

## PREPARATIVE SCALE GAS CHROMATOGRAPHY BY A LABORATORY ROTATING UNIT

### IV. SEPARATION OF CLOSE BOILING MIXTURES AND CRUDE REACTION PRODUCTS

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#### INTRODUCTION

Some earlier papers<sup>1,2</sup> describe a new gas chromatographic process and the development of an apparatus<sup>3</sup>, the "Roto-Chrom" (Fig. 1), in which a continuous separation is carried out by rotating a bundle of columns between the feeding and the collecting systems, both of which are stationary. The efficiency of the preparative unit is comparable to that of an analytical column.

It was also shown that the Roto-Chrom can be successfully applied to the resolution of isomers<sup>4</sup>. The present communication is concerned with the possibility of using our large scale preparative unit as an alternative method to high efficiency fractional distillation.

#### COMPARISON BETWEEN LARGE SCALE PREPARATIVE GAS CHROMATOGRAPHY AND FRACTIONAL DISTILLATION

We selected as an example the separation of a mixture of 95 % *n*-pentane and 5 % isopentane. In order to obtain the bottom product at 99.99 % purity and the top product at 99, by laboratory continuous fractional distillation, 85 actual plates would be required\* ; a one-inch Oldershaw column would allow a take-off rate of about 40 ml/h.

The Roto-Chrom Mod. U3\*\* when used for this separation gave a 52 ml/h feed rate and *n*-pentane of 99.99 % purity and isopentane of 99.8 % purity.

In order to realize this feed rate, the Roto-Chrom would need 800 theoretical plates: in spite of this, as the values of H.E.T.P. are very low in gas chromatography, the overall dimensions of the apparatus are not larger than those of a distillation unit.

#### SEPARATION OF HYDROCARBONS

The Roto-Chrom can easily be used for the purification of hydrocarbons, which are usually obtained by distillation. We have obtained, *e.g.*, at purities always higher

\* As the relative volatility of the components is 1.3, 48 theoretical plates are required; but the plate efficiency for an Oldershaw column is about 60%. Reflux ratio is 50:1.

\*\* Details of the Mod. U3 are given in the Experimental section. Octoil S was used for the separation: on this stationary phase the *n*-pentane-isopentane separation factor is 1.3.

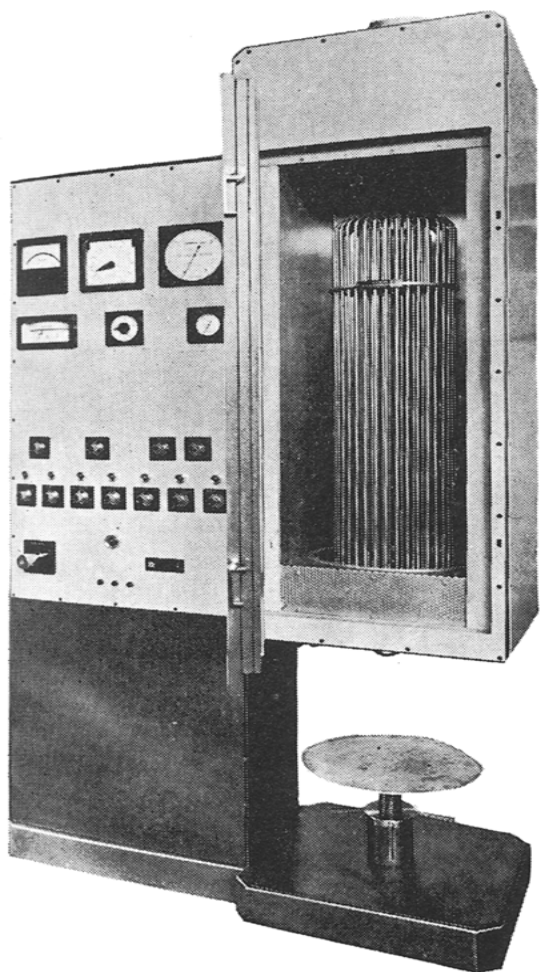


Fig. 1.

Fig. 1. The preparative-scale unit "Roto-Chrom" Mod. U<sub>3</sub>.

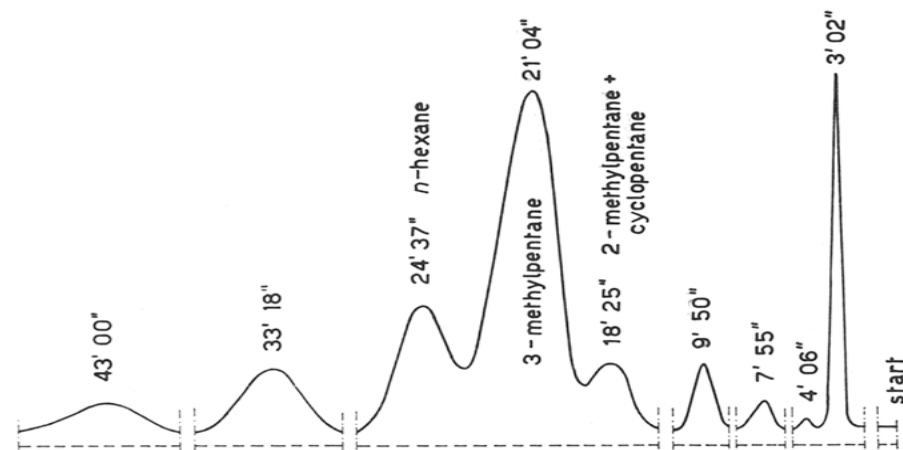


Fig. 2.

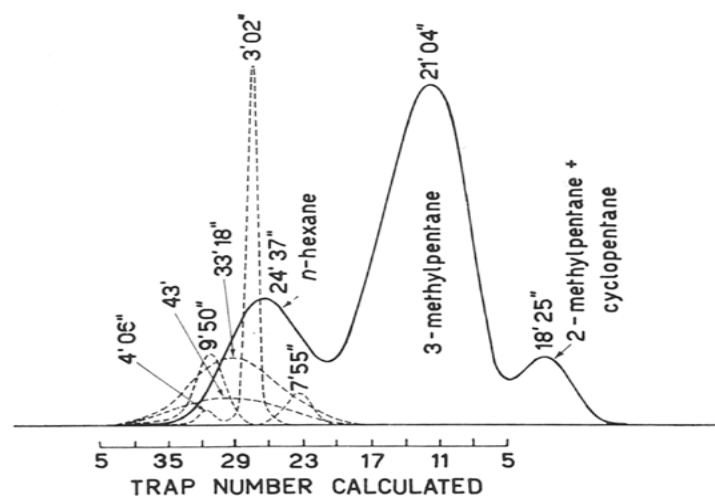


Fig. 3.

Fig. 2. Chromatogram of the "tops of *n*-hexane distillation".

Fig. 3. Roto-Chrom program for the separation of 3-methylpentane.

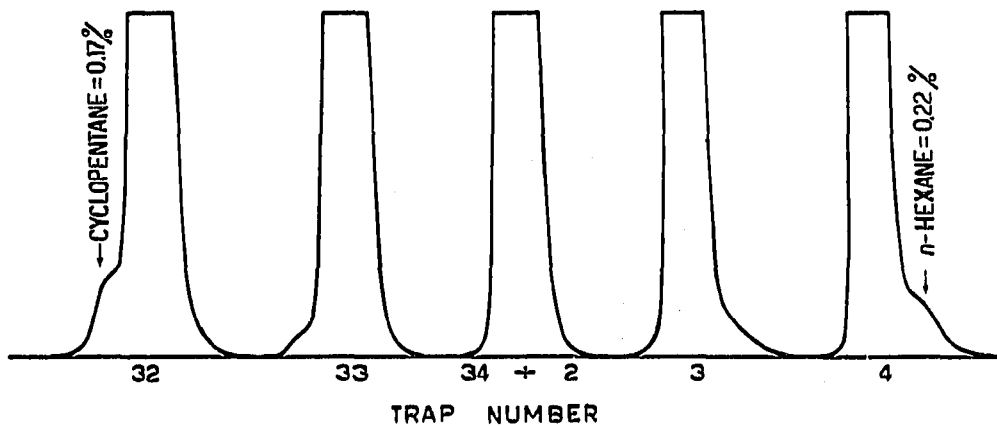


Fig. 4. 3-Methylpentane distribution in the trapping system.

than 99.99 % and in amounts ranging from 0.1 to 2 l, *n*-hexane (f.r.\* = 78), cyclohexane (f.r. = 28.5) and *n*-octane (f.r. = 15.5).

Furthermore we have been able to isolate pure hydrocarbons from distillation cuts which are usually discarded. In the two following examples the separation by distillation would be very difficult owing to the large number of components and the low values of relative volatility ( $\alpha = 1.1 \div 1.2$ ).

#### *Separation of 3-methyl-pentane from tops of n-hexane distillation*

The analytical chromatogram of the starting mixture is shown in Fig. 2: the 3-methyl-pentane content is 66.4 % and the retention time of the components ranges from 3 to 43 min.

The Roto-Chrom working conditions (stationary phase Octoil S 30 %,  $l = 2.2$  m, c.g.f. = 60 ml/min,  $t = 60^\circ$ , r.p.h. = 6.6)\* had been selected in such a way that all unwanted impurities overlap; in other words the program compels the unit to work as if the chromatogram were that shown in Fig. 3. This shows the versatility of the apparatus.

By operating at a feed rate of 23.7 ml/h, the 43 % of the substance collected was 3-methyl-pentane 98.8 % pure. In another run, feeding a richer cut (95 % of 3-methyl-pentane) at a rate of 40 ml/h, we obtained 350 g of 99.99 % pure 3-methyl-pentane. As the Roto-Chrom can subdivide a single band into many fractions it is possible to recover a substance at different degrees of purity. Fig. 4 clearly shows that 3-methyl-pentane collected in the central traps is very pure, while the product recovered in the side cuts is less pure owing to the presence of substances which elute so that they partially overlap with the 3-methyl-pentane.

#### *Separation of cyclopentane from residues of an n-pentane distillation*

In order to recover cyclopentane from a mixture of the following composition: *n*-pentane 29.2 %, 2,2-dimethyl-butane 6.3 %, cyclopentane 64.5 %, the Roto-Chrom was run under the following conditions: stationary phase = 1,2-bis(2-cyanoethoxy)ethane 30 %,  $l = 2.4$  m, c.g.f. = 40 ml/min,  $t = 39^\circ$ \*. 1,2-bis(2-cyanoethoxy)ethane was chosen because on this stationary phase *n*-pentane and 2,2-dimethyl-butane elute together.

With a 45 ml/h feed rate the distribution shown in Fig. 5 was obtained: cyclopentane was recovered at a purity higher than 99.9 % and comprised 62 % of the feed mixture. With a continuous run we obtained 600 g of pure product.

### RESOLUTION OF CRUDE REACTION PRODUCTS

The resolution of crude reaction products demonstrates an important feature of our process, namely the possibility of collecting at the same time a number of pure components of a mixture. Two such separations are described below.

#### *Separation of the addition products after reaction of cyclopentadiene and isoprene*

PLATÉ AND BELIKOVA<sup>5</sup> reported that the separation of the products of the Diels Alder reaction between isoprene and cyclopentadiene is difficult because the codimers

\* For abbreviations see List of symbols.

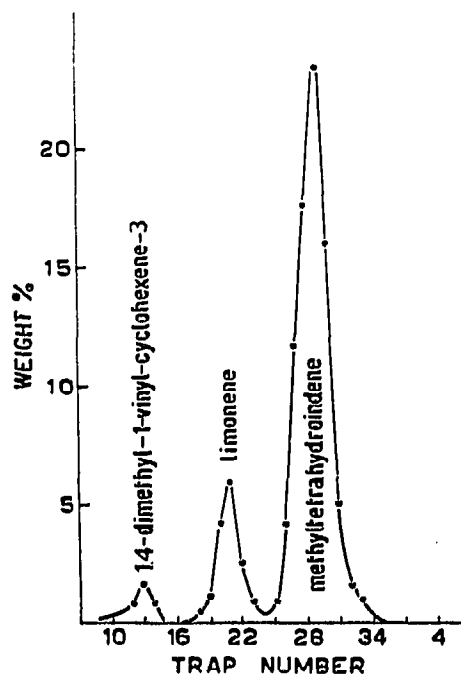
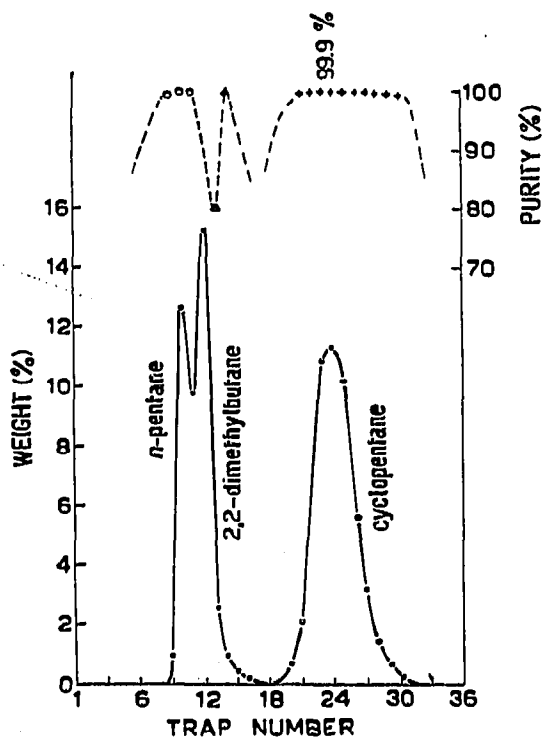


Fig. 5. Distribution in the trapping system of the cyclopentane cut.

Fig. 6. Distribution in the trapping system of the addition products of cyclopentadiene and isoprene.

have the same number of C atoms as the dimers of isoprene and cyclopentadiene. These authors have isolated, from a preliminary cut, methyltetrahydroindene on a column having 100 theoretical plates.

Analysis of an analogous cut, obtained as described by PLATÉ AND BELIKOVA, has given the following composition:

1,4-dimethyl-1-vinyl-cyclohexene-3	6 %
limonene	19 %
methyltetrahydroindene	71 %
other compounds	4 %

The main components of this mixture had different structures and therefore an effective separation could be expected on a suitable stationary phase; therefore a separation on the Roto-Chrom was tried. Polyethylene glycol 400 and Octoil S were found suitable for the purpose. The first stationary phase allows higher feed rates and lower operating temperatures, the second gives a better separation because it resolves two peaks which are eluted together on polyethylene glycol 400.

Since we wanted to show that a separation was possible at a temperature ( $110^{\circ}$ ) lower than the average boiling point ( $180^{\circ}$ ) of the mixture, the first stationary phase was selected. With the following working conditions: s.f.\* = P.E.G. 400, l = 1.9 m, c.g.f. = 100 ml/min, t =  $110^{\circ}$ , r.p.h. = 2, f.r. = 4 ml/h, we obtained the distribution shown in Fig. 6 and the percentages obtained are given in Table I.

\* For abbreviations see List of symbols.

The gas chromatographic analysis on Octoil S confirmed the sharpness of the separations; on the other hand the purity of methyltetrahydroindene was somewhat

TABLE I

<i>Component</i>	<i>Analysis on P.E.G. 400 (per cent found)</i>
1,4-Dimethyl-1-vinyl-cyclohexene-3	99.5
Limonene	99.98
Methyltetrahydroindene	99.94

lower (98.5%), owing to the above mentioned overlapping of a minor constituent (probably vinylnorbonene) on P.E.G. 400. A further purification would be possible by recycling on Octoil S. This has been done in the following case:

A mixture (obtained by fractionating through a Podbielniak Hyper-Cal Column a crude addition product of butadiene and cyclopentadiene) of 98.4% tetrahydroindene and 1.6% vinyl-norbonene was fed into the Roto-Chrom (s.f.\* = Octoil S 30%, l = 1.9 m, c.g.f. = 86 ml/min, t = 144°, r.p.h. = 2, f.r. = 8 ml/h). The eluted tetrahydroindene was > 99.9% pure.

#### *Separation of dicyclopentadiene hydrogenation products*

Hydrogenation of dicyclopentadiene gave a mixture of the following composition:

dicyclopentadiene	20.7 %
dihydrodicyclopentadiene	76.9 %
other components	2.4 %.

When this mixture was fed into the Roto-Chrom (s.f.\* = methyl silicone rubber S.E.30 20%, l = 1.90 m, c.g.f. = 80 ml/min, t = 140°, r.p.h. = 3.75, f.r. = 6 ml/h) > 99.9% pure dihydrodicyclopentadiene was obtained.

The last example, although not very significant, has been reported since, as in the above mentioned case of tetrahydroindene, such high purities cannot be obtained by fractional distillation owing to the very similar boiling points.

#### DISCUSSION

We believe the above reported examples to be fairly indicative of the possible practical applications of our large scale preparative gas-chromatographic unit (the Roto-Chrom).

The apparatus is a remarkable alternative to high efficiency laboratory-fractional distillation columns, since at equal feed rates it yields purer fractions and more than one pure component may be collected at the same time.

It may be noted that the feed rates reported in the present communication are much higher than those reported previously<sup>4</sup> in the separation of isomers which could be resolved by other means.

\* For abbreviations see List of symbols.

As well as the 36 column unit, which has been used for the separations described in this and previous communications, a 100 column unit has been operated successfully in our laboratory.

The following separations may be mentioned among those carried out by the use of this unit:

(a) > 99.9 % pure isoprene has been obtained, at a 175 ml/h feed rate, from a mixture containing pentenes (~ 10 %).

(b) Germanium tetrachloride has been separated from arsenic trichloride and silicon tetrachloride (~ 5 %) at a 550 g/h feed rate.

Large scale preparative gas chromatography may thus become a useful tool for the production of very pure chemicals.

#### LIST OF SYMBOLS

s.f. = stationary phase

l = column length

c.g.f. = carrier gas flow rate (ml/min)

t = temperature of thermostatic chamber

r.p.h. = number of revolutions per hour of the bundle of columns

f.r. = feed rate (ml/h)

#### EXPERIMENTAL

In all the separations which have been reported the following conditions have been held constant:

The bundle consisted of 36 columns; the columns were stainless steel with a 6 mm internal diameter; all stationary phases were supported on Fire Brick C<sub>22</sub> (60-80 mesh); and the carrier gas was dry nitrogen.

#### SUMMARY

The effectiveness of preparative scale gas chromatography in the resolution of close boiling mixtures is compared with laboratory fractional distillation.

Some examples of separations of close boiling hydrocarbon mixtures and crude reaction products are reported; these show the versatility, the high purity levels and the remarkable feed rates obtainable with the rotating unit.

Moreover two examples are reported in which, by the use of a larger gas chromatographic apparatus, exceptionally high feed rates are obtained.

#### REFERENCES

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