Infinite Circular Gas Chromatographic Columns[1]

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The use of infinite circular columns in gas chromatography has been proposed by Martin[2] in his address, "Past, Present and Future of Gas Chromatography," before the first International Symposium on Gas Chromatography (ISA). He suggested that "if you have two columns and two substances that are very difficult to separate, you can arrange to drive the pair of substances into the first column and then, when it gets near one end, you connect it to the other column and you continue blowing until it's gone right into the second column, monitoring its passage with an extremely small detector, probably a katharometer in this case. When it is safely in the second column, you disconnect the first column and start blowing in the end of the second column and carry on until it's started into the first one again. And so you go on, round and round and round."

Porter and Johnson[3,4] utilized a circular column to obtain data for extractive distillation. Using a pump to circulate the gas into the column, they were thus able to use volatile liquids as partitioning solvents.

The search for a chromatographic column suitable for the separation of components with very small separation factors, such as nitrogen isotopes, has been going on in these laboratories for the last few years. Some of the very long columns used exhibited extremely high retention times (up to nine hours in some cases). Appreciable pressure drops were required, and a rapid decrease in the efficiency of the column occurred because of the evaporation of the liquid phase.

As these difficulties are obviously absent in circular infinite columns, it was of interest to study other characteristics of such systems. The effect of column length, i. e., the number of cycles, on the width of the peaks was examined, both by theory and experiment, and the feasibility of utilizing this technique for the separation of components was investigated.

Apparatus

Two mechanisms for circulating the sample gas in the column were compared.

A) An Infinite Column with Externally-supplied Carrier Gas.—Figure 1 illustrates the system used. Two short columns, with a thermal conductivity cell (T. C. C.) at each end, were connected head to tail. Two pairs of electrically-operated valves were used to direct the flow in a closed circuit. One of the valves of each pair was connected to the carrier gas cylinder, while the other vented to the atmosphere. Once the sample reached the end of one column, a signal from the T. C. C. energized one pair of valves and simultaneously de-energized the other pair. The sample was thus directed into the second half of the circuit, and vice versa. A delay-relay unit (Fig. 2) was incorporated in the system to ensure the delayed operation of the valves. This was achieved by deactivating a triggering micro-switch set in the recorder for the time

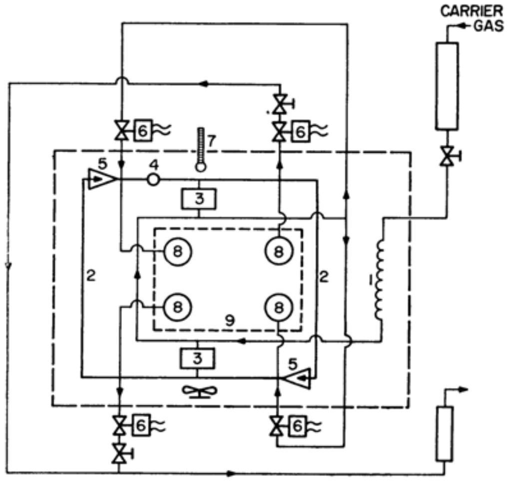

Fig. 1. Schematic diagram of an infinite circular gas chromatographic column of the "two half cycles" type.
1 : Preheating coil 2 : Chromatographic column 3 : T. C. C. 4 : Sample injection block 5 : Check valve 6 : Solenoid valve 7 : Thermometer 8 : Pressure gauge 9 : Pressure gauge panel

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[1] Part of this work was presented at the 29th Meeting of the Israel Chemical Society: S. Sideman, *Bull. Res. Coun. Israel*, **10A**, No. 3, 20 (1961).

[2] A. J. P. Martin, "Gas Ghromatography," 1957, Coates et al. Eds., Acad. Press, New York (1959), p. 243.

[3] R. S. Porter and J. F. Johnson, *Nature*, **183**, 391 (1959).

[4] R. S. Porter and J. F. Johnson, *Ind. Eng. Chem.*, **52**, 691 (1950).

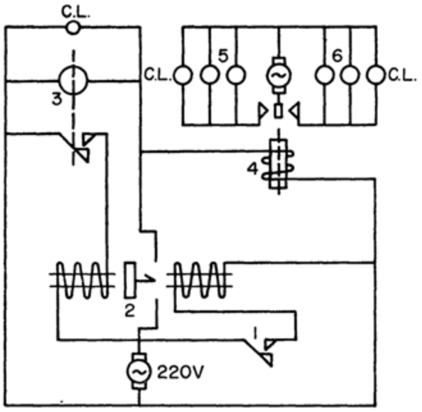

Fig. 2. Wiring diagram of delay-relay unit and operating valves.
1 : Triggering microswitch (in recorder)
2 : Mechanical latch-relay 3 : Electric timer (motor) 4 : Electromagnet affecting the changing of the solenoid valves 5 : Solenoid valves of first half cycle 6 : Solenoid valves of second half cycle C. L.: Control lamp

needed for the sample to pass through the T. C. C. By this arrangement the leading peak in each half-cycle entering the T. C. C. triggered the micro-switch, which in turn alternated the electric valves.

Some experiments were conducted with one T. C. C. only. In this arrangement the two half-columns were so connected that the reference and sample sides of the T. C. C. alternated for each half cycle. The base line drift caused by peak broadening discouraged further work with this arrangement; therefore, two T. C. C.s were connected, one at the end of each half-circuit. Figure 3 illustrates the wiring of the two T. C. C.s.

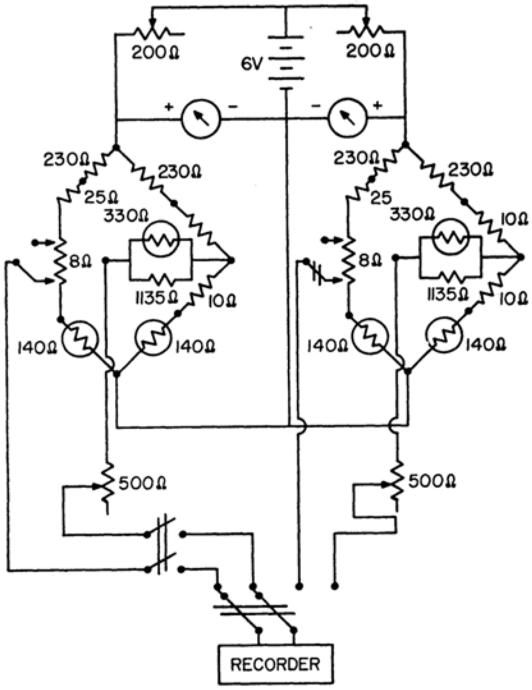

Fig. 3. Wiring diagram of the two T. C. C.s.

B) An Infinite Column with Gas Circulation Pump.—The arrangement of the apparatus is illustrated in Fig. 4. Except for a short length of unpacked tubing which passed through the squeeze pump (a Sigmamotor type), the column and the T. C. C. were housed in an air-thermostat. The plastic tubing used was coated with polyvinyl alcohol to prevent losses of the compound tested by diffusion through the wall. A rotameter was used to calibrate the gas flow through the column. Pressure gauges across the pump provided pressure drop measurements. These were connected to the column through copper capillaries, thus ensuring a minimum voidage in the column. The rotameter was taken out of the system after the desired flow rate had been fixed. Variations in the flow caused by the removal of the rotameter were sufficiently small to be disregarded. By opening two needle valves (at the inlet and outlet of the pump), the apparatus could be used as a standard gas chromatograph.

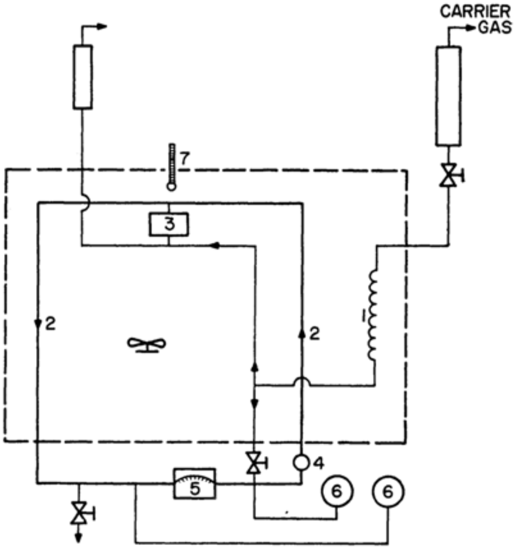

Fig. 4. Schematic diagram of an infinite circular gas chromatographic column of the "pump" type.
1 : Preheater coil 2 : Chromatographic column 3 : Thermal conductivity cell 4 : Sample injection block 5 : Squeeze pump 6 : Pressure gauge 7 : Thermometer

Advantages and Disadvantages of the Above Mechanisms

The obvious advantage of the "half-cycle," method A, over the "pump" method, B, is that there is no risk of mixing the sample, since it does not require an external pump and since it can be constructed with a minimum dead volume. The disadvantages, however, are discouraging. An elaborate apparatus is needed, and the control mechanism is rather complicated. A base line shift occurs when the valves are alternated at each half-cycle, and this has to be corrected for either manually or automatically. Moreover, pressure waves due to sudden pressure variation at each half-cycle cause the sample to contract in the gas-phase only, thus disturbing the equilibrium and broadening the peak. Under these conditions, no efficient separation seems feasible.

The main advantage of the pump technique is its simplicity. It is easy to operate at various absolute pressures. The main disadvantage is, of course, the mixing of the sample as it passes through the pump, which may result in undesired peak broadening.

The Effect of the Number of Cycles on Peak Width

Theoretical. — Under ideal conditions gas chromatographic peaks closely approach the normal distribution curve; i. e., the curve approaches the base-line (or zero concentration line) asymptotically. Thus, theoretically, the width of the peak is infinite. In practice, the width is measured at some convenient place. The common procedure is to measure the width between the intercepts of the tangents to the peak passing through the inflection points at the base-line. The width thus obtained is equal to 4σ, where σ is the standard deviation.

For the usual case where the volume of the sample S is negligible ($0.5 > S/v\sqrt{n}$), the width of the peak, W, has been shown (Van Deemter et al.[5]) to be:

$$W = 4v\sqrt{n} \tag{1}$$

where v is the volume of one theoretical stage and n is the number of theoretical plates in the column. The retention volume, V_r, has also been shown to be:

$$V_r = vn \tag{2}$$

The combination of these two equations enables us to determine the theoretical number of stages by the well-known relation:

$$n = 16(V_r/W)^2$$

where both W and V_r are measured in the same units (volume, time or length).

Assuming that the number of stages in the column is directly proportional to the length of the column, Eq. 1 can be written:

$$W = K'\sqrt{NL + L'} \quad \text{or:} \quad W^2 = K(NL + L') \tag{3}$$

where K is a proportionality constant, N is the number of cycles (starting from the T. C. C.), L is the length of the column, and L' is the length of the fragment of the column from the injection block to the T. C. C. When the apparatus is so constructed that $L' = 0$

$$W^2 = KNL \tag{3a}$$

or, when $L' = 1/2L$

$$W^2 = KL(N + 1/2) \tag{3b}$$

Equation 3 indicates that the higher the number of cycles, the wider the peak becomes.

The assumption of the linear proportionality of n and L can be experimentally verified for non-overlapping peaks. Let subscript i represent the number of the consecutive peaks. Then, from Eq. 1, the ratio of the widths of two consecutive peaks is:

$$\frac{W_{i+1}}{W_i} = \frac{\sqrt{n_{i+1}}}{\sqrt{n_i}} = \frac{\sqrt{L_{i+1}}}{\sqrt{L_i}} \tag{4}$$

Now, if L is expressed in half-cycles, i. e., $L_1 = (1/2)L(=L')$, $L_2 = (3/2)L$, $L_3 = (5/2)L$, etc., substitution in Eq. 4 gives:

$$\frac{W_{i+1}}{W_i} = \sqrt{\frac{2i+1}{2i-1}} \tag{4a}$$

which is the theoretical value of the ratio of the widths of two consecutive peaks.

Experimental.—An example of the chromatograms obtained using the first mechanism is given in Fig. 5. No attempt was made to draw quantitative conclusions from these experiments.

Figure 6 shows a chromatogram obtained using the pump technique with a sample of ethyl methyl ketone. The column was 8 m. long, was packed with polyethylene powder, 50~70 mesh, which was coated with 15% glycerol. A polyethylene packing was chosen for this work because of its low pressure-drop characteristics. The column was flushed for about two hours with carrier gas before each

TABLE I. THE RELATIONSHIP BETWEEN CONSECUTIVE PEAKS

Peak No.	Width W, mm.	Retention volume V_r, mm.	W_{i+1}/W_i Exp.	W_{i+1}/W_i Theor.
1	27	56	1	1
2	47.6	150	1.76	1.73
3	58.6	243.5	1.23	1.29
(4)	69*	337	1.18	1.18
(5)	84*	431		1.13

* Uncertain values due to a base-line shift upwards.

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[5] Van Deemter et al., *Chem. Eng. Sci.*, 5, 271 (1956).

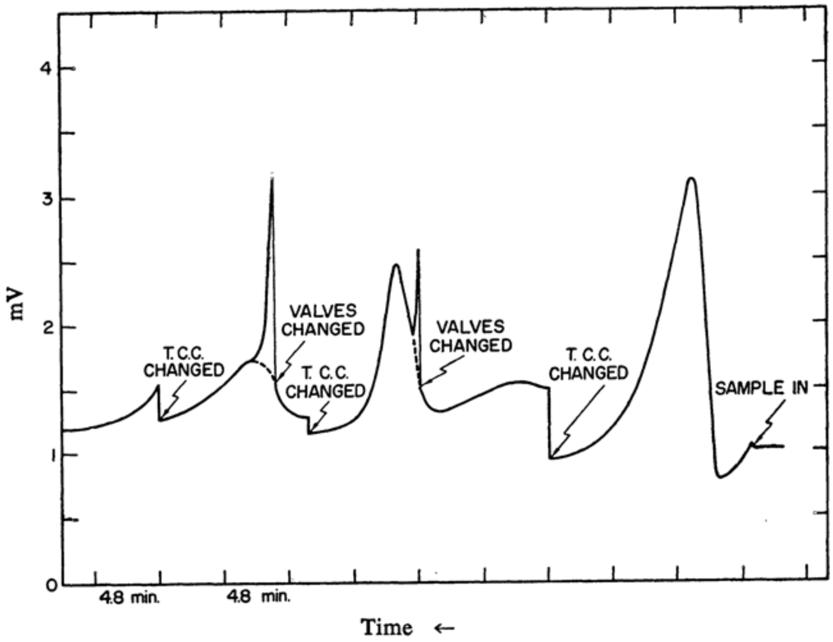

Fig. 5. Chromatograms obtained with the "two half cycles" type of column. Ether, 41°C, nitrogen gas, 55 cc./min.

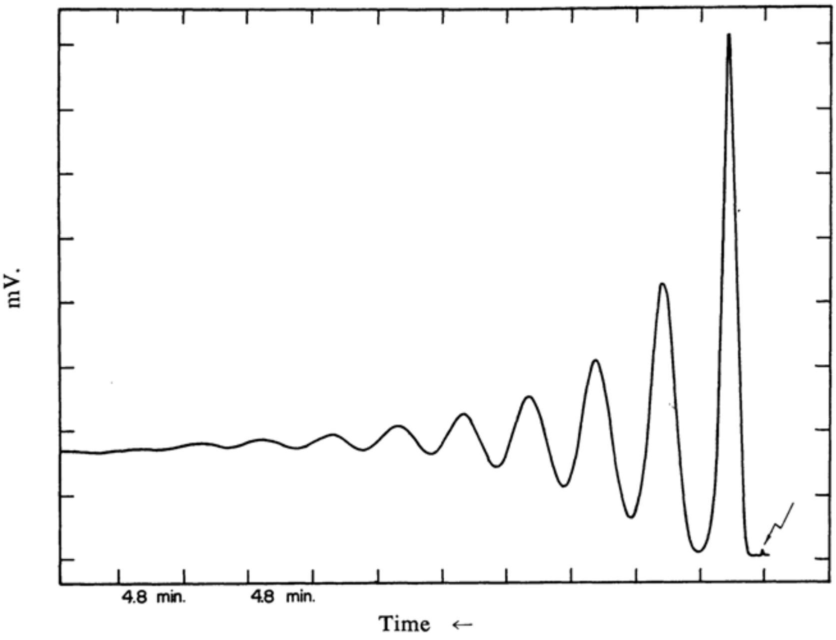

Fig. 6. Chromatograms obtained in a circular column of the "pump" type. Sample: M.E.K. Column: Polyethylene powder 50∼70 mesh, 15% glycerol, 45°C

run to remove traces of material left over from previous experiments.

A set of measurements from an experimental run with a sample of *n*-heptane is given in Table I. Only the first three peaks could be measured with a fair degree of reliability. Once the peaks met head to tail, the base-line shifted upwards; consequently, accurate measurement was not possible.

Figure 7 was drawn according to Eq. 3b and shows good agreement between experiment and theory. Agreement is also evident in Fig. 8,

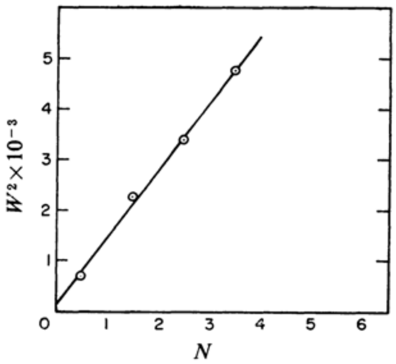

Fig. 7. Relationship between peak width (measured at zero base line) and number of cycles.
$W^2=KL(N+1/2)$

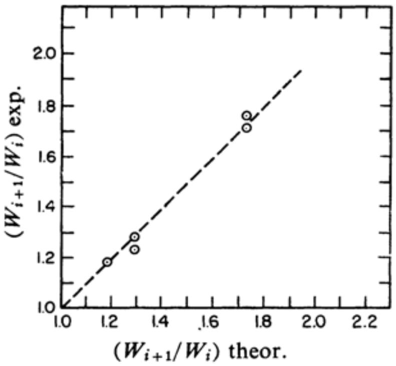

Fig. 8. Theoretical vs. experimental peak width ratio of consecutive peaks.
Sample gas : *n*-Heptane, 45°C

which shows the experimental versus theoretical width ratio of the consecutive peaks given in Table I.

Discussion and Conclusions

The characteristics and performance of infinite circular columns in gas chromatography have been studied. Two mechanisms for gas circulation in the column have been experimentally compared. The half-cycle-type mechanism proved to be rather unsuccessful because of intermittent pressure drops inherent in this mode of operation. The pump mechanism was found easy to operate and was used for most of the experimental work conducted. The separate effect of mixing due to pump action is yet to be studied. The theoretical relationship of the width to the number of cycles has been experimentally verified.

The results obtained in this study discourage the use of low-efficiency columns, with about 100 theoretical plates, for separation purposes. This is in agreement with our previous report⁶⁾ that separation is feasible only with high-efficiency columns, where the width of the peak is less than a half, and preferably a quarter, of the retention volume of the first peak. With the low-pressure, low-efficiency polyethylene column used in this work, head and tail mixing of the consecutive peaks occurred and no separation was feasible. Other packed columns with a higher number of theoretical plates could not be used with the given pump mechanism because of the higher pressure drops required. Nevertheless, the reported pump mechanism, though presently limited only to low-pressure, low-efficiency columns, may be used for some particular applications, where the following advantages may be utilized:

(1) The use of short circular columns instead of the usual long columns eliminates the high pressure differential between inlet and outlet.

(2) Absolute retention times can be read directly, with no need for dead volume corrections, sometimes even without pressure corrections.

(3) Volatile solvents can be used as column coating with practically no aging of the column.

(4) Uniform coating can be made in situ.

(5) The behaviour of ternary systems can be easily studied, and separation factors applicable to extractive distillation can be evaluated.

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6) S. Sideman, *Chem. Eng. Sci.*, **18**, 95 (1963).