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NEW APPROACH TO CHROMATOGRAPHIC OPTIMIZATION IN GLASS CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A system for achieving mechanically valved recycle chromatography in small bore glass capillary columns is described. The system is capable of achieving extreme resolution in comparatively short times (*e.g.* over 2,000,000 theoretical plates in 16 min) and can be designed to permit optimization of column length and liquid phase polarity.

INTRODUCTION

Column efficiency, measured in theoretical plates per meter, should (according to the Van Deemter or Golay equations) be independent of the column length when the average linear gas velocity is optimized. Because longer columns operate at higher pressure drops, this generalization would seem questionable, and indeed it has been challenged^{1,2}. Giddings³, however, reasoned that the conclusion was essentially correct, largely because if the average linear gas velocity is optimized, changes in the diffusion coefficient due to the changes in pressure that accompany decompression of the sample as it passes through the column compensate for the negative effects of decreasing velocity; this reasoning was supported by Sternberg⁴.

Yabumoto and VandenHeuvel⁵ studied the efficiencies of different length segments from the same glass capillary column at different gas velocities. They concluded that at \bar{u}_{opt} , variation in column length had little effect on h , but at increased flow velocities, longer columns had much larger h values. Hence shorter columns possess an advantage in their higher optimum practical gas velocities (OPGV)^{1,7} but they are obviously limited in the total number of theoretical plates that they can deliver.

Partially resolved eluates have been recycled through the same column to achieve more complete high-performance liquid chromatographic separations. The

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recycle concept has also been applied to gas chromatography (GC). Deford⁷ achieved up to six passes in preparative GC recirculation; Reid⁸ reported up to three cycles in an analytical system equipped with a 6-ft. packed column, and recycling with capillary columns has been suggested⁹.

The present study was directed toward developing a recycle unit, utilizing a mechanical flow switching valve whose internal passage diameters are consistent with those of the capillary column¹⁰ to achieve increased resolution, and to explore the prospects of using this device to optimize the GC system.

MATERIALS AND METHODS

Switching valve

Deans¹¹ raised several objections to the use of mechanical valves for flow switching in high resolution columns, and Bertsch *et al.*¹² have also commented on the difficulties normally encountered with mechanical valves. As pointed out by Miller *et al.*¹⁰, mechanical valves also enjoy several advantages which tend to favor their use, provided their major disadvantage (band broadening caused by the valve) can be eliminated. The valve used in this study was an experimental model produced by Valco Engineering (Houston, Texas, U.S.A.)¹⁰. Flow channels in the valve rotor were approximately 0.15 to 0.20 mm in cross section, and each port was fitted with zero dead volume connections, terminating in 2-cm lengths of 0.25 mm O.D. platinum-iridium tubing, in precise alignment with these channels.

Columns

Initial work utilized 0.25 mm I.D. glass capillary columns; to facilitate the connection between the glass capillary and the platinum-iridium tubing, later efforts utilized 0.32 mm I.D. columns. All columns were coated with methyl silicone SP-2100 and were supplied by J & W Scientific.

Gas chromatography

A Hewlett Packard 5720 chromatograph, equipped with a J & W inlet splitter (operating at a split ratio of *ca.* 1:100) and utilizing flame-ionization detector, was adapted to receive the recycle unit by drilling a hole through the oven wall to accommodate the torque transfer assembly of the flow-switching valve. The valve, with column segments attached (Fig. 1), was located in the oven proper.

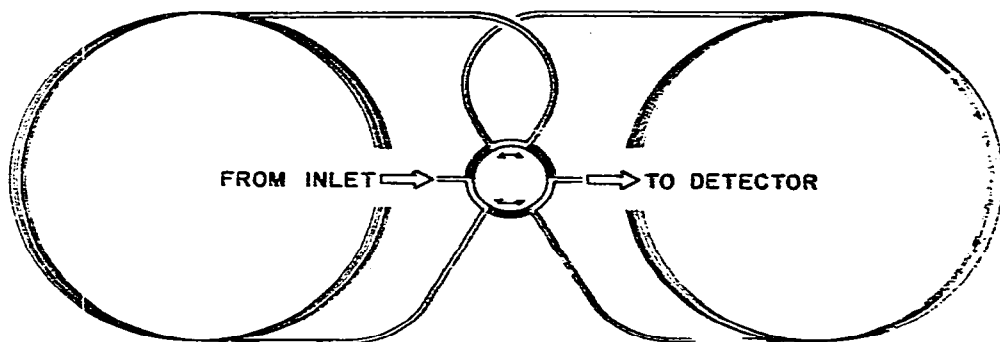


Fig. 1. Schematic representation of a recycle unit. See text for details.

RESULTS AND DISCUSSION

Fig. 1 shows a schematic representation of the recycle unit. Obviously, flow characteristics in the valve become critically important to the performance of this unit. Because the valve contains transfer passages that do not normally possess chromatographic (*i.e.* partitioning) properties, some degree of band broadening should be anticipated for each passage through the valve. Provided the degree of component separation achieved from each pass through the column exceeds the degree of component remixing occasioned by each passage through the valve, the net effect would be a gain in separation for each recycle pass. This concept is illustrated by Fig. 2. Hence it is desirable that flow conditions in the valve passage match as nearly as possible those that are encountered in the column; in particular, minute unswept volumes or areas of lower velocity in the valve would be expected to have a deleterious effect. In an earlier evaluation, two $7.5 \text{ m} \times 0.25 \text{ mm}$ segments were installed on the recycle unit by expanding the column ends to fit over the 0.24 mm O.D. platinum-iridium tubing and fused. A 15-m segment of that same column exhibited $55,000 \pm 3000$ theoretical plates on butane at $\bar{u} = 37 \text{ cm/sec}$. A single pass through the six-valve ports, three valve channels and two 7.5-m column segments gave for butane $54,000 \pm 3000$ theoretical plates¹³. As used in this study, 0.32 mm I.D. glass capillary columns were slipped over the 0.25 mm O.D. platinum-iridium valve connections and fused, so that gas velocities through the valve exceeded those experienced in the column. Using two $25 \text{ m} \times 0.32 \text{ mm}$ I.D. column segments that possessed coating efficiencies of $100 \pm 3\%$, a butane injection yielded a minor component, 90% resolved

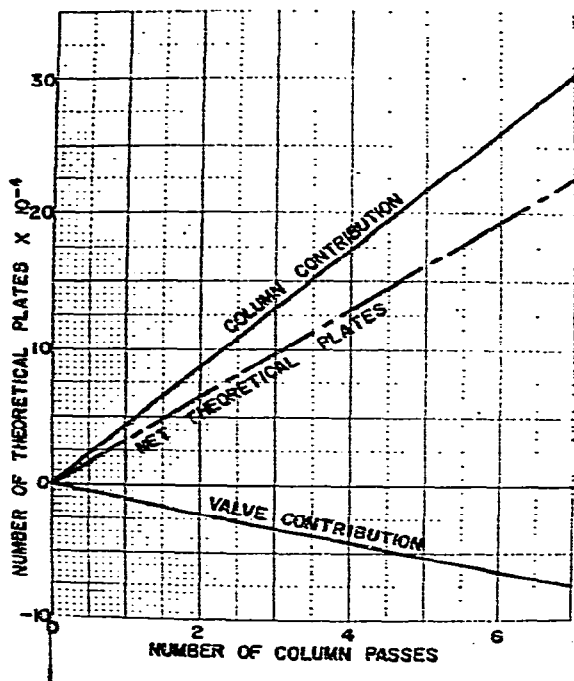


Fig. 2. Column and valve contributions to net overall efficiency of the system.

from the major peak; the latter exhibited $250,000 \pm 7000$ theoretical plates in a single pass. After eight passes (*i.e.* seven cycles involving 14 valve switchings and 16 min of operation), six minor components were separated, and the major peak exhibited $2.01 \cdot 10^6$ theoretical plates. There is no reason to believe that a limit has yet been reached. We were unable to demonstrate any loss of efficiency occasioned by passage through the valve.

Because of the considerations detailed above and illustrated in Fig. 2, as valve efficiency and column efficiency are increased, shorter column segments can be utilized in the multiple pass unit. In their study correlating chromatographic efficiency and column length, Yabumoto and VandenHeuvel⁵ emphasized that the OPGV increased as column length decreased. Fig. 3, constructed on points recalculated from their data, suggests that as short columns are made still shorter, the separation between two components as a function of time increases sharply. (There must, of course, be a limit to this phenomenon, and one limiting factor would be the length of the sample plug injected.) These considerations lead to the conclusion that by recycling at high velocity (OPGV) through short column segments, one could achieve large plate numbers and much shorter analysis times; in addition, column length can be treated as an operational parameter rather than a design parameter.

Another limit to recycling is that as a sample is recycled to achieve increased separation, components falling within the "containment envelope" are limited to

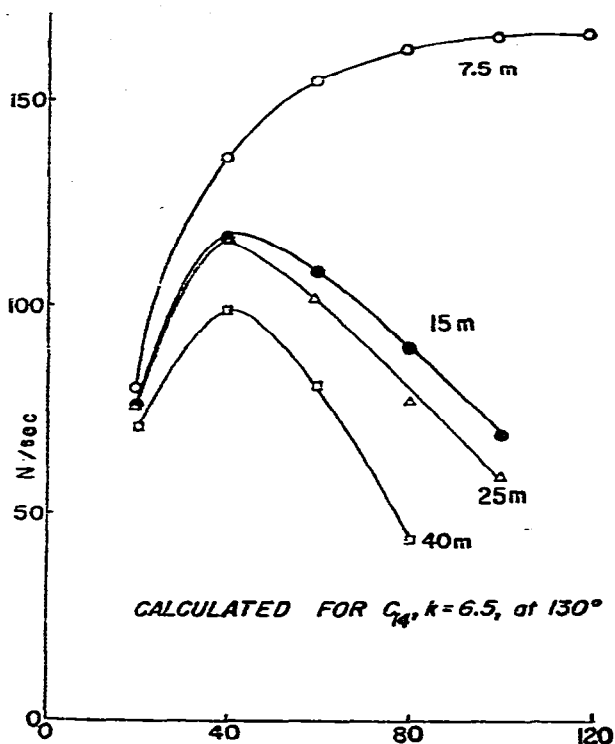


Fig. 3. Efficiencies, as effective theoretical plates per second, for different length segments of the same column. Recalculated from data presented by Yabumoto and VandenHeuvel⁵.

smaller and smaller ranges of k (i.e. fewer components can be resolved). Compounds that fall outside the containment envelope will be cut out by the valve and passed to the detector.

It can be shown that—provided the valve switching interval is properly programmed—the distance between any two components A and B is

$$d_{AB} = n_{cyc} \frac{k_B - k_A}{k_B + 1} L_{seg}$$

where n_{cyc} is the number of cycles, L_{seg} is the length of one column segment ($L_{seg1} = L_{seg2}$) and k_A and k_B represent the partition ratios of the two components. Rearranging, this can be written as

$$\frac{d_{AB}}{L_{seg}} = n_{cyc} \frac{k_B - k_A}{k_B + 1}$$

When $d_{AB} = L_{seg}$, the limit of the system has been reached; hence the number of cycles that A and B can be subjected to before one of them exceeds the envelope of the system is limited to

$$n_{cyc} = \frac{k_B + 1}{k_B - k_A}$$

In Fig. 4 the recycle unit is shown in tandem with an analytical column. The

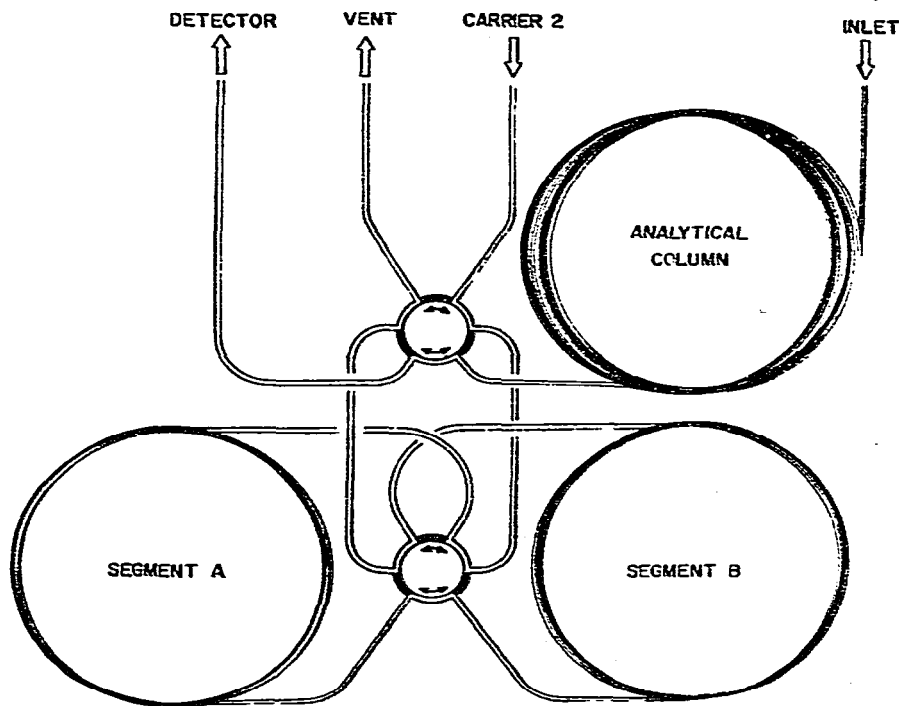


Fig. 4. Schematic representation of a recycle unit in conjunction with an analytical column. See text for details.

recycle unit is provided with a separate carrier gas, which permits it to be operated at its OPGV which, because of its shorter length, is considerably higher than that of the analytical column. Anything that can be separated by the analytical column is allowed to proceed in normal mode to detection; unresolved or suspect peaks are shunted to the recycle unit, subjected to any desirable degree of recycling, and either switched to the normal detector, or allowed to proceed to "vent", which can be a mass spectrometer or a selective detector. Because the flow switching device does not depend on balanced gas flows, the unit can be programmed in a normal manner. For some applications, separate ovens for the analytical and recycle columns would be desirable, which would permit adjustment of the partition ratios of the components being recycled.

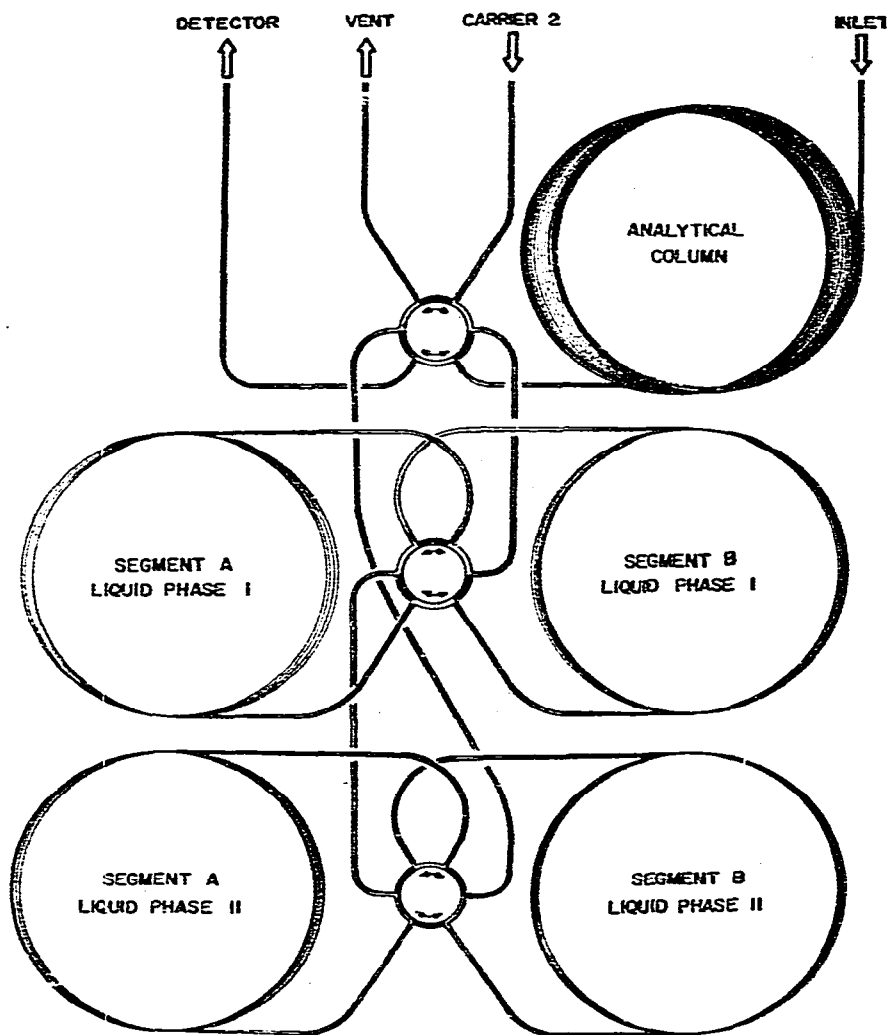


Fig. 5. Schematic representation of two recycle units (containing different liquid phases) in conjunction with an analytical column. See text for details.

There is yet another—and major—advantage that could be realized with recycle chromatography. Laub and Purnell^{14,15} described a novel system of “window diagramming” to establish what proportions of any two liquid phases would achieve the best separation of any given mixture. The prediction required the preparation of several packed columns, containing different ratios of the two liquid phases. Similar results can be obtained by adjusting the lengths of two capillary columns connected in series to control the proportion of time spent in each of the two liquid phases. More elegantly, two recycle units, one coated with liquid phase I, the other coated with liquid phase II, could be connected, together with an analytical column, through valves as shown in Fig. 5. Window diagrams¹⁴ could be constructed from data collected by varying the ratio of time spent in liquid phase I to the time spent in liquid phase II. From that diagram, one could predict what ratio of recycle passes in liquid phase I to recycle passes in liquid phase II would achieve the best separation; in essence, liquid phase “polarity” can be made an operational, rather than a design parameter.

A major difficulty with the recycle apparatus as it now exists lies in determining just when the recycle valve should be activated. This can be done pneumatically through an electronic timer, but any error in that set switching interval is cumulative and is evident when a portion of a peak is eventually excluded from the switched mainstream and proceeds instead to the detector. Minor variations in gas velocity or temperature would cause similar problems. A non-destructive in-line detector whose flow characteristics matched those of the column and which could be used to trigger the switching valve would greatly extend the capability of this unit. We are currently investigating the feasibility of such a detector.

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REFERENCES

- 1 D. H. Desty, A. Goldup and W. T. Swanton in N. Brenner, J. E. Callen and M. D. Weiss (Editors), *Gas Chromatography 1962*, Academic Press, New York, 1962, p. 105.
- 2 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1979) 515.
- 3 J. C. Giddings, *Anal. Chem.*, 36 (1964) 741.
- 4 J. C. Sternberg, *Anal. Chem.*, 36 (1964) 921.
- 5 K. Yabumoto and W. J. A. vandenHeuvel, *J. Chromatogr.*, 140 (1977) 197.
- 6 R. P. W. Scott and G. S. F. Hazeldean, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, Washington, 1960, p. 144.
- 7 D. Deford (Phillips Petroleum Co.), *U.S. Patent*, 3,455,090, July 15, 1969.
- 8 A. M. Reid, *J. Chromatogr. Sci.*, 14 (1976) 203.
- 9 *Switching Valve Applications*, Valco Engineering Bulletin, Valco, Houston, Texas, 1970.
- 10 R. J. Miller, S. D. Stearns and R. R. Freeman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 55.
- 11 D. R. Deans, *Chromatographia*, 1 (1968) 18.

- 12 W. Bertsch, E. Anderson and G. Holzer, *Chromatographia*, 10 (1977) 449.
- 13 W. G. Jennings, J. R. Settlage and R. J. Miller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, in press.
- 14 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 799.
- 15 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 1720.