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PREPARATIVE-SCALE CIRCULATION GAS CHROMATOGRAPHY

COMPARISON OF LONG PACKED COLUMNS WITH COLUMNS INCORPORATED INTO CIRCULATION SCHEMES

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SUMMARY

The theoretical treatment has been performed to enable columns incorporated into circulation schemes to be compared with normal columns of equivalent length and performance. The influence of the particle diameter of the support on the parameters of both separation systems has been determined. The theoretical conclusions have been confirmed experimentally by the separations of isomeric pairs using short columns incorporated into the circulation system. The effectiveness and the separation achieved were comparable with those for open tubular columns. The first preparative-scale separation of isomers having very similar properties ($\alpha = 1.035$) has been achieved with circulation chromatography and the components have been isolated in high purity.

INTRODUCTION

Contemporary qualitative analysis and synthetic organic chemistry often involve the preparative-scale separation of substances which possess very similar physical properties. If the separation factor for two compounds is close to unity, very long columns (tens of meters) or circulation chromatography may be necessary[1,2]. The suitability of circulation schemes in preparative-scale chromatography has already been discussed[3–5], but under the conditions described there was not a linear relation between the number of semi-cycles and the number of theoretical plates. Recent investigations[6,7] showed the possibility of employment of relatively short columns. The advantages of using circulation systems to separate substances having very similar properties are discussed here.

THEORY

The productivity, W, of a preparative-scale column is determined according to the equation

$$W = \frac{Q}{t_R} \tag{1}$$

where Q is the quantity of mixture to be separated at the column exit and t_R is the time required to obtain separation R:

$$t_R = \frac{16R^2}{(\alpha - 1)^2} \cdot \frac{\text{HETP}}{u} \cdot \frac{(1 + k')^3}{(k')^2} \tag{2}$$

Here α is the separation factor (only the case of $\alpha - 1 \ll 1$ is considered), HETP is the height equivalent to a theoretical plate, u is the mean carrier gas flow-rate and k' is the partition ratio. If there is no loss of substance in the separation process,

$$Q = \text{HETS} \, (S_g \cdot C_{g,1} + S_l \cdot C_{l,1} + S_g \cdot C_{g,2} + S_l \cdot C_{l,2}) \tag{3}$$

where the subscripts 1 and 2 are related to the first and the second components of the mixture, C_g and C_l are the concentrations in the gas and in the liquid phases, S_g and S_l are the cross-sectional areas occupied by the gas and the liquid and HETS is the height equivalent to a theoretical separation step, *i.e.*, the step in which the separation characterized by the factor α is achieved.

The relationship

$$\text{HETS} = \text{HETP} \cdot \frac{1 + k'}{2k'} \tag{4}$$

was established in ref. 8. Assuming that $C_{g,1} = C_{g,2}$ for $\alpha - 1 \ll 1$,

$$Q = 2 \, \text{HETS} \cdot S_g \cdot C_g (1 + k') \tag{5}$$

Substituting for t_R and Q in eqn. 1, we obtain for $k' \geqslant 3$,

$$W = \frac{\pi d^2}{64} \cdot \left(\frac{\alpha - 1}{R} \right)^2 \cdot \varkappa \cdot C_g \cdot u \tag{6}$$

where d is column diameter, the fraction $\varkappa$ of which is occupied by the cross-sectional area of the gas.

It can be seen that W increases with increasing flow-rate of the carrier gas. An increase in the carrier-gas flow-rate simultaneous with a decrease in the minimum HETP value and with a reduction in the separation time may be achieved by decreasing the content of the liquid phase in the column[9,10].

The experimental results of many workers show that the term A in the Van Deemter–Jones equation[11] and the term describing the resistance of the liquid phase to mass transfer are negligible for analytical columns of silicate-type solid supports loaded with 1–5% of liquid phase, in comparison with the terms describing the molecular diffusion and the resistance of the gas phase to mass transfer[11]. For such columns, the Van Deemter–Jones equation may be written in the following form[11] for $k' \geqslant 3$,

$$\text{HETP} \approx \frac{2\gamma D_g}{u} + \frac{2d_p^2}{D_g} \cdot u = \frac{B}{u} + c_2 u \tag{7}$$

where γ is the eddy diffusion factor, d_p is the particle diameter and D_g is the molecular diffusion coefficient in the carrier gas. B and c_2 are the coefficients in the Van Deemter–Jones equation[11].

For preparative-scale columns the expression for HETP is[12]

$$\text{HETP} = A + \frac{2\gamma D_g}{u} + \frac{8}{\pi^2} \cdot \left(\frac{k'}{1+k'}\right)^2 \cdot \frac{d_p^2}{D_g} \cdot u + \frac{2k'}{3(1+k')^2} \cdot \frac{d_l^2}{D_l} \cdot u + \frac{cd^2}{4D_g} \cdot u \quad (8)$$

where d_l is the thickness of the liquid film and D_l is the diffusion coefficient of the liquid phase. It is probable that, for a 1–5% loading of liquid phase, eqn. 9 can be written by analogy with packed analytical columns when $k' \geqslant 3$:

$$\text{HETP} \approx \frac{2\gamma D_g}{u} + \frac{8}{\pi^2} \left[1 + \frac{\pi^2 c}{32}\left(\frac{d}{d_p}\right)^2\right] \cdot \frac{d_p^2}{D_g} \cdot u \quad (9)$$

We shall limit the consideration to the case when

$$\frac{\pi^2 c}{32}\left(\frac{d}{d_p}\right)^2 = 1 \quad (10)$$

for which eqn. 9 becomes

$$\text{HETP} \approx \frac{2\gamma D_g}{u} + \frac{16}{\pi^2} \cdot \frac{d_p^2}{D_g} \cdot u = c_2' u + \frac{B}{u} \quad (11)$$

where $c_2' \approx c_2$. It follows from the eqn. 11 that for an infinite increase in carrier-gas flow-rate, u, the first term becomes very small and HETP becomes proportional to the flow-rate; the value of HETP/u is constant, equal to c_2. In attempting to reduce the separation time, it would not be appropriate to increase the flow-rate since, although the quantity HETP/u is not decreased, that of HETP is increased.

Assuming that the influence of the B/u term in eqn. 11 is negligible when it becomes an order of magnitude smaller than $c_2' \cdot u$, one can define a term u_m which corresponds to an acceptable compromise between the speed of separation and the column efficiency. u_m can be derived from

$$10 \cdot \frac{2\gamma D_g}{u_m} = \frac{16}{\pi^2} \cdot \frac{d_p^2}{D_g} \cdot u_m \quad (12)$$

Eqn. 12 defines the minimum value of HETP/u in eqn. 2, for which the considerable increase in flow-rate does not result in a proportional increase in HETP with a consequent loss of resolution. On combining eqns. 11 and 12, we obtain

$$u_m = \pi \cdot \sqrt{\frac{\gamma}{0.8} \cdot \frac{D_g}{d_p}} \quad (13)$$

$$\text{HETP} = 4.83 \cdot d_p \quad (14)$$

The expression for the productivity of the circulation mounting (W_c) must take into account the loss of substance caused by carrier-gas take-off between the columns, which is necessary to ensure optimum working conditions[7]. Using the data of ref. 6, we obtain

$$W_c = \frac{Q\left(1 - \frac{\theta_{opt.}}{100}\right)^{m-1}}{t_R} \tag{15}$$

$$\theta_{opt.} = \frac{2(P_c - 1)}{3P_c + 1} \cdot 100 \tag{16}$$

where P_c is the ratio of the inlet (p_i) and outlet (p_o) pressures in the circulation column and m is the number of semi-cycles given[6] by

$$m = \frac{1}{3} \cdot \frac{1}{\alpha - 1} \cdot \frac{1 + k'}{k'} \tag{17}$$

Using eqn. 16 when $k' \geqslant 3$, we may write

$$W_c \approx \frac{\pi d^2}{4} \cdot \left(\frac{\alpha - 1}{R}\right)^2 \cdot \varkappa \cdot C_g \cdot u_{m,c} \left[\frac{P_c + 3}{3P_c + 1}\right]^{m-1} \tag{18}$$

$$u_{m,c} = \pi \sqrt{\frac{\gamma}{0.8} \cdot \frac{D_{g,c}}{d_p}} \tag{19}$$

Therefore we obtain[11]

$$\frac{W}{W_c} = \frac{u_m}{u_{m,c}} \cdot \left[\frac{3P_c + 1}{P_c + 3}\right]^{m-1} \tag{20}$$

$$\frac{u_m}{u_{m,c}} = \frac{D_g}{D_{g,c}} = \frac{D_{g,0}}{D_{g,0,c}} \cdot \frac{j}{j_c} \tag{21}$$

where $D_{g,0}$ is the diffusion coefficient of the gas at P_c (the subscript c refers to the circulation scheme) and j is the compressibility factor. The carrier-gas take-off does not necessarily result in loss of substance, as for example when a semipermeable membrane is used. Palladium foil allows take-off of the necessary quantity of hydrogen without loss of any other substance[13].

The optimum conditions in circulation chromatography correspond[6] to $P_c \leqslant 1.4$, *i.e.*[11]

$$j_c = \frac{2}{P_c + 1} \tag{22}$$

For long columns,

$$j = \frac{3}{2} \cdot \frac{P_{hl}^2 - 1}{P_{hl}^3 - 1} \tag{23}$$

where the subscript hl signifies a conventional column of greater length. From the ratio

$$\frac{D_{z,0}}{D_{g,0,c}} = \frac{P_{0,c}}{P_0} = \frac{p_{i,c}}{p_i} \cdot \frac{P_{hl}}{P_c} \tag{24}$$

we obtain

$$\frac{u_m}{u_{m,c}} = \frac{4}{3} \cdot \frac{p_i}{p_{i,c}} \cdot \frac{P_c}{P_c+1} \cdot \frac{P_{hl}^3 - 1}{P_{hl}(P_{hl}^2 - 1)} \tag{25}$$

In order to exclude $p_i/p_{i,c}$ from eqn. 25, known relations between the parameters can be used.

The pressure drop in a column of any kind is determined by Darcy's law:

$$\Delta p = \frac{\eta}{K} \cdot L \cdot u_m \tag{26}$$

$$\Delta p_c = \frac{\eta}{K} \cdot 2L_c \cdot u_{m,c} \tag{27}$$

The column permeability, K, may be defined[11] as

$$K = \frac{d_p^2}{180} \cdot \frac{\varkappa^3}{(1 - \varkappa)^2} \tag{28}$$

where η is the gas viscosity, which has been tabulated in many sources[9]. The column length required in normal (L) of circulation (L_c) chromatography is determined[6,9] by

$$L = \frac{16}{(\alpha - 1)^2} \cdot \text{HETP} \cdot \left(\frac{1 + k'}{k'}\right)^2 \tag{29}$$

$$2L_c = \frac{2 \cdot 48}{\alpha - 1} \cdot \text{HETP} \cdot \left(\frac{1 + k'}{k'}\right) \tag{30}$$

where the resolution, R, is assumed to be equal to 1. These equations lead to

$$\frac{p_{i,c}}{p_i} = 6(\alpha - 1) \cdot \frac{u_{m,c}}{u_m} \cdot \frac{P_{hl} - 1}{P_c - 1} \cdot \frac{P_c}{P_{hl}} \cdot \frac{k'}{1 + k'} \tag{31}$$

dividing eqn. 25 by 31 we obtain

$$\frac{u_m}{u_{m,c}} \approx 2.12 \sqrt{\frac{P_c + 1}{P_c - 1} \cdot (\alpha - 1) \cdot \frac{k'}{1 + k'} \cdot \frac{(P_{hl}^2 - 1)(P_{hl} - 1)}{P_{hl}^3 - 1}} \tag{32}$$

Introducing eqn. 32 into 20 when $k' \geqslant 3$ we finally obtain

$$\frac{W}{W_c} \approx 2.12 \cdot \sqrt{\frac{P_c + 1}{P_c - 1} \cdot (\alpha - 1) \cdot \frac{(P_{h1}^2 - 1)(P_{h1} - 1)}{P_{h1}^3 - 1}} \cdot \left(\frac{3P_c + 1}{P_c + 3}\right)^{m-1} \tag{33}$$

In these calculations we have assumed that $p_1 = p_{1,c}$ which corresponds (from eqns. 31 and 32) to

$$P_c = \sqrt{\frac{1}{1 - 8(\alpha - 1) \cdot \dfrac{P_{h1}^3 - 1}{P_{h1}^2 (P_{h1} + 1)}}} \tag{34}$$

Thus knowing P_{h1} one can easily calculate P_c and thence W/W_c. A set of parameters calculated by means of eqn. 34 is given in Table I. The time for one semi-cycle can be determined from

$$\tau = \frac{t_R}{m} \tag{35}$$

The influence of particle size was evaluated using

$$\frac{\Delta p_1}{\Delta p_2} = \frac{P_{h1,1} - 1}{P_{h1,2} - 1} = \left(\frac{d_{p,2}}{d_{p,1}}\right)^2 \cdot \frac{D_{g,1}}{D_{g,2}} \tag{36}$$

and

$$\frac{D_{g,1}}{D_{g,2}} \approx \frac{P_{h1,2}}{P_{h1,1}} \tag{37}$$

where $P_{h1} \geqslant 5$.

The employment of the circulation technique leads to an increase in the separation time and a decrease in the productivity as shown in Table I. However, the productivity per unit of sorbent volume, W' (ref. 14), increases considerably due to the drastic shortening of the column. This is of great importance as decreasing the sorbent volume results in a saving in equipment volume and in the time and labour required to prepare the columns. A decrease in particle size results in a decrease in column length and a reduction in separation time. The optimum value of the gas flow-rate is practically unchanged since it is the result of simultaneous changes in the particle size and in the diffusion coefficients according to eqns. 13 and 19.

The inlet pressure, p_1, increases with decreasing particle size. The ratio W/W_c is almost constant. Eqns. 6 and 15, together with the data in Table I, show the remaining productivity parameters are also almost constant. Nevertheless the quantity of separated substance which enters the trap at the end of the chromatographic process decreases appreciably with decreasing particle diameter. Generally, the em-

TABLE I

COMPARISON OF LONG PACKED COLUMNS (hl) WITH COLUMNS INCORPORATED INTO CIRCULATION SCHEMES (c)

Data for the calculation: $\alpha = 1.02$; $R = 1$; $x' = 10$; $\kappa = 0.41$; $\gamma = 0.6$; $\eta \cdot 10^{10} = 2.34$ kg·sec/cm^2. Column temperature, 150°. Carrier gas, nitrogen. Column, 4 m × 10 mm I.D.

Calculated parameter	$d_p = 0.0174$ cm		$d_p = 0.0304$ cm		$d_p = 0.0434$ cm	
	hl	c	hl	c	hl	c
Diffusion coefficient, $D_g \cdot 10^2$ (cm^2/sec)	2.17	1.47	3.65	2.52	5.0	3.51
Permeability factor, $K \cdot 10^7$ (cm^2)	3.45	3.45	9.54	9.54	21.4	21.4
HETP (mm)	0.77	0.77	1.3	1.3	1.9	1.9
Column length, L (m)	37.2	2.06	65.1	3.64	92.4	5.14
Carrier-gas flow-rate (mean), u (cm/sec)	3.75	2.54	3.6	2.46	3.44	2.42
Number of theoretical plates, $n \cdot 10^{-2}$	486	27.0	486	27.0	486	27.0
Number of semi-cycles, m	—	18	—	18	—	18
Separation time, t_R (h)	3.08	4.57	5.5	8.12	8.16	11.62
Semi-cycle time, τ (min)	—	15.2	—	27	—	38.8
Inlet pressure, p_i (kg/cm^2)	9.3	9.3	5.14	5.14	3.48	3.48
Ratio of inlet to outlet pressure, P	10.3	1.07	6.14	1.065	4.48	1.062
Compressibility factor, j	0.146	0.965	0.239	0.967	0.322	0.970
Optimum eluate take-off, θ_{opt} (%)	—	3.33	—	3.10	—	2.96
Productivity	$W_b = 1.08W$	$0.374W_b$	$W_a = 1.04W$	$0.4W_a$	W	$0.42W$
Productivity per unit of sorbent volume	W'_b	$3.39W'_b$	W'_a	$3.54W'_a$	W'	$3.77W'$
Recovery in the trap	$Q_b = 0.4Q$	$0.56Q_b$	$Q_a = 7Q$	$0.59Q_a$	Q	$0.6Q$

ployment of a support with a particle size of 60–80 mesh is considered to be optimal under the circumstances discussed. In this case the separation time is sufficiently short and the length of the circulation columns is quite reasonable for practical purposes. At the same time, the inlet pressure and the loss of separated material are not too high.

EXPERIMENTAL

The possibilities of circulation chromatography arising from the above theo-
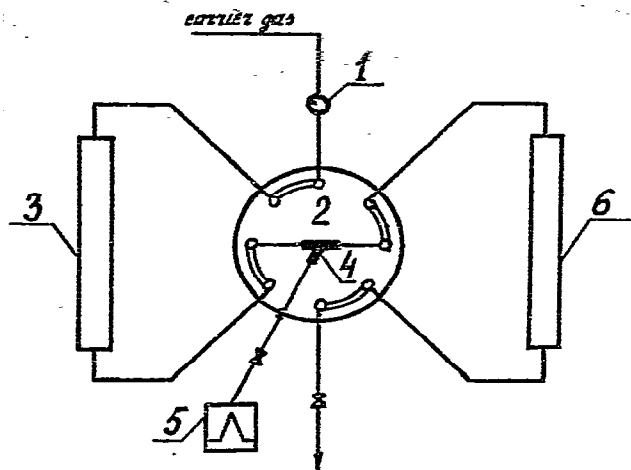
Fig. 1. Circulation scheme: 1 = injection port; 2 = circulation valve; 3 and 6 = columns; 4 = flow splitter; 5 = flame ionization detector.

retical treatment will now be illustrated by two examples of the separation of mixtures of two isomers which have very similar properties.

The separations were made by use of the circulation scheme in Fig. 1. A flame ionization detector (FID) was used to which a small proportion of the separated substances was directed in a stream of the carrier gas. The circulation valve was made of stainless steel and PTFE to permit chromatography at temperatures up to 230°. The outlet pressure was controlled by means of a special valve. The circulation scheme employed allows the most difficult pair of components to be separated from the initial mixture and circulated long enough for adequate resolution to be obtained. Components other than the ones chosen for circulation could be directed out of the system. When a multicomponent mixture is to be separated ,a preliminary separation may be made by use of the whole length of the column. The more difficult components can then be separated by means of the circulation method.

Separation of the methyl esters of 1,3-dimethylcyclohexene-3-carboxylic and 1,4-dimethylcyclohexene-3-carboxylic acids

The above mixture of isomers was obtained by Diels-Alder condensation of isoprene and methyl methacrylate[15]. Two steel columns (3 m × 4 mm I.D.) were used to separate this mixture. Chromosorb W (70–100 mesh) loaded with 5% polyethylene glycol succinate was used as the packing. Optimum conditions for chromatography were established as described in ref. 16. The column temperature was 127°. The inlet and outlet pressures were $p_{i,c} = 9.2$ kg/cm^2 and $p_{o,c} = 8.7$ kg/cm^2, respectively ($p_c = 1.05$). The carrier gas (nitrogen) flow-rate was 60 ml/min. The mean gas velocity, $u = 1.32$ cm/sec, was measured by the injection of methane.

The chromatogram obtained is shown in Fig. 2. The resolution achieved after 8 semi-cycles was $R = 1.044$. The values of $k' = 1.74$ and $\tau = 10.4$ min were determined from the chromatogram. The efficiency of separation corresponds to the total number of plates, $n = 23600$ (HETP = 0.1 cm) and the separation factor, $\alpha = 1.044$.
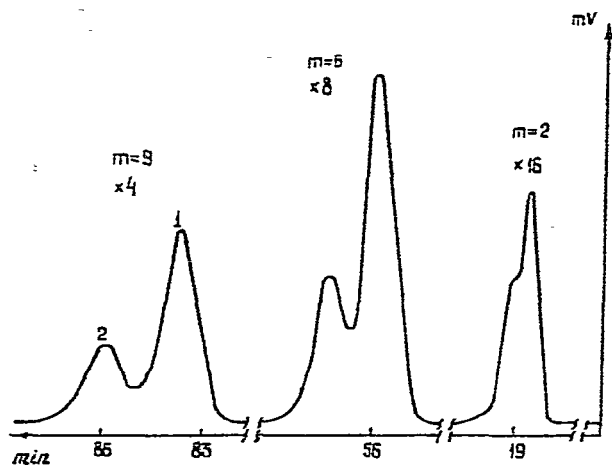
Fig. 2. Circulation chromatographic separation of the mixture of methyl esters of 1,3-dimethylcyclo-hexene-3-carboxylic acid (1) and 1,4-dimethylcyclohexene-3-carboxylic acid (2) methyl esters.

The time for complete separation was $t_R = 89$ min, the calculated value (from eqn. 2) being 79 min. Thus there is sufficient correspondence between experimental and calculated values. There was also satisfactory correspondence between the experimental and calculated values of the length of column occupied by the analyzed mixture at the end of the circulation (experimental, $L_c = 201$ cm; calculated from eqn. 30, $L_c = 167$ cm at $R \neq 1$).

The same isomeric mixture has previously been separated using an open tubular column[17] with polyethylene glycol, or a packed column containing silver nitrate solution and having ca. 4000 plates[15].
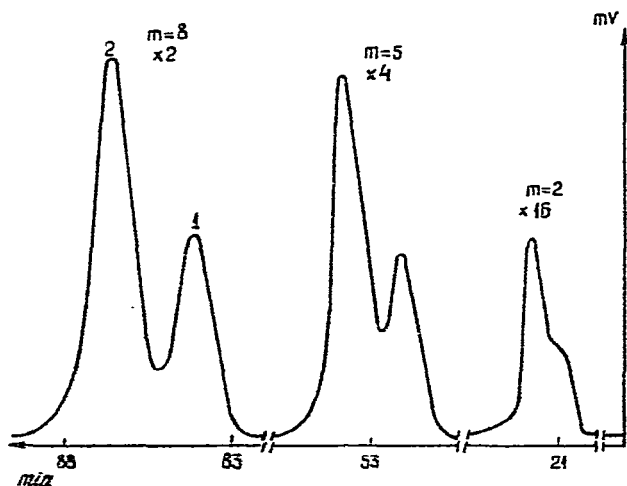

Fig. 3. Circulation chromatographic separation of the mixture of durene (1) and isodurene (2) with a 4-mm I.D. column.
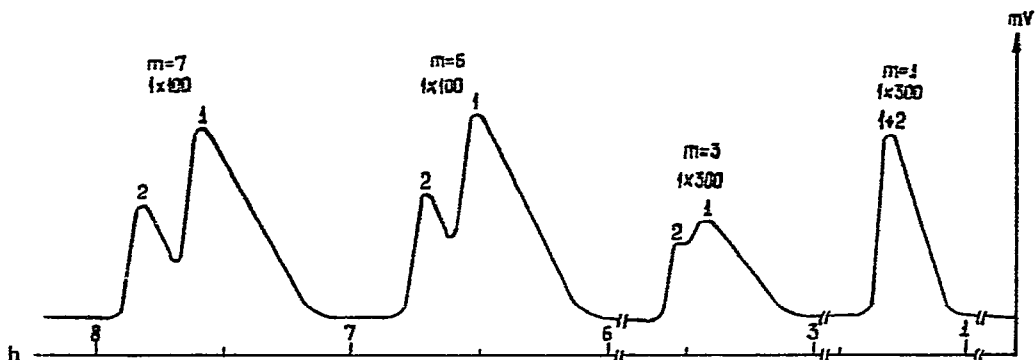
Fig. 4. Preparative-scale circulation chromatographic separation of a mixture of durene (1) and iso-durene (2) using a 10-mm I.D. column.

Separation of isomeric tetramethylbenzenes

The mixture to be separated consisted of durene (1,2,4,5-tetramethylbenzene) and isodurene (1,2,3,5-tetramethylbenzene). It was obtained through isomerization of isodurene in the presence of aluminium trichloride. The separation was achieved using the same installation and under the same conditions as described above. The resulting chromatogram is given in Fig. 3. The resolution $R = 1.025$ was achieved after 9 semi-cycles. The following values were calculated from the chromatogram: theoretical plate number, 26000; $k' = 1.56$; $\alpha = 1.046$ and $\tau = 9.6$ min. The complete separation required 89 min, the value calculated from eqn. 2 being 72 min. A good separation of this mixture has been previously achieved by using an open tubular column coated with polypropylene glycol[18] and having 3000 theoretical plates.

In order to demonstrate the potential of the circulation technique for preparative-scale separations, the same mixture was separated on a set of columns (each 2 m × 10 mm I.D.) installed within the same circulation scheme. Approximately 0.1% of eluate was directed into the detector. In addition, *ca.* 1% of the flow of carrier-gas was constantly removed in order to ensure the optimum conditions[7]. The columns were packed with silanized Chromaton N (particle size, 0.2–0.25 mm) and loaded with 15% Carbowax 6000. The column temperature was 150°. The carrier-gas (nitrogen) flow-rate was 120 ml/min. The inlet and outlet pressures were $p_{i,c} = 6.42$ kg/cm^2 and $p_{o,c} = 6.22$ kg/cm^2, respectively. Samples of 45 mg of the mixture in benzene were injected for each run. The trap temperature was 0°.

The resulting chromatogram is shown in Fig. 4. The resolution $R = 0.6$ was achieved after 7 semi-cycles. *ca.* 20 mg of durene with >98% purity was collected in the trap. In order to evaluate the parameters of the process, the chromatogram was obtained without overloading and the dead time of the system was determined by methane injection. The values of the partition ratio, separation factor and HETP were 10, 1.035 and 0.1 cm, respectively.

DISCUSSION

Gas chromatographic preparative-scale separation of isomers having $\alpha \geqslant 1.02$ can be performed by means of long packed columns of high separating power or by

"impulseless" circulation chromatography. The theoretical comparison of these two methods in the present work shows that the productivity of long packed column chromatography is about 2.5 times better than circulation chromatography having similar characteristics. On the other hand, the productivity per unit of sorbent volume is about 3.5 times greater for circulation chromatography due to the actual column length being about 9 times smaller. The decrease in sorbent volume leads to a decrease in the equipment volume and makes the column preparation easier.

The experimental data obtained demonstrate that "impulseless" circulation chromatography is promising for the preparative-scale separation of pairs of isomers. The performance of ordinary columns (4–10 mm I.D.) used in this work did not differ considerably from that of analytical packed columns. This is in accordance with the assumption made in eqn. 10. The complete separating power of the process achieved here was *ca.* 25000, comparable with the performance of open tubular columns, and makes possible the achievement of resolutions, R, greater than unity for mixtures having $\alpha \approx 1.04$. "Impulseless" circulation gas chromatography has permitted the first preparative-scale separation of isomeric tetramethylbenzenes ($\alpha = 1.035$) and their isolation in high purity.

ACKNOWLEDGEMENT

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