

## THE EFFECT OF PRESSURE DIFFERENTIALS ON GAS CHROMATOGRAPHY SEPARATION

R. O. HELLYER AND H. KEYZER

*The Museum of Applied Arts and Sciences, Sydney (Australia)*

### INTRODUCTION

Difficulties may be experienced in the separation and collection of the components of volatile mixtures by gas chromatography, which neither increase in column length nor change of stationary phase can overcome.

Little attention appears to have been paid to the effect of pressure changes in the carrier gas at a point in the gas chromatography column intermediate between inlet and outlet, the pressure at the latter being held constant.

An investigation of the effects of such intermediate pressure changes on column efficiency has now been carried out, using a modified analytical gas chromatography apparatus. This study has led to applications which can facilitate the collection of pure components.

### APPARATUS

The instrument used throughout was a Bodenseewerk Perkin-Elmer Fraktometer Model 154C in conjunction with a Hartmann and Braun Linecomp recorder with a 5 mV full scale deflection. 8,000  $\Omega$  thermistors were used in the detector block. The columns were packed with Celite 545 impregnated with 20% Silicone D.C. 550 fluid by the conventional slurry method and dried at 100°. Helium was used as the carrier gas, and a soap bubble flowmeter was used in conjunction with the rotameter in the instrument. The samples were injected with Hamilton syringes of 10  $\mu$ l and 50  $\mu$ l capacities. The following modifications were made to the instrument.

#### *The monitoring system (see Fig. 1)*

The normal gas inlet was fed directly into the sample injection block (F), without the bypass into the reference thermistor chamber, by unscrewing the T-piece and sealing the bypass outlet. A hole was drilled from the front face of the detector block (T) to the original reference thermistor chamber (H). This hole was tapped and a brass elbow (S), with a column connection at one end, was screwed into it. A three-way brass elbow was screwed into the original reference thermistor inlet. This arrangement allows the gas stream to pass directly over the original reference thermistor now called the monitoring thermistor.

#### *The multichannel stopcock (see Fig. 2)*

The stopcock was constructed from two brass discs held together on a brass spindle (U). One disc (V) was faced and the disc (X) had a Teflon insert (W), which was also faced.

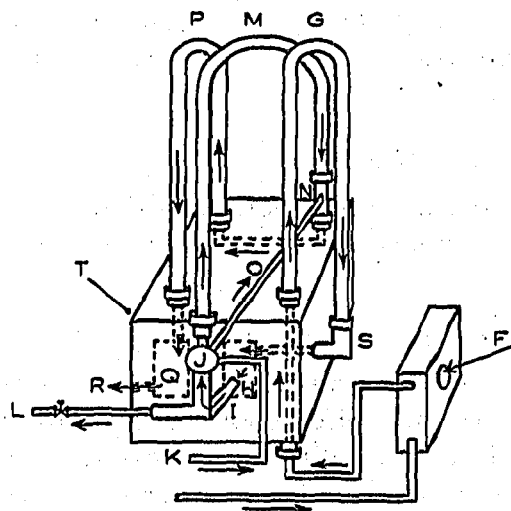


Fig. 1. Detector block assembly.

Disc (V) had four holes drilled into its edge which coincided with four holes drilled into its face. Copper tubes (I), (O), (M) and (K) were soldered into the holes in the edge of the disc. Two grooves were cut into the Teflon face (W). Face (V) was fixed and face (W) revolved, its movement being controlled by a switch (Z) connected by a castle system (Y) to the spindle (U). The multichannel stopcock will now be referred to as m.c. stopcock.

*The gas inlets (see Figs. 1 and 4)*

A gas regulator (B<sub>1</sub>), connected to the gas cylinder (A), controlled the supply to both the fine gas regulator in the instrument (D) and the gas regulator (B<sub>2</sub>) for the second-

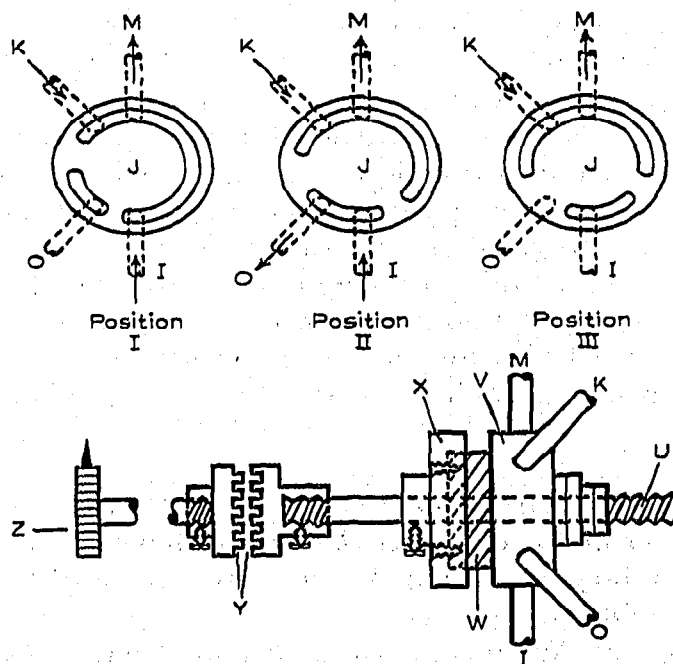


Fig. 2. Multichannel stopcock.

ary gas inlet (K). A copper tube (O.D.  $\frac{1}{4}$  in.) with a two-way brass stopcock led from the secondary gas inlet regulator through the instrument's gas sampling port to tube (K) in the m.c. stopcock (J).

*The bypass system (see Figs. 1 and 2)*

One of the tubes (O) on the m.c. stopcock was connected by a copper tube (O.D.  $\frac{1}{8}$  in.) to a brass column connection (N) which was fixed to a port on the detector block.

*The secondary gas outlet stopcock (see Figs. 1 and 2)*

The secondary outlet stopcock was manufactured in a manner similar to that of the m.c. stopcock except that here only one groove was made in the Teflon face to permit connection of the inlet and outlet in the open-to-atmosphere position. The outlet tube on the stopcock was constricted by crimping to prevent too abrupt pressure adjustments when the stopcock was opened. The inlet of the stopcock was connected by a copper tube (O.D.  $\frac{1}{8}$  in.) to tube (I) (Fig. 2) on the m.c. stopcock (J).

*The column arrangement (see Fig. 1)*

Three packed aluminium columns (I.D. 4 mm) were used in the modified fractometer. The columns were connected as follows: Column (G) led from the inlet port on the detector block to elbow (S) leading to chamber (H). Column (M) led from the m.c. stopcock (J) to the bypass connection (N) attached to the detector block. Column (P) joined the remaining two ports on the detector block, one being the outlet port leading to the original detecting thermistor.

The monitoring system allowed the operator to check on the behaviour of a sample and enabled precise cutting just before the sample reached the m.c. stopcock. A typical trace so obtained on the recorder is shown for a mixture of  $\alpha$ -pinene and  $\beta$ -pinene (Fig. 3). Here the base line was run in the middle of the chart and the response of the monitoring thermistor to the sample was shown as a negative signal, (dashed curve), whereas the response of the original detecting thermistor was shown as a positive signal (full curve). A range of intermediate pressures can be obtained by adjusting the secondary gas inlet regulator. Tube (O) permitted column (M) to be bypassed if so desired. The monitoring detector, m.c. stopcock and bypass were placed in the column line at a distance of approximately one third of the total column length from the normal inlet. A shorter distance was found to be unsatisfactory in view of the poor resolution of some multicomponent mixtures at the monitor. A greater distance could give rise to overlapping of monitor and final detector responses on the chart, especially with regard to a mixture with a wide range of retention times. The m.c. stopcock was to provide a choice of several paths to a sample (see Fig. 4).

*Gas flow paths*

When a sample is injected into block (F) it is carried by the gas stream through column (G), monitor thermistor chamber (H) and either by tube (I) to m.c. stopcock (J) or through the secondary outlet (L). If the latter is closed to the atmosphere, the following paths are possible:

*Position I* (see Fig. 2). With or without a gas stream from the secondary gas inlet (K), the sample passes through columns (M) and (P), thermistor chamber (Q),

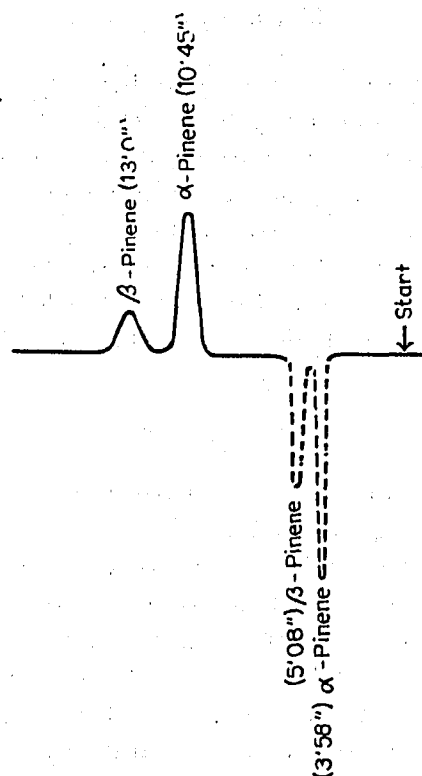


Fig. 3. Chromatogram of a mixture of  $\alpha$ - and  $\beta$ -pinene. Temperature:  $138^\circ$ ; normal inlet pressure:  $2.5 \text{ kg/cm}^2$ ; column length: 2.8 m; attenuation: 32; chart speed: 300 mm/h; sample volume:  $7 \mu\text{l}$ .

and normal outlet (R), except in the case where the intermediate pressure is equal to the normal inlet pressure.

*Position II* (see Fig. 2). The sample passes through bypass tube (O), connection (N), column (P), chamber (Q) and outlet (R). Simultaneously a separate gas stream from inlet (K) can be made to pass through columns (M) and (P).

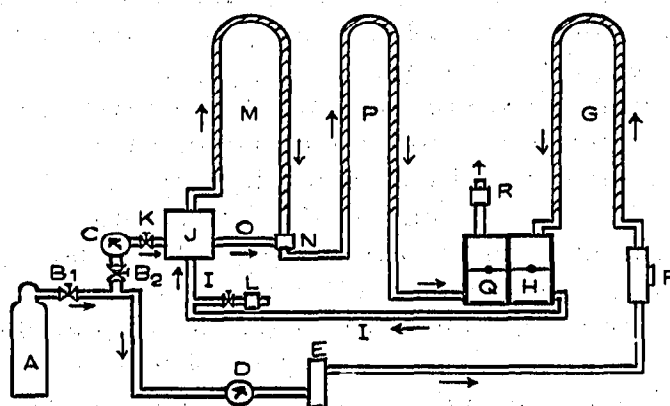


Fig. 4. Gas flow diagram.

*Position III* (see Fig. 2). Sample cannot enter (J), hence may be eluted from the secondary outlet (L). Simultaneously a stream of gas can be passed from inlet (K) through columns (M) and (P).

## EXPERIMENTAL

The m.c. stopcock was held in Position I affording use of the columns according to normal gas chromatography procedure except that the intermediate pressure could be adjusted. The intermediate pressure was brought to the desired level by adjusting the secondary pressure regulator ( $B_2$ ) (Fig. 4) with stopcock (K) closed, after which it was opened. The fine pressure regulator in the apparatus and the regulator on the gas cylinder were at all times adjusted to the same pressure; thus the intermediate pressure could not be made to exceed the normal inlet pressure. The rotameter (E) was calibrated against the soap bubble flowmeter for flow rate measurements.

## RESULTS

At maximum sensitivity (attenuation 1) a sudden pressure change caused an abrupt recorder response followed by a gradual base line adjustment to its original position. At lower sensitivities (*e.g.* attenuation 32) with a sudden pressure change, the base line remained constant except for an instantaneous negative and positive deflection of the recorder pen. Sudden pressure changes caused no deterioration of the thermistor beads, which was also observed by BORFITZ<sup>1</sup>. When the intermediate pressure was raised in the column, while outlet and normal inlet pressures were held constant, a decreased flow in the column before the secondary inlet, and an increased flow in the column after the secondary inlet was observed. When the intermediate pressure was made equal to the normal inlet pressure, gas flow ceased in the column before the secondary inlet.

Raising the intermediate pressure prior to the injection of a compound had the effect of increasing its retention time, as well as broadening its elution curve. Raising the intermediate pressure after the compound had passed the secondary gas inlet, a slight drop in retention time accompanied by a slight sharpening of the elution curve was noted.

Raising the intermediate pressure, whilst the compound was retained in column (G), caused much the same effects as in the case where the intermediate pressure was raised prior to sample injection. Column efficiency dropped markedly when the pressure gradient in column (G) was small.

When the intermediate pressure was raised just after the first component of a binary mixture, almost completely resolved at the monitor, had passed the secondary inlet, no appreciable change was observed in the retention times and shapes of the elution curves, except when the pressure gradient in column (G) was small. Under the latter condition the difference in retention times of the two components was considerably increased, but column efficiency for the second component dropped below a useful limit. When the pressure gradient was zero a compound could be held stationary in column (G). However, when it was stationed just before the secondary inlet, diffusion effects caused it to leak into column (M). On reducing the secondary inlet pressure the compound, which was held up, resumed its passage. This effect was studied on single compounds, *e.g.* ethyl alcohol, benzene and *n*-butyl acetate, and the results are shown in Fig. 5. The period for which the compound was held stationary was called the hold-up time,  $H_t$ . The total residence time  $R_t$ , less the hold-up time,  $H_t$ , was called the travelling time,  $T_t$ , *i.e.*,  $R_t - H_t = T_t$ . To obtain some measure of the effect of

the hold-up time, the concept of column efficiency was used. For this purpose the column efficiency was measured by the number of theoretical plates (KEULEMANS<sup>2</sup>) which was adapted by replacing retention time by travelling time in the equation; column efficiency =  $(4 T_e/W)^2$ , where  $W$  (in mm) is the base of the triangle on the base line obtained by drawing the tangents to the inflection points of the elution curve.

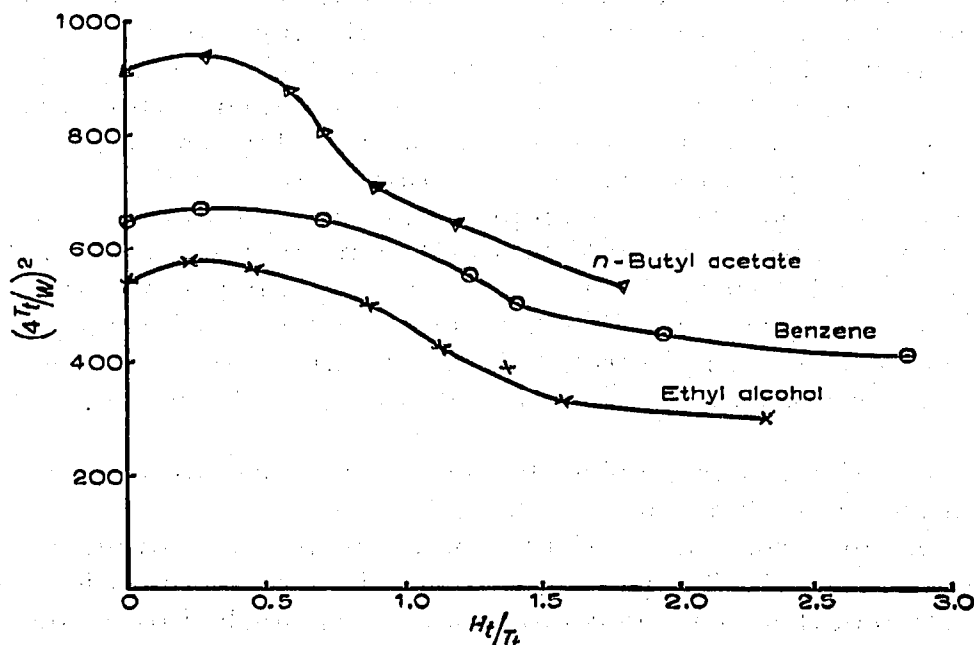


Fig. 5. Effect of hold-up time on column efficiency. Normal inlet pressure: 2.5 kg/cm<sup>2</sup>; column length: 3 m; temperature: 139°, except for *n*-butyl acetate: 130°.

Travelling time,  $T_t$ , is converted to length units by multiplying by the chart speed. Column efficiency was then plotted against the ratio of hold-up time to travelling time. It was noted that column efficiency did not drop appreciably until the hold-up time equalled approximately three quarters of the travelling time. Beyond this value the column efficiency decreased considerably and was probably due to the fact that diffusion of the zone became more marked during the hold-up period.

Therefore the effect of intermediate pressure changes on the separation of components is of little use unless a hold-up technique can be used.

#### APPLICATIONS

By using the gas chromatography apparatus as outlined in the Experimental section, only one application, which has little practical value, is possible, namely further separating components which are already resolved at the secondary gas inlet. This application may be repeated by the following technique. The zero pressure gradient is obtained in column (G) (Fig. 4), by switching m.c. stopcock to Position III and simultaneously using the secondary gas inlet, instead of using Position I. However, both suffer from the disadvantage that the monitor and final thermistor responses interfere with each other. By using the above gas chromatography apparatus with the secondary outlet and bypass for samples in which the total range of retention times lies within certain limits, the above disadvantage may be eliminated.

In view of the observation that a component can be held stationary under pressure for a limited period without great loss of column efficiency, the modified apparatus may be used for the following applications.

Using the secondary outlet any component of a mixture can be flushed out to atmosphere during a run. In the case of a binary mixture (*e.g.*  $\alpha$ - and  $\beta$ -pinene), where the second component with the longer retention time *i.e.*  $\beta$ -pinene, was flushed out, bleeding back of  $\alpha$ -pinene was prevented by switching the m.c. stopcock from Position I to Position III, prior to the flush-out period. This example is shown in Fig. 6. A reduction of approximately 20% in run-time is gained in this way. A further reduction in time can be obtained by the use of the secondary gas inlet.

The bypass allows any component of a mixture to be eluted from the column before any preceding components. For example in the case of  $\alpha$ - and  $\beta$ -pinene, (Fig. 7), the  $\alpha$ -pinene is allowed to pass through column (M), with m.c. stopcock in Position I, then  $\beta$ -pinene is channelled through the bypass by switching to Position II and is eluted before the  $\alpha$ -pinene. Switching back to Position I now allows  $\alpha$ -pinene to be eluted. The  $\alpha$ -pinene can be made to travel along column (M) by using the secondary gas inlet with m.c. stopcock in Position II and this again leads to a reduction in total run-time.

The secondary outlet and the bypass become particularly useful with regard to partially resolved and multicomponent mixtures.

An example of the former is a mixture of  $\alpha$ -pinene and camphene, (Fig. 8a) which was partially resolved after passing through the total column length of 3 m. The undesired portion of this partially resolved mixture is flushed from the secondary outlet. This leads to a mechanical separation of fractions of  $\alpha$ -pinene and camphene (Fig. 8b), the purity of which is checked by the final thermistor without the necessity of recirculating part of the fractions. If required, the portion flushed from the secondary outlet may be collected and recirculated. This technique should have value if only a small initial amount of sample is available. A reduction in run-time could have been attained had the bypass also been used.

An example in which both the bypass and secondary outlet are used is afforded by the case of a mixture of  $\alpha$ -pinene,  $\beta$ -pinene and ocimene, (Fig. 9).  $\beta$ -Pinene plus some  $\alpha$ -pinene and ocimene were flushed from the secondary outlet and ocimene was channelled through the bypass, while  $\alpha$ -pinene was held stationary in column (M). Compared with a normal run on the above mixture, this technique gave a reduction in run-time of approximately 20%. The run-time could have been reduced further by allowing  $\alpha$ -pinene to travel along column (M) during the flush-out and bypass period.

The use of the modified apparatus allows collection of components of a mixture in less than normal run-time if required. Such a reduction in time may be important in the case of repetitive sample collection. If a reduction in run-time is not of primary importance the components of a mixture may be separated to such a degree that contamination during collection is completely avoided. In general the separation of pure components from partially resolved and multicomponent mixtures can be carried out in a comparatively simple manner. This technique becomes particularly useful if only a small initial amount of sample is available, and where no complete resolution of components has been achieved even by the use of the most efficient available stationary phases and conditions. Furthermore recirculation becomes unnecessary as

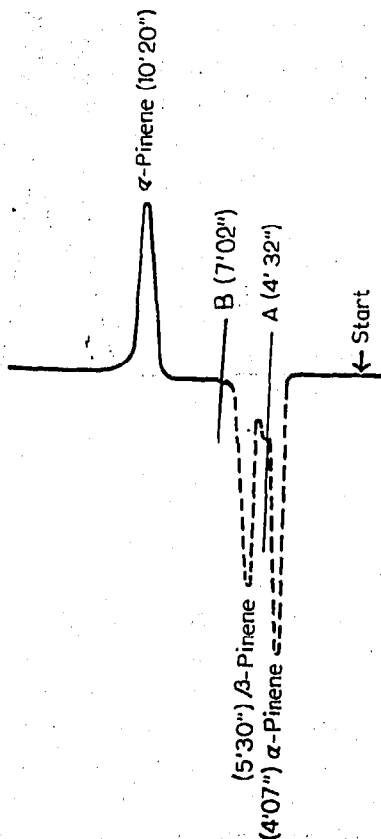


Fig. 6. Chromatogram of a mixture of  $\alpha$ - and  $\beta$ -pinene. Conditions as for Fig. 3. (A) m.c. stopcock: Position III; secondary inlet pressure; 2.0 kg/cm<sup>2</sup>; secondary outlet: open. (B) Secondary outlet: closed; m.c. stopcock: Position I; secondary inlet: closed.

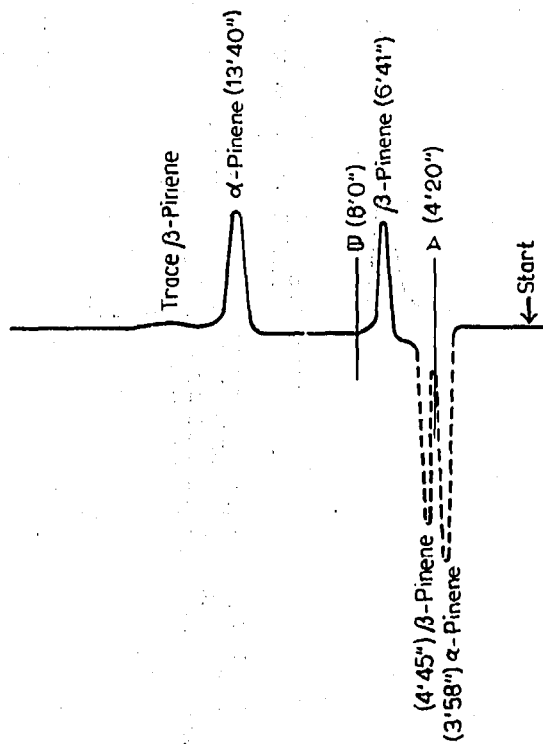


Fig. 7. Chromatogram of a mixture of  $\alpha$ - and  $\beta$ -pinene. Conditions as for Fig. 3. (A) m.c. stopcock: Position II; (B) m.c. stopcock: Position I.



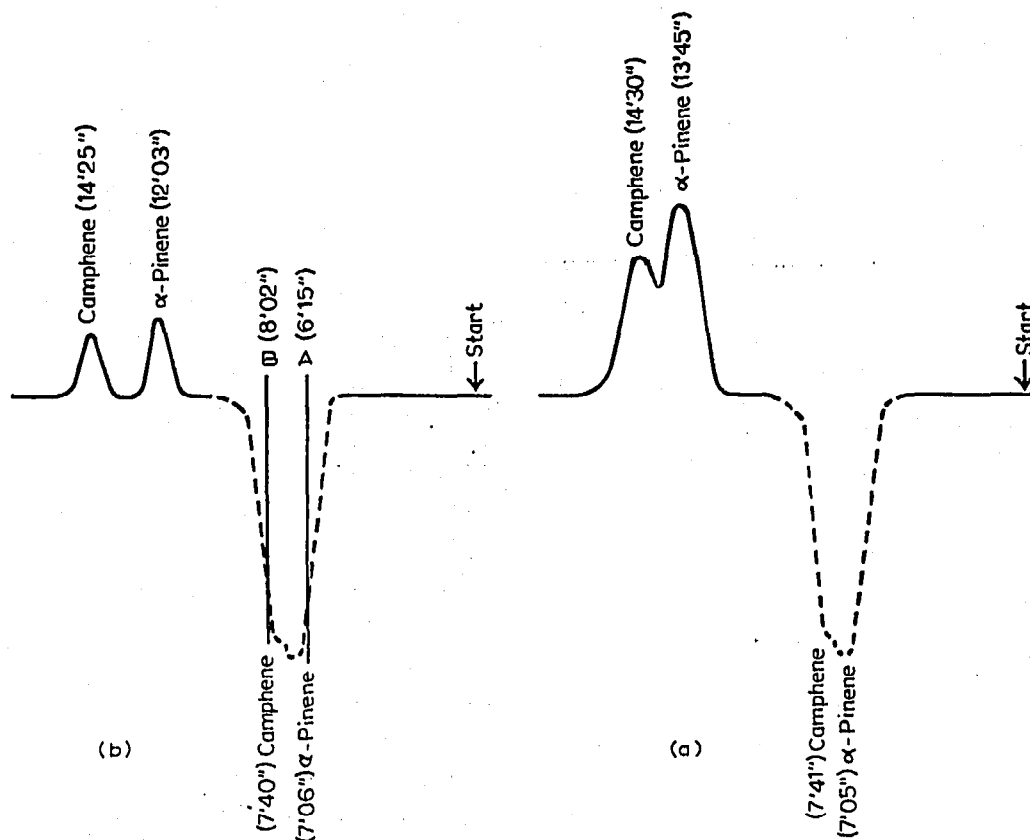


Fig. 8. Chromatogram of a mixture of  $\alpha$ -pinene and camphene. (a) Temperature:  $133^{\circ}$ ; normal inlet pressure:  $2.5 \text{ kg/cm}^2$ ; column length: 3 m; attenuation: 64; chart speed: 300 mm/h; sample volume:  $16 \mu\text{l}$ . (b) Conditions as for (a). (A) m.c. stopcock: Position III; secondary outlet: open. (B) Secondary outlet: closed; m.c. stopcock: Position I.

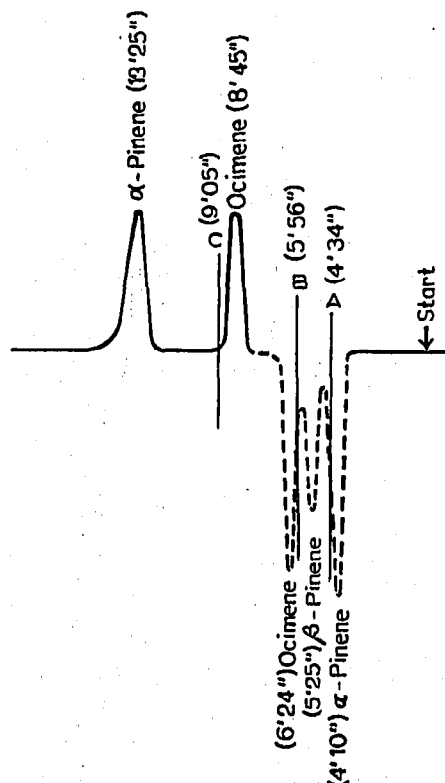


Fig. 9. Chromatogram of a mixture of  $\alpha$ -pinene,  $\beta$ -pinene and ocimene. Conditions as for Fig. 3; sample volume:  $9 \mu\text{l}$ . (A) m.c. stopcock: Position III; secondary outlet: open. (B) Secondary outlet: closed; m.c. stopcock: Position II. (C) m.c. stopcock: Position I.

the purity of the component has already been checked by the final thermistor. The modified apparatus may be used for ordinary runs by rearranging the columns.

A disadvantage arises if two components in the system pass over the monitoring and final thermistor at the same time, thus adversely affecting the recorder response. Also, to achieve a successful run, some experience is needed in the manipulation of the various controls.

#### ACKNOWLEDGEMENTS

We wish to thank the Director and the Trustees of this Museum for permission to publish this work. We are indebted to Mr. E. E. DESBRUSLAIS for assistance in modifying the apparatus, and Mr. H. H. G. MCKERN and the Museum staff for their helpful advice and assistance.

#### SUMMARY

A series of experiments on volatile samples in a gas chromatography column were carried out to determine the effect of pressure changes at a point intermediate between the normal inlet and outlet, while pressures at the latter were held constant. To facilitate these experiments, a number of modifications were made to a conventional analytical fractometer. No major intrinsic alterations were necessary in modifying the apparatus, and the accessories used were of simple construction.

Of the above series of experiments the only case leading to useful applications was found to be that in which the intermediate pressure was made equal to the normal inlet pressure. The effect of holding a compound stationary under such pressure is discussed in terms of column efficiency and the ratio of hold-up time to travelling time.

From the above study certain applications became evident of which several examples are given. Some of these applications were found to be of considerable value with regard to partially resolved and multicomponent mixtures. The advantages and disadvantages of the modified apparatus are discussed.

#### REFERENCES

<sup>1</sup> H. BOREFIZ, *Anal. Chem.*, 34 (1962) 167.

<sup>2</sup> A. I. M. KEULEMANS, *Gas Chromatography*, Reinhold Publ. Corp., New York, 1959, p. 138.