IMPROVED RESOLUTION IN GAS CHROMATOGRAPHY THE USE OF RECIRCULATION COLUMNS

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INTRODUCTION

In recirculation columns the sample is eluted through several comparatively short columns, the columns being used in cyclic alternation as often as is required. In this way, though the actual length of column in the apparatus is small, the total length of column traversed by the sample may be as large as is required. The idea is almost as old as gas chromatography itself. It has been suggested periodically by several authors (see *e.g.* MARTIN[1,2], SAUNDERS[3] and SAKODYNSKI[4] but it is only relatively recently that GOLAY and his co-workers[5] have reported the successful construction and operation of a simple but elegant recirculation device. However, no further practical devices have since been reported, and interest in this aspect of gas chromatography seems to have waned. Since recirculation offers a potentially attractive means of improving the available resolution of gas chromatography columns, particularly in preparative work, it is useful to examine the advantages and also the limits of the method.

THEORY

Consider a gas chromatography column defined by the following parameters:
Dead volume $= v_M$, ml/plate
Active substrate $= m$, g/plate
Flow-rate $= \dot{V}$, ml/sec
Specific retention volume for component $x = V_g^x$, ml/g at column temperature.
Let the peak centre pass $\bar{n}$ plates in t seconds: the peak centre passes $\bar{n}m$ grams of substrate.
The apparent retention volume V' is given by:
$V' =$ total flow—dead volume $= \dot{V}t - \bar{n}v_M$.
But the specific retention volume for component x is given by:

$$V_g^x = \frac{V'^x}{\bar{n}m}$$

Thus,

$$V_g^x = \frac{\dot{V}t - \bar{n}v_M}{\bar{n}m}$$

Whence

$$\bar{n} = \frac{\dot{V}t}{V_g^x m + v_M} \qquad (1)$$

Now consider any peak after $\bar{n}$ plates: it may be shown[6-8] that the elution curve in gas chromatography approximates to a gaussian distribution. The distance w between the points of intersection at the base of the gaussian curve of the tangents to the inflexion points is:

$$w = 4\sigma$$

where σ is the standard deviation of the gaussian curve. In an elution curve, this width w may be expressed in terms of theoretical plates:

$$\bar{n} = 16\left(\frac{\bar{n}}{4\sigma}\right)^2$$

Thus

$$\sigma = \sqrt{\bar{n}} \qquad (2)$$

and

$$w = 4\sqrt{\bar{n}}$$

A gaussian distribution may be considered[9] to have an effective width of 6σ; 99.73 % of the area of a gaussian curve lies within the $\pm 3\sigma$ limit. Thus, any peak, after travelling $\bar{n}$ plates, effectively occupies $6\sqrt{\bar{n}}$ plates in the column. This distribution is independent of all the usual column variables; peaks appear to alter in width with changes in flow rate, component (*i.e.* partition coefficient), temperature, and the like, because the peak width is conventionally measured in terms of gas volume occupied beyond the column. This latter quantity depends on the variables mentioned above, whereas the number of plates which the peak occupies in the column is (for constant $\bar{n}$) independent of these variables, and depends only on the number of plates which the peak centre has passed.

There are two factors which are significant in this context: (a) the number of plates required for a given separation; and (b) the efficiency with which these plates are used. These factors are discussed below.

(*a*) *The number of plates required for a given separation*

Consider the separation of two components 1 and 2. These are completely separated when their centres are $3(\sigma_1 + \sigma_2)$ plates apart (Fig. 1), but

$$3(\sigma_1 + \sigma_2) = \bar{n}_2 - \bar{n}_1 \qquad (3)$$

From eqn. (1) follows:

$$\bar{n}_1 = \frac{\dot{V}t}{(V_g^1 m - v_M)} \text{ and } \bar{n}_2 = \frac{\dot{V}t}{(V_g^2 m - v_M)}$$

Thus

$$\bar{n}_1 = \bar{n}_2\left(\frac{V_g^2 - \frac{v_M}{m}}{V_g^1 - \frac{v_M}{m}}\right) = \frac{V_g^2}{V_g^1}\bar{n}_2$$

if V_g^1 and $V_g^2 \gg v_M/m$, as is normally justified.

The minimum number of plates ($\bar{n}_{min}$) required to separate any two components can now be found by combining eqns. (2), (3) and (4):

$$3(\sqrt{\bar{n}_1} + \sqrt{\bar{n}_2}) = \bar{n}_2 \left(1 - \frac{V_0^2}{V_0^1}\right)$$

whence

$$3\sqrt{\bar{n}_2} \left(1 + \sqrt{\frac{V_0^2}{V_0^1}}\right) = \bar{n}_2 \left(1 - \frac{V_0^2}{V_0^1}\right)$$

Thus

$$\bar{n}_{min}(= \bar{n}_2) = 9 \left(\frac{1 + \sqrt{\frac{V_0^2}{V_0^1}}}{1 - \frac{V_0^2}{V_0^1}} \right)^2 \tag{5}$$

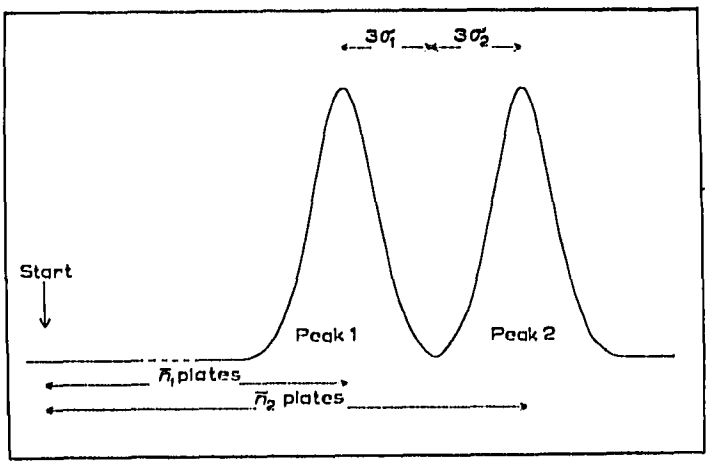

Fig. 1. Peak parameters at the moment of separation.

This equation is related to those derived by PURNELL[6-8] using a slightly different frame of reference and set of assumptions.

(*b*) *The efficiency of use of plates*

Consider equations (3) and (4):

$$\bar{n}_2 - \bar{n}_1 = 3(\sigma_1 + \sigma_2) = \bar{n}_2 \left(1 - \frac{V_0^2}{V_0^1}\right)$$

The number of plates, (n_f), occupied by both components at the instant of separation is given by:

$$n_f = 6(\sigma_1 + \sigma_2)$$

Hence, the fraction, F, of the total number of plates which is actually occupied at the instant of separation is given by:

$$F = \frac{n_f}{\bar{n}_{min}} = 2 \left(1 - \frac{V_0^2}{V_0^1}\right) \tag{6}$$

Fig. 2 shows the total number of plates (n_f) occupied by solute at the instant of separation as a function of the total number of plates ($\bar{n}$) needed to effect a separation. In Fig. 3 the quantity $F(= 100n_f/\bar{n})$ which is a measure of the efficiency of use of the plates in the column is plotted against the separation factor V_g^2/V_g^1. It is clear that this efficiency drops regularly as the separation factor approaches unity. This aspect

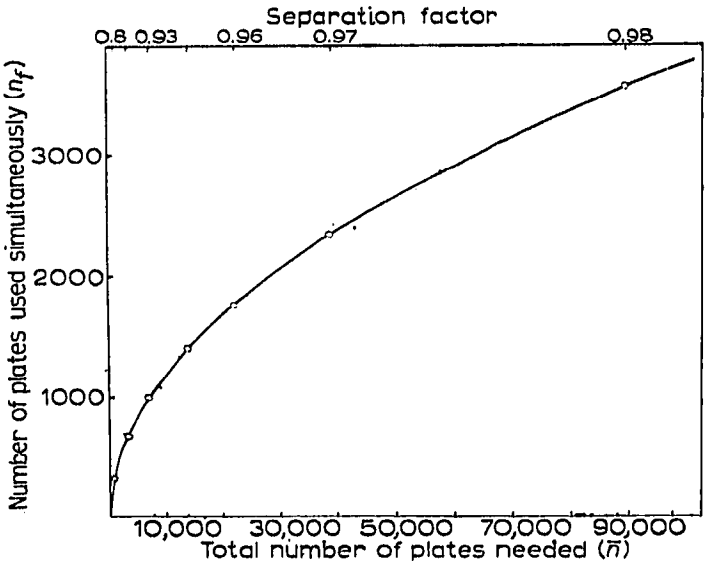

Fig. 2. Plates filled during a separation.

has been pointed out by VAN DEEMTER *et al.*[10] who state that only those plates actually occupied by solute are effective in separations. The number of plates occupied by solute for a given separation is of the order of the number of plates required for counter-current continuous distillation[10], which can be seen in Fig. 2. VAN DEEMTER *et al.*[10] also point out that although counter-current continuous distillation is more efficient in the use of plates, the considerably larger number of plates required in gas chromatography is much more easily realised in practice. This is generally true for

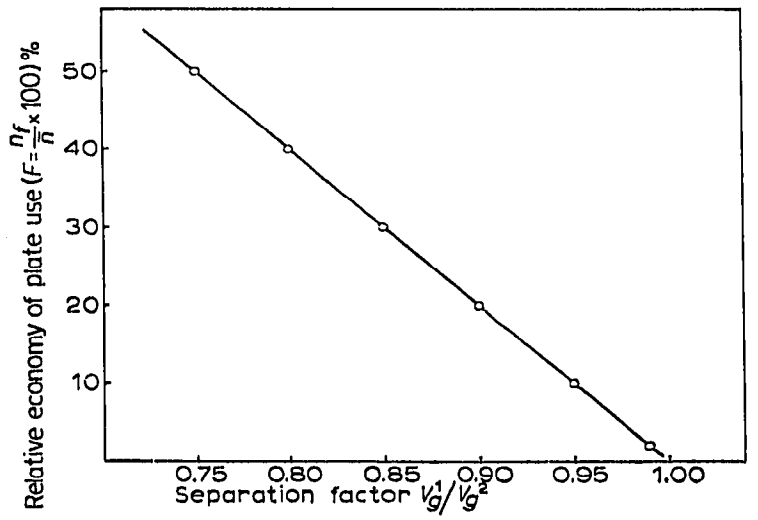

Fig. 3. The fraction of plates which are effective during a separation.

packed columns and moderate separations, and indeed for capillary columns even with the most difficult separations. However, capillary columns are limited as to sample size, and packed columns become impracticable above about 40,000 plates, largely as a result of the adverse high pressure required to produce appreciable gas flow.

(c) Discussion

It can be seen from the preceding two sections that more and more difficult separations may be achieved by using longer and longer columns. However, at the same time, the result is greater and greater waste in the sense that not more than a moderate portion ($\sqrt{n}$) of the total number of plates are ever occupied by solute simultaneously. For example, the resolution of a column may be doubled by multiplying its length by four. Of this factor of four, a factor of two goes on increasing the resolution, and a factor of two goes to increasing the waste. One would like to keep the former factor, but eliminate the latter. One way in which this may bed one is by using recirculation columns, which are described in the following section.

RECIRCULATION COLUMNS

Introduction

Recirculation devices involving a pump linking the output and input ends of a single column have been successfully used by PORTER AND JOHNSON[11–13]. These however do not lead directly to enhanced column resolution, for their chief application is in allowing the use of very volatile stationary phases.

GOLAY *et al.*[5] have described a three stage recirculation device with back-flushing to remove unwanted components. The device works manually, though it could be modified for automatic operation. The device described below has been designed specifically for automatic recirculation.

Continuous recirculation

Consider a number of GC columns (A–F) joined in series end to end to form a continuous loop as in Fig. 4. Between each pair of columns there is an inlet/outlet tube (a–f) controlled by a valve which can either join both columns and block access to the inlet/outlet tube (as at b), or else can separate two contingent columns and join one or other of them to the inlet/outlet tube (as at a and f). Gas which enters the system by tube a passes in turn through columns A to E and emerges through tube f. No gas can enter into or escape from column F, which can be thought of as a barrier between the inlet and outlet tubes. It is clear that this barrier is moveable; correct switching can make columns A, B, C etc. in turn act as barriers.

Now consider a peak situated in column C, say, of Fig. 4. As gas passes through the system, this peak will move in a clockwise direction and, providing that the appropriate valves are changed at the correct times, the peak can be kept indefinitely mid-way between inlet and outlet. Thus the peak undergoes continuous recirculation. The process bears some resemblance to counter-current distribution, for, relative to a stationary inlet/outlet system and a stationary peak midway round the system, it is as if the mobile phase was moving clockwise, and the stationary phase in an anti-clockwise direction.

The sections which follow describe the design and construction of a continuous switching device and report on its operation.

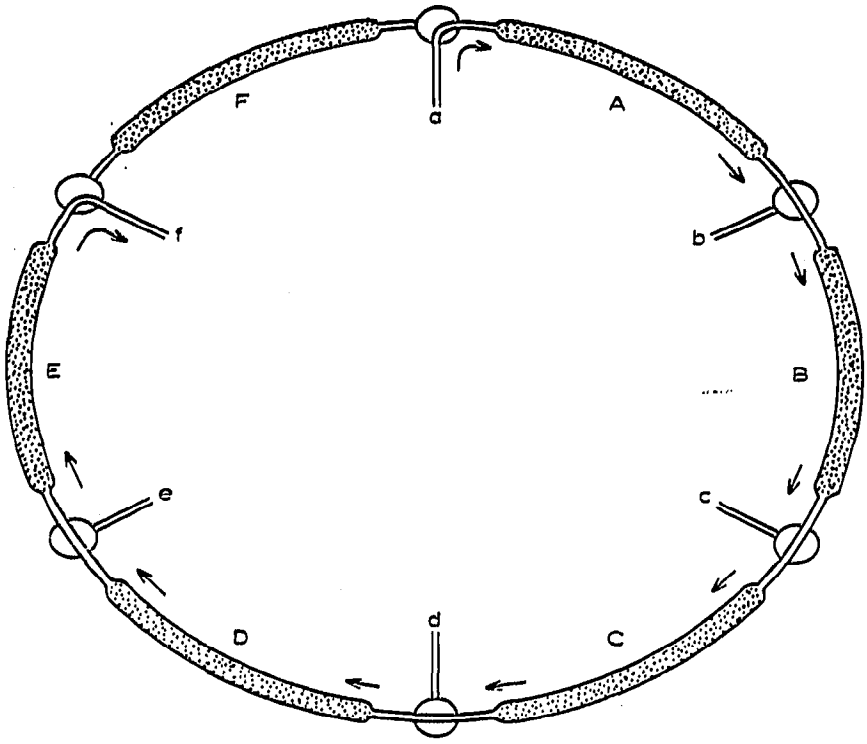

Fig. 4. Recirculation scheme.

The recirculation valve

This is shown in Fig. 5. A pointer P and marks a to e are shown to clarify the description below. The design allows a cyclic sequence of six functions, five of which operate when P is directed towards each of the positions a to e. These are:

(i) pointer to a joins tubes C + D
(ii) pointer to b joins tubes B + C + D
(iii) pointer to c joins tubes B + C
(iv) pointer to d joins tubes A + B + C
(v) pointer to e joins tubes A + B.

The sixth function which operates between e and a closes off the valve completely; in this position—o—the pointer is directed between tubes B and C.

Tube A leads to the detector, tube B to the outlet of one column, tube C to the inlet of the next, and tube D to the gas input. This valve has all the features of the valve required in Fig. 4. Indeed it has some functions not demanded previously in that it can connect the outlet of one column and the inlet of the next simultaneously to either the gas input (b) or to the detector (d). This ensures a smooth switch-over as the inlet and outlet traverse the circle of columns in Fig. 4.

The switching sequence

The change-over portion of a circle of many columns and valves is shown in Fig. 6. Seven valves are shown in order. The two outside ones (1 and 7) are in position c, as also are all the remaining valves (not shown) which lie between 7 and 1 the long

way round the circle. These valves (all in position c) serve to join columns in sequence. Valve 2 (in position d) joins the outlet from column 2 and also the inlet of column 3 to the detector inlet; valve 3, (in position e) joins the outlet of column 3 to the detector inlet. Valve 4 is completely shut off, in position o. Thus columns 4 and 5 are both cut off from the gas flow line. Valve 5 (in position a) and valve 6 (in position b) mirror valves 2 and 3, and are concerned with gas inlet.

The switching operation for recirculation is controlled by the large partially-toothed central wheel (X in Fig. 6) which meshes with smaller continuously toothed wheels attached to the valves. The design of the valves is such that all but two of the operations require valves to be moved through 1/10 of a revolution. The remaining two (o to e and a to o) need 3/10 of a revolution, and consequently three times as many teeth on X have to move past during these operations as are needed for the others. The sequences of teeth and gaps on X are so arranged that during the first 2/10 of a revolution of o to e and a to o all the other valves remain untouched; the final 1/10 of a revolution completes these two changes and at the same time switches all the other valves which need to be moved for recirculation.

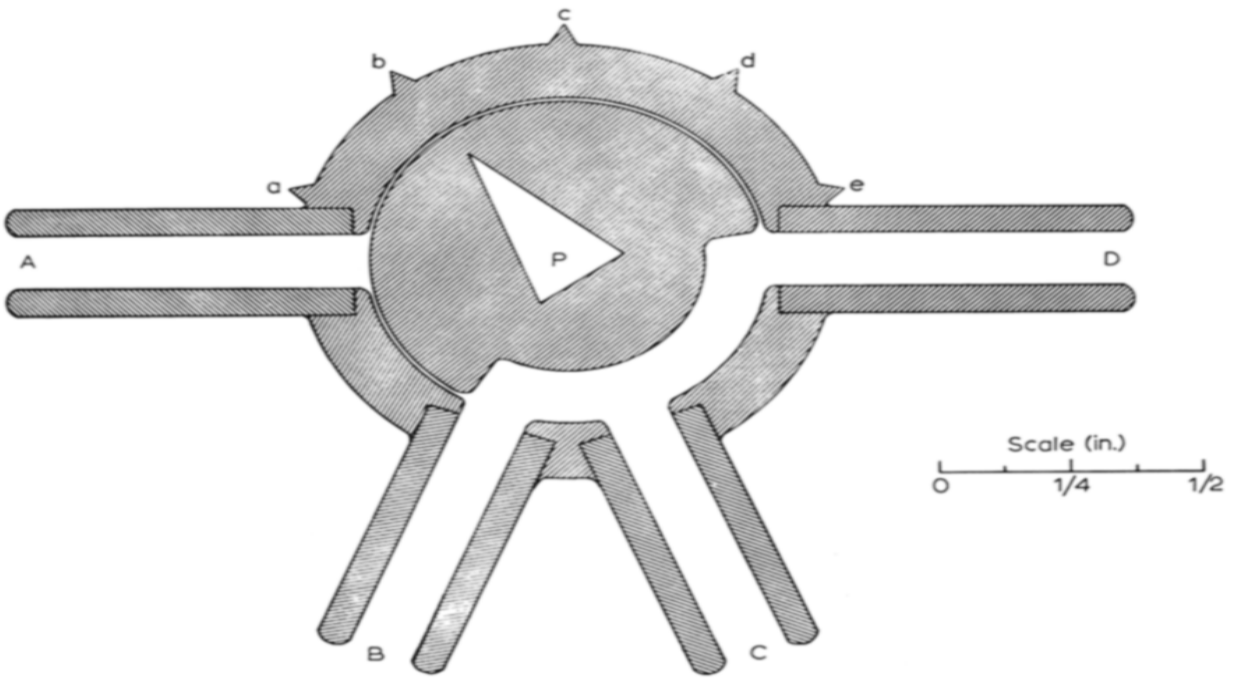

Fig. 5. The recirculation valve. D = 0°; e = 18°; d = 54°; c = 90°; b = 126°; a = 162°; A = 180°; B = 250°; C = 290°.

Thus as X moves clockwise in Fig. 6, its first 12° of movement affects only valves 4 and 5 which complete two thirds of their required changes o to e and a to o. The next 6° of movement of X completes these changes in valves 4 and 5 and also changes valves 2, 3, 6 and 7. The overall effect is to move each of the valves 2–7 anticlockwise from its initial configuration to that previously shown by its left-hand neighbour. If positions d and b joining three valve channels were not available, such a change would completely arrest the gas flow and then suddenly release the pressure which had built up. Thus the value of these triple connection positions is in keeping a constant and smooth flow of gas through the system.

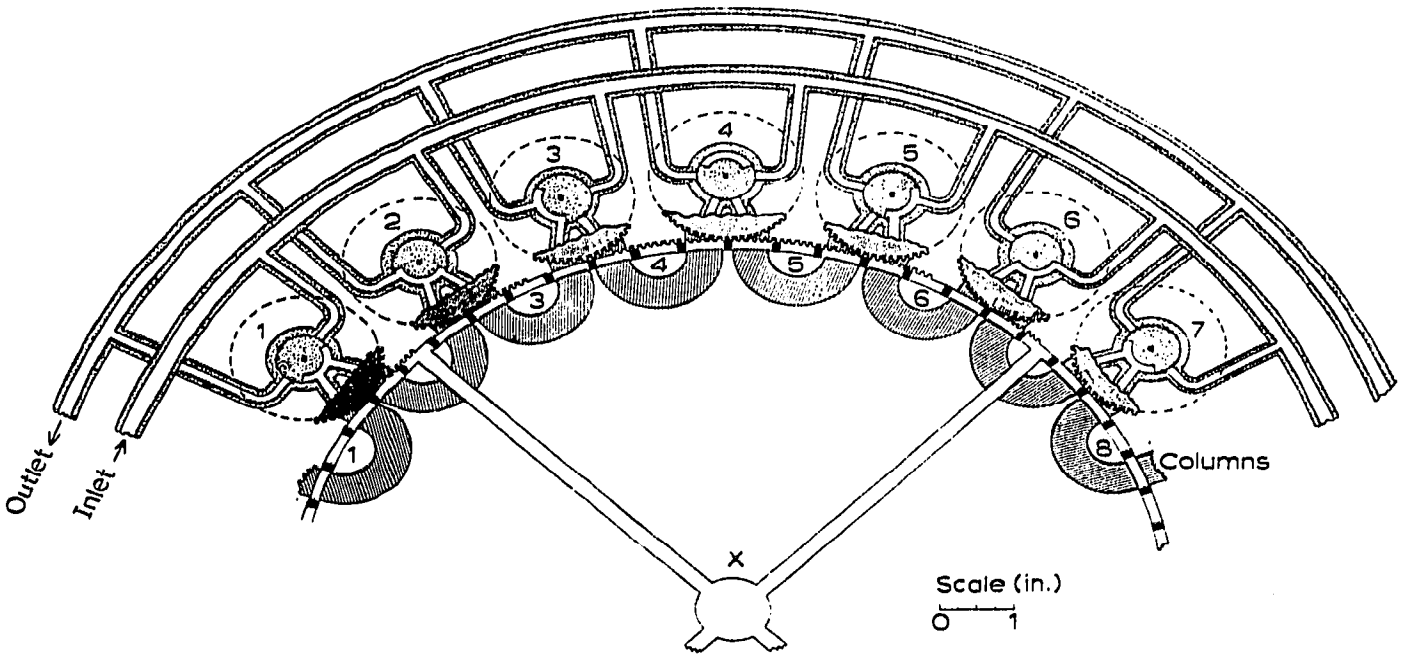

Fig. 6. Valves at the change-over point. X 12 in. diameter, one tooth for each degree of arc. Valve control wheels 2 in. diameter, one tooth for 6 degrees of arc = 60 teeth. Angular separation of valves = 18° of arc.

The chromatography columns

Four inch lengths of ½ in. diameter columns are joined to the valves by 1/8 in. I.D. tubing. The overall length of column joined in a circle is about 7 ft. The columns are packed with 10% tritolyl phosphate impregnated Celite and columns and valves are kept at 100° in an oil bath.

RESULTS

The system was tested in the separation of methyl thiocyanate and methyl isothiocyanate MeNCS and MeSCN. These have a separation factor of 0.905 on tritolyl phosphate at 100°; methyl thiocyanate, MeNCS, emerges first.

A sample (0.1 ml) of a 1:1 mixture of MeSCN and MeNCS was chromatographed with recirculation. The wheel X was manually operated at a rate appropriate to the carrier gas flow-rate. The course of the separation over nearly an hour is shown in Fig. 7. During this time the peak was circulated four times over and passed ~ 3,500 plates spread over nearly 30 ft. Pure samples of methyl thiocyanate and methyl isothiocyanate were collected at the outlet.

The column packing is not very efficient; it gives an HETP of ~ 2.5 mm. However, with relative ease it is possible to achieve efficient separations in a simple and compact apparatus that would require an unacceptably bulky construction in normal chromatography. It is possible that the presence of the valves enhances rather than diminishes the column performance, for several workers have reported an increase in column efficiency which results from columns in sections joined by narrow restrictions[14–16], though it has been suggested[17] that with recirculation beyond a total column length of 50 ft. the resolution is limited and ultimately perhaps even diminished by the presence of the valves.

CONCLUSIONS

The usefulness of recirculation columns needs no further mention. There are however some improvements which might profitably be incorporated. In the first place, the valves could be switched by a continuous motor. Secondly it would be possible to monitor a recirculation separation continuously if a non-destructive detector, such as a katharometer, was incorporated into the circle of valves and columns. This would give a good indication of the progress of a separation. Finally a recirculation device could be made part of a conventional apparatus. The outlet from a normal column could be switched into recirculation wherever an awkward separation was needed. The switched components would then be able to circulate for any required length of time until they were separated, and could then be re-introduced into the normal column output to take advantage of any suitable gap in the chromatogram.

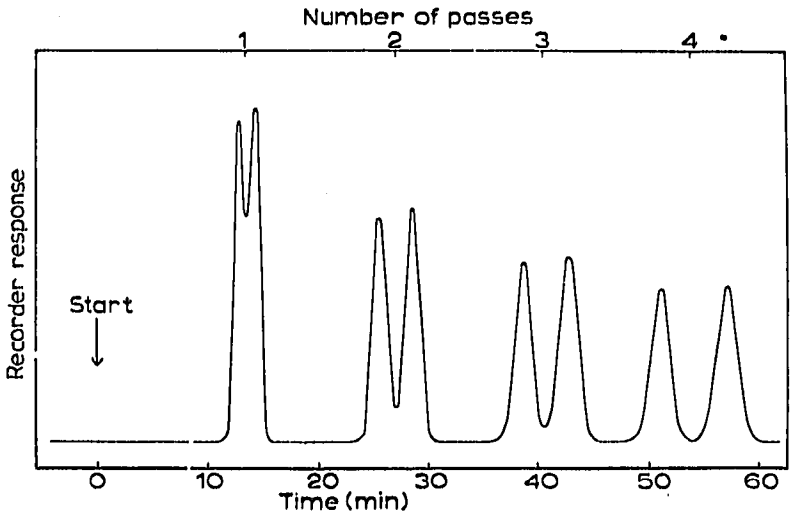

Fig. 7. The separation of methyl thiocyanate and methyl isothiocyanate using recirculation.

The limiting separation which can be effected on a particular recirculation column can quite easily be calculated. For example a column of 2,000 plates, used to the utmost efficiency, could separate two components with a retention ratio of 0.965. After 14 recirculations through such a column, the components would be just separated and would completely fill the 2,000 plates available. Attempts at more difficult separations would not succeed, for the available plates would be filled before the two components were completely separated. Continued recirculation under such conditions would result in a renewed mixing of components already separated.

The resolution of a normal GC column is proportional to $(\bar{n})^{\frac{1}{2}}$ where $\bar{n}$ is the number of plates in the column; the optimum resolution of a recirculation column is directly proportional to $\bar{n}$. While recirculation chromatography cannot rival the great speed of analysis of capillary chromatography, it does have one advantage, for there is no reason why columns should not be scaled up to any desired extent, and as a result be able to handle quite appreciable samples. It is in the field of preparative chromatography that recirculation would appear to have its potentially most beneficial application.

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SUMMARY

The theoretical bases of recirculation columns are examined, and the construction and use of a practical recirculation device is described.

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