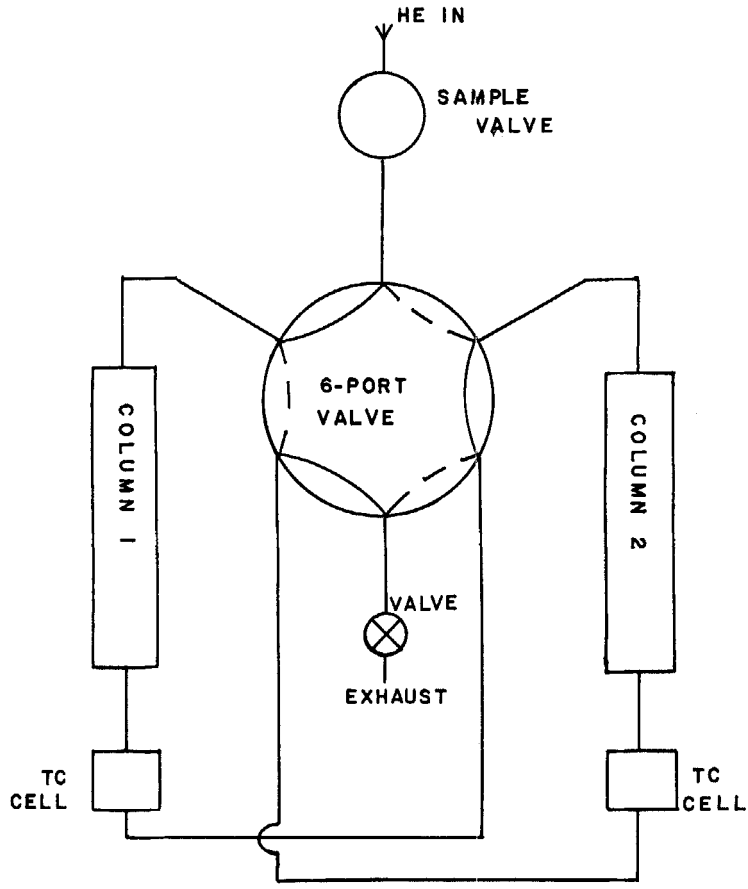

FIG. 1. Recycle apparatus.

recorder the peak eluting from one column and then manually turned on a relay to actuate the switching valve. In the computer mode the computer searched for a threshold on the back side of the last peak. Then, after a fixed time, the valve was actuated.

Calculations

The retention time of a peak was calculated by a 15-point least-squares fit about the top of the peak. Grams polynomials (*26*) were used to calculate the coefficients of the second-order equation used in the fit.

The average linear flow in the column was calculated by

$$\bar{\mu} = L/t_{R_0} \tag{5}$$

where L is the column length and t_{R_0} is the retention time of a nonretained species. The number of theoretical plates was calculated by

$$N = 5.54(t_R/W)^2 \tag{6}$$

where t_R is the retention time of the solute and W is the width at half height. The height equivalent to a theoretical plate was calculated by

$$H = L/N \tag{7}$$

RESULTS

Outlet at Atmospheric Pressure

Initial experiments with the recycle apparatus were carried out with the outlet at atmospheric pressure. The number of cycles obtained before the sample overflowed a single column was small, typically 5 to 10 column lengths for a single component. In order to determine if the solute capacity ratio affected the maximum number of cycles obtained, *n*-alkanes from butane to octane were chromatographed on 100/120 mesh, 20% SE-30 columns. There was not a substantial difference in behavior, as all five solutes overflowed in the seventh cycle. In all subsequent experiments either *n*-hexane or 3-methyl pentane was used as the solute.

One reason for the low number of cycles was a loss in efficiency caused by switching the column inlets as shown in Table 1. Note that after switch-

TABLE 1

Effect of Switching on Column Efficiency[a]

	No switching			Switching		
$\mu_{1/2}$ (cm/sec)	t_{R_2} (sec)[b]	W_2 (sec)	N	t_{R_2} (sec)[b]	W_2 (sec)	N
3.84	137.5	15.24	1970	147.7	16.54	1790
6.26	79.0	8.08	2480	86.5	9.02	2170
7.03	69.4	7.05	2570	77.1	8.09	2170

[a] Columns, 1.5 m, 20% SE-30 on 40/60 mesh Chromosorb W; solute, 3-methyl pentane.

[b] Retention time for second column.

ing, the retention time of the sample in the second column was larger than if there had been no switch because of gas compressibility effects. For example, the retention time of 3-methyl pentane in the first column was 149.8 sec and in the second column it was 137.5 sec without switching and 147.7 sec with switching. The shorter residence time (faster linear flow rates) reflected the lower pressure, averaged over the volume of the sample, while in the second column. Unfortunately, the increase in the retention time obtained by switching was offset by a larger increase in the peak width which caused a net decrease in the number of theoretical plates. The loss in efficiency was largest at the higher flow rates where changes in gas compressibility were largest. Hence, at a flow rate of 3.84 cm/sec, 9.1% fewer plates were generated when the columns were switched, while at 7.03 cm/sec, 15% fewer plates were generated.

Table 2 summarizes the effects of column length on the maximum number of cycles obtained before overflow. By doubling the column length a small decrease, about 1 cycle, in the number of cycles was observed. Although exact measurements were not made, more theoretical plates were generated on the longer columns because of the increased column length.

Table 3 summarizes the effects of solid support mesh size and carrier gas flow rate on the maximum number of cycles obtained for 3-methyl pentane before overflow. As the particle size increased, H at the minimum of the Van Deemter plot increased as shown in Fig. 2, but more cycles were obtained before overflow. As a result, the total number of plates obtained before overflow for columns of coarser particles was usually greater at a given flow rate. At a flow rate of 3.84 cm/sec, 11 cycles were obtained on the 40/60 mesh column, while at the same flow rate only 7

TABLE 2

Effect of Column Length on the Maximum Number of Cycles[a]

Length (m)	$\mu_{1/2}$ (cm/sec)	H_1 (mm)[b]	Cycles
1.5	4.4	1.28	9
	6.0	0.83	7–8
	9.7	0.87	5–6
3.0	3.4	0.79	7
	6.2	0.69	7
	9.9	0.92	4–5

[a] 60/80 mesh Chromosorb W, 20% SE-30; solute, 3-methyl pentane.

[b] H of the first column length.

TABLE 3

Effect of Mesh Size and Flow Rate on the Number of Cycles Obtained before Overflow and the Maximum Number of Plates Achieved[a]

Mesh size	$\mu_{1/2}$ (cm/sec)	U_0 (cm/sec)	Inlet pressure (psig)	H_1 (mm)	Cycles	N_{max}[b]
100/120	3.84	4.49	21.1	0.83	7	2720
	6.27	7.62	36.0	0.58	5–6	3020
	9.70	12.1	60.5	0.63	4–5	2070
60/80	3.44	3.78	9.7	1.28	9	Not measured
	6.16	7.14	17.8	0.83	7–8	Not measured
	9.90	12.2	30.4	0.87	5–6	Not measured
40/60	3.84	4.04	5.3	1.54	11	3410
	6.26	6.81	8.4	1.20	8	2920
	7.02	7.70	9.0	1.15	7	2740

[a] 1.5 m columns, 20% SE-30, P_{out} = 1 atm; solute, 3-methyl pentane.
[b] Maximum number of theoretical plates obtained.

cycles were obtained on a 100/120 mesh column. The increase in the number of cycles with coarser particles was again a consequence of gas compressibility, which was determined by the ratio of the column inlet and outlet pressures. With finer size particles the pressure drop was much larger than that for the coarser particles; hence compressibility factors were more important. For the 100/120 mesh column the pressure drop across the columns at a flow rate of 3.84 cm/sec was 21.1 psi, corresponding to a ratio of 2.4. At the same flow rate the pressure drop across the 40/60 mesh column was 5.3 psi or a ratio of 1.4 for the inlet and outlet pressures. The fact that the largest number of cycles for any given mesh size was obtained at the lowest flow rate, not at the minimum of the Van Deemter plot, again confirmed that the most cycles were obtained under conditions which minimized compressibility effects.

When the outlet of the recycle apparatus was maintained at atmospheric pressure, the number of theoretical plates did not increase over the entire range of cycles. As shown in Fig. 3, the maximum number of theoretical plates was not achieved in the final cycle, but instead N went through a maximum so that additional cycles actually caused a decrease in the number of plates. This loss in theoretical plates with increased column length

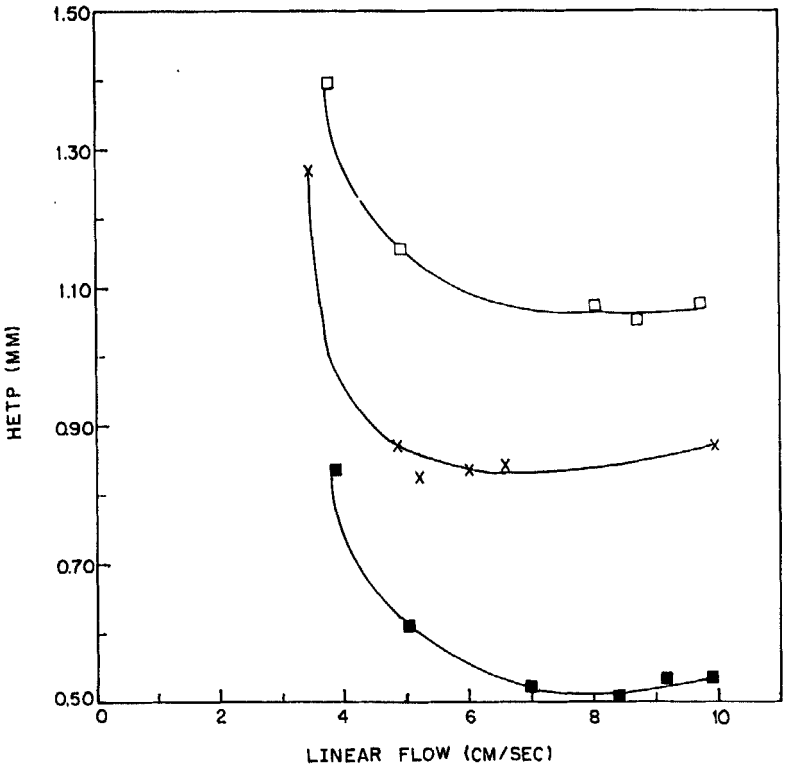

FIG. 2. Effect of solid support particle size on column efficiency. Columns, 1.5 m, 20% SE-30; solute, *n*-hexane; outlet at atmospheric pressure. (□) 40/60 mesh. (×) 60/80 mesh. (■) 100/120 mesh.

resulted because the peak retention time increased in a roughly linear rate, while the peak width increased disproportionately faster with each additional cycle.

Note that, during the first few cycles, the increase in N was roughly linear. On the 100/120 mesh column the maximum on N was achieved on the third cycle. For the coarser particles the linear section was longer, and at 3.84 cm/sec the maximum in N occurred at the seventh cycle. Furthermore, although the decrease in N after the maximum was very rapid for the 100/120 mesh column, the decrease was more gradual for the 40/60 mesh column.

In order to compare the results in Table 3 with those predicted theo-

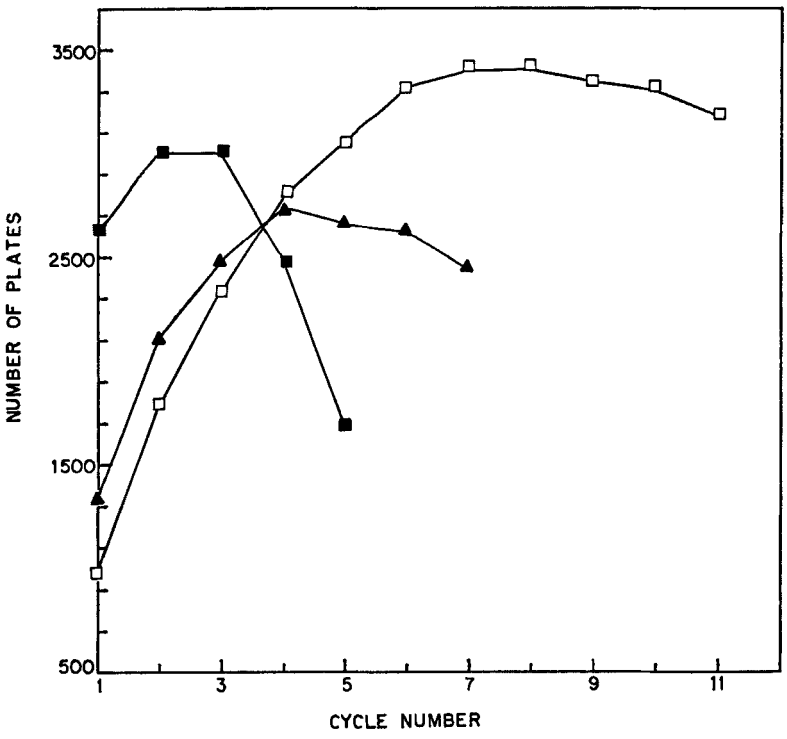

FIG. 3. Number of theoretical plates as a function of cycle number, Outlet at atmospheric pressure. Columns, 1.5 m, 20% SE-30; solute, 3-methyl pentane. (■) 100/120 mesh, 6.27 cm/sec. (□) 40/60 mesh, 3.84 cm/sec. (▲) 40/60 mesh, 7.02 cm/sec.

retically, the number of cycles obtained before overflow was calculated from Eqs. (1)–(4). The width of the peak at overflow was approximated by the retention time of the solute in the first column. For a flow rate of 3.84 cm/sec in the first column on the 40/60 mesh column, a value for m of 12 cycles was calculated which compared well to the value of 11 cycles obtained experimentally. The results of experiments with the column outlet at atmospheric pressure demonstrated that only a relatively small number of cycles could be obtained, and that the total number of theoretical plates generated was small. It was noted that both of these quantities were maximized under conditions which minimized carrier gas compressibility effects. In addition, N increased more nearly linearly with cycle number when compressibility effects were smaller.

Outlet at Higher Pressures

By adding a valve to restrict the flow of gas at the exit to the atmosphere, the outlet pressure of the recycle apparatus could be increased. This resulted in a smaller and more nearly constant pressure drop across the two columns at a given flow rate. Decreased compressibility effects were observed after the inlet-to-outlet pressure ratio had been lowered.

Figure 4 shows that, as the outlet pressure was increased, the minimum of the Van Deemter plot shifted to a lower linear flow rate and to a lower value of H. Compared to atmospheric outlet pressure where the minimum corresponded to a linear flow of 8 cm/sec and a H of 1.04 mm, the minimum occurred at a flow of 2 cm/sec and a H of 0.85 mm at an outlet

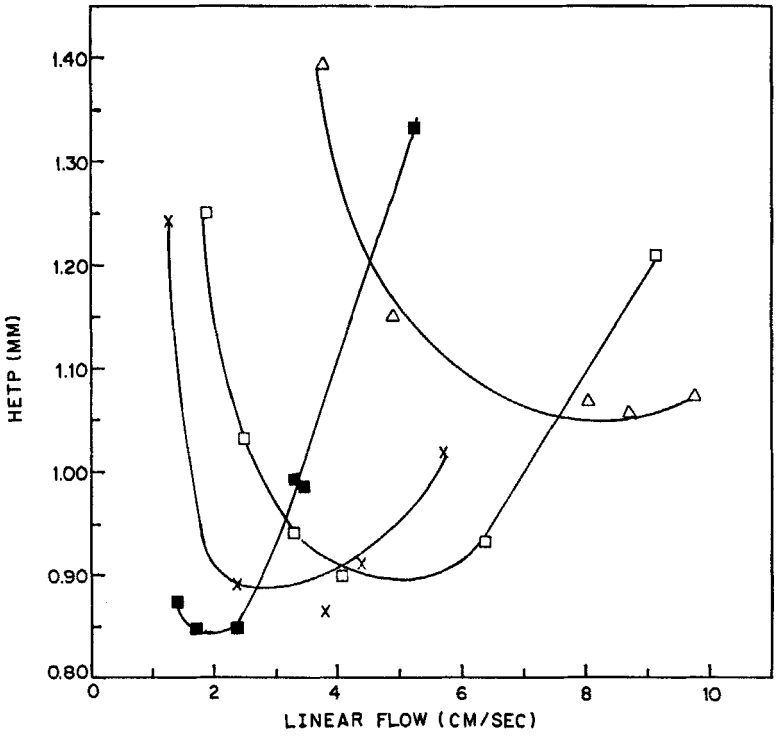

FIG. 4. Effect of outlet pressure on column efficiency. Columns, 1.5 m, 20% SE-30; solute, *n*-hexane. (△) P_{out} = 0 psig. (□) P_{out} = 25 psig. (×) P_{out} = 45 psig. (■) P_{out} = 90 psig.

pressure of 90 psig. These shifts reflected a decrease in the B term of the Van Deemter equation.

At higher outlet pressures, switching of the column outlets had only a small effect on the number of plates obtained after the second column length. With the outlet at 45 psig and a flow rate of 3.9 cm/sec, 3010 plates (no switch) were degraded only to 2870 plates when the columns were switched, a 5% loss in plates. At about the same flow the loss was 9% when the outlet was at atmospheric pressure.

More important, Fig. 5 shows that with the column outlet at 45 psig, the column efficiency, H, for the first and second column lengths became equal within experimental error in the absence of switching. To insure that

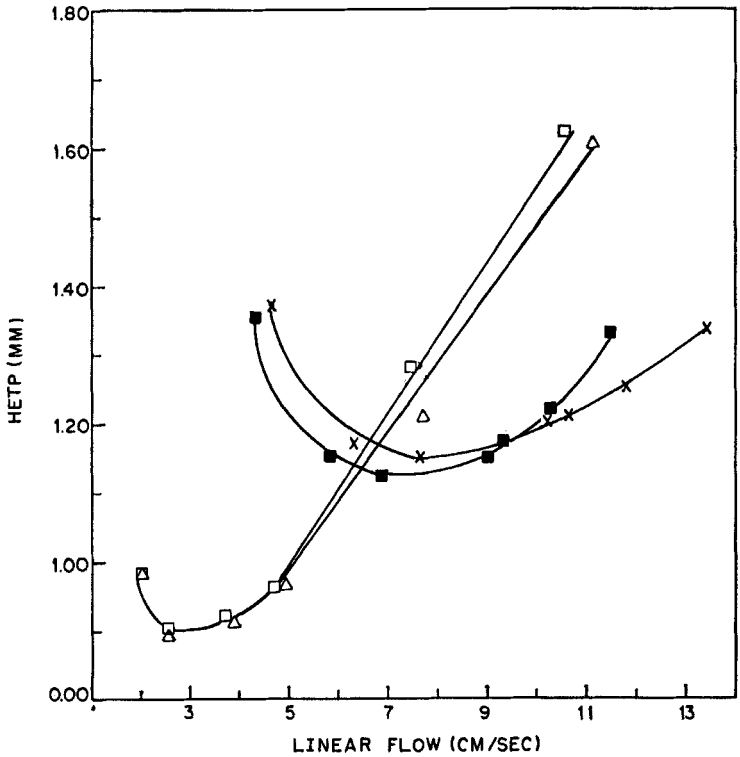

FIG. 5. Column efficiency after first and second column lengths without switching. Column, 1.5 m, 40/60 mesh Chromosorb W, 20% SE-30; solute, 3-methyl pentane. (■) Column 1, P_{out} = 0 psig. (×) Column 1 + 2, P_{out} = 0 psig. (□) Column 1, P_{out} = 45 psig. (△) Column 1 + 2, P_{out} = 45 psig.

TABLE 4

Effect of Outlet Pressure on the Number of Cycles before Overflow[a]

Outlet pressure (psig)	$\mu_{1/2}$ (cm/sec)	H_1 (mm)	Cycles	Time (hr)
0	3.8	1.54	11	0.5
	4.9	1.20	8	0.4
	7.0	1.15	7	0.2
25	1.9	1.25	23	2.2
	3.5	0.94	19	1.3
	6.4	0.93	15	0.8
45	1.2	1.24	34	5.9
	2.4	0.88	33	2.6
	3.8	0.88	21	1.3
	4.3	0.91	18	0.8
	5.7	1.02	14	0.6
90	1.4	0.87	50	6.5
	2.4	0.85	45	3.5
	5.3	1.33	15	0.7

[a] Column, 1.5 m, 40/60 mesh Chromosorb W, 20% SE-30; solute, *n*-hexane.

these results were not a reflection of a difference in the individual columns, the column positions were switched and similar results were obtained.

The increased outlet pressure had a dramatic effect on the maximum number of cycles which could be achieved. Table 4 shows that at an outlet pressure of 1 atm a maximum of 11 cycles were observed while at an outlet pressure of 90 psig up to 50 cycles were obtained. For any given flow rate it was possible to obtain more cycles at a higher outlet pressure, as illustrated by the data at a flow rate of 2.4 cm/sec where 33 cycles were obtained with the outlet at 45 psig and 50 cycles were obtained at 90 psig. That gain was due to two factors. First, gas compressibility effects decreased as the ratio of the inlet and outlet pressures approached unity. Second, the efficiency increased at lower flow rates because of the smaller B term on the Van Deemter plot. As a consequence, there was a large increase in the time required to achieve a separation. It required 6.5 hr to obtain 50 cycles at a flow rate of 1.4 cm/sec with the outlet at 90 psig. Fortunately the retention time increased linearly with cycle number under these conditions, thereby making easier the automation of the process based upon the retention time of the first cycle.

In order to compare the results in Table 4 with those predicted theoretically from Eqs. (1)–(4), the number of cycles obtained before overflow

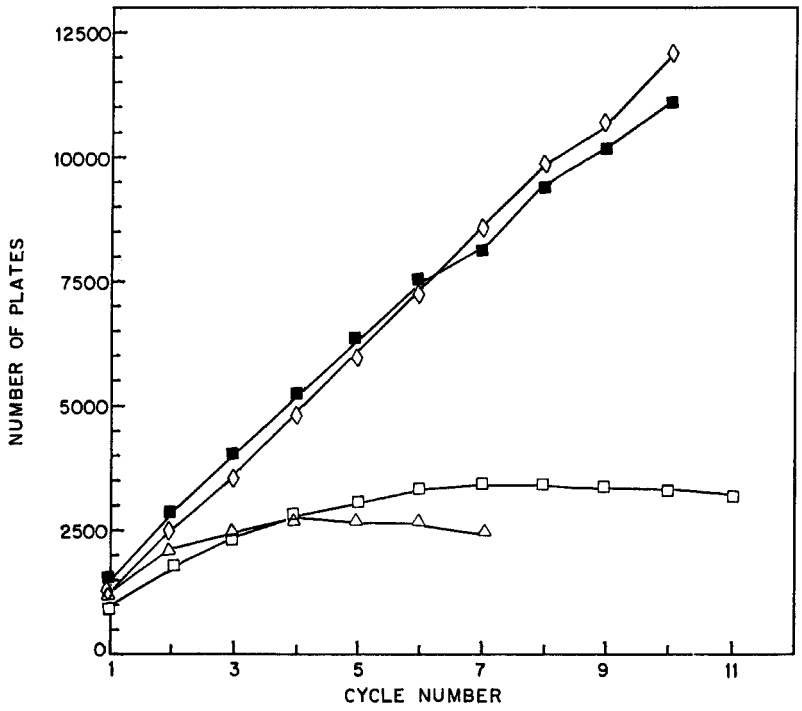

FIG. 6. Number of theoretical plates as a function of cycle number. Column, 1.5 m, 20% SE-30, 40/60 mesh Chromosorb W; solute, 3-methyl pentane. (△) P_{out} = 0 psig, 7.02 cm/sec. (□) P_{out} = 0 psig, 3.84 cm/sec. (■) P_{out} = 45 psig, 3.9 cm/sec. (◇) P_{out} = 45 psig, 1.4 cm/sec.

was calculated for the case of a $\mu_{1/2}$ of 1.9 cm/sec and an outlet pressure of 25 psig. From Eq. (1), 27 cycles were predicted while 22 were actually observed. As expected from the work of Chizhkov et al. (*14*), increasing the column outlet pressure caused the increase in N with cycle number to become more linear as shown in Fig. 6. As noted earlier, when the column outlet was maintained at atmospheric pressure, more total plates were achieved at a lower flow rate of 3.84 cm/sec than at a flow rate, 7.02 cm/sec, which corresponded to the minimum of the Van Deemter plot. It is also interesting to note that at 7.02 cm/sec, more plates were achieved initially than at the lower flow rate, but that after the fourth cycle they were equal. At the lower flow rate, N continued to increase, while at the higher flow it began to decrease.

A similar crossover was observed at higher outlet pressures where a higher, more efficient flow based on the first column length gave fewer total plates than a slower, less efficient flow. For example, with the column outlet at 45 psig, a flow rate of 3.89 cm/sec initially gave more plates than a flow of 1.44 cm/sec. After six cycles they had both generated the same number of plates and after the sixth cycle, N continued to increase linearly with cycle number for the lower flow whereas N for the higher flow rate began to fall off. As the ratio of the inlet to outlet pressure approached unity, the linear section of the plot of N vs cycle number extended to more cycles. For an outlet pressure of 90 psig, over 55,000 plates were generated at a flow rate of 1.4 cm/sec on 40/60 mesh Chromosorb.

DISCUSSION

The present study has independently confirmed the major findings of Chizhkov et al. First, compressibility is a major factor that can affect the number of cycles and, therefore, the total number of plates. Second, the use of a valve at the exit end served to minimize compression problems by permitting the ratio of inlet pressure to outlet pressure to approach close to unity. Under those conditions the number of plates increases linearity with the number of cycles.

In addition, the present study led to new information that should be helpful in extending the application, as well as the further study, of recycling. First, by using a single compound rather than two, we were relieved of having to find a suitable combination of chemical components and operating conditions for testing the system. Second, contrary to our expectations, our best results (i.e., the largest number of cycles and the largest total of plates) were obtained by working at flow rates less than that at the minimum of the Van Deemter curve for the first (or second) column in a series. For example, the use of the flow rate at the minimum Van Deemter plot gave more plates per cycle and more total plates only in the first few cycles, and then both values fell below those for a slower flow rate. In fact, when operated with the outlet at atmospheric pressure and at a flow rate that gave the maximal number of plates after the first column, the total number of plates actually went through a maximum and then decreased before the sample overflowed the system. However, at higher outlet pressures, where the ratio of inlet to outlet pressure approached closer to unity, the crossover occurred at larger numbers of cycles and total plates, and the total number of plates was still increasing when the sample overflowed the column capacity.

Chizhkov et al. (*21*) recommended the use of 60/80 mesh packings. Our best results were obtained using 40/60 mesh but probably only because it was the coarsest packing we had available. The combination of coarser particles and longer columns represents a promising direction to be explored in a future study. As is well known, for a given mesh size, a longer column will produce more plates. In our study, because we obtained nearly the same number of cycles in a system using longer columns, the total number of plates obtained before overflow was larger than for a recycling system composed of shorter columns. Hence, by using coarser particles, it should be possible to use longer columns before increasing the pressure drop to the point where poorer separations resulted. Although it is not reasonable to believe that one can continue indefinitely to increase the particle size and the column length, that combination has yet to be optimized. There is already an indication in the early work of Root, Lee, and Rowland (*10*) that the use of longer columns and coarser mesh may be advantageous.

When using very long columns, it may be necessary to operate at higher pressures than Chizhkov or we did in order to maintain the ratio of inlet to outlet pressure close to unity. Even in the present study it would have been interesting to explore the use of higher pressures. Unfortunately, the transducers and controllers we had available limited our ability to make careful studies at significantly higher pressures.

Acknowledgments

The work was supported by the National Science Foundation under Grant MPS 74–23609. We also wish to thank the University of Georgia for a Graduate Assistantship to R.E.P.

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Received by editor August 30, 1976