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HEATER-DISPLACEMENT CHROMATOGRAPHY

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SUMMARY

The classical displacement gas chromatographic method has been modified by using a moving heater which eliminates the need for the displacer substance normally required pure and in large quantity. The technique is particularly suitable for trace concentration and for preparative work on a continuous basis, and by using catalysts as adsorbents it is also possible to carry out reaction and separation in one operation.

INTRODUCTION

There have been many examples of the use of elution gas chromatography (GC) for preparative work[1], of which the most successful (*e.g.*, ref. 2) would appear to be that of the ERAP-SRTI process (ELF, Solaize, France) now used for the production of high-purity products on the scale of up to 3 kg/h. As was shown some years ago, displacement GC is a powerful alternative and has certain peculiar advantages[3]. These include:

(1) The fact that displacement chromatography operates best under conditions of high vapour concentration where there is competition between molecules, for, *e.g.*, surface sites on an adsorbent, *i.e.*, in the region of marked curvature in the Langmuir-type adsorption isotherm. Thus 50-g samples are readily separated on 350 g of activated charcoal adsorbent[3].

(2) The enhanced selectivity of adsorbents over normal GC liquids which makes possible the tailoring of columns for particular difficult separations. This selectivity can usually be determined most rapidly first of all by simple elution experiments.

(3) The use of these adsorbents at lower temperatures in displacement than in elution chromatography. This will in general enhance the separations, but is most important in reducing the risk of chemical reactions occurring on a column packed with an active adsorbent.

(4) The possibility of using buffer substances (*e.g.*, added artificially to the mixture to be separated) which will form displacement bands between the substances to be separated, and which can then be easily removed, *e.g.*, by some simple chemical or solution methods.

(5) The concentration of trace impurities (*e.g.*, of alkenes in alkanes by a factor of 10^5) (ref. 3).

The original displacement method suffers, however, from two disadvantages:

(1) A large quantity of pure displacer material is required to displace the sample from the column.

(2) The column needs to be regenerated and the displacer material recovered by heating up the column after the end of the displacement experiment. These two disadvantages can be overcome, as we have now shown, by use of a heater moving along the column. The function of the heater is to drive all the sample substances ahead of it along the column in a manner similar to the analytical device of Turner[4] as distinct from having the sample within the heater zone as in the chromatothermographic technique of Turkeltaub[5]. In this manner the most strongly adsorbed component of the mixture displaces the next most strongly adsorbed component, etc. In the case of a thermolabile sample, it may be necessary to add a small amount of a displacer substance (more strongly adsorbed than any of the components of the sample) which serves to protect the thermolabile substances from the heater by ensuring that they will always be in the colder parts of the column some distance ahead of the heater.

It is also possible to use the heater to induce reactions on the column itself so that reaction and separation of products can be effected in one operation on the preparative and possibly on the production scale. Some preliminary examples of this mode of operation and using catalysts as adsorbents are described in the latter part of the paper, while the earlier part is concerned with examples involving preparative separation only.

EXPERIMENTAL AND RESULTS

The experiments quoted in this paper have been carried out using a small-scale prototype heater-displacement apparatus with a glass column of 1 m length and 1 cm I.D. This has been packed or partly packed with adsorbents such as activated charcoal, activated alumina, silica (Porasil), Pt–Al$_2$O$_3$, Ni–SiO$_2$, and porous polymer (Porapak). The column is mounted vertically in an air oven which can be maintained at controlled temperatures between room temperature and 130°. An electrical-resistance heater, 6 cm long, fits loosely around the column and moves downwards under its own weight on slide rails attached to the side of the oven. The rate of movement of the heater is controlled by a motor and pulley system between 10 and 80 cm h^{-1}. The heater temperature can be varied between 100 and 500°, and thermocouple measurements inside the column show that the temperature rises quite sharply (over about 3 cm) into the heater zone. Better and more efficient operation would be expected using direct dielectric heating of the adsorbent. Carrier gas flow-rates have been varied between 10 and 300 cm^3 min^{-1}. The effluent from the column passes through a heated sampling valve which is operated automatically so as to inject samples via a splitter into a rapid GC analytical column consisting of a 20 ft. × 1/100 in. stainless-steel capillary column coated with squalane.

Samples have been introduced to the column either by direct injections or via a saturator. With single injections of relatively large samples great care has to be taken to avoid liquid running down the inside wall of the column. The majority of runs have been made with batch introduction of sample, but it has proved possible to continue to introduce fresh sample on to the cooled parts of the column while the heater is still

moving down the rest of the column. This means that the process can be carried out on a continuous basis, as is envisaged schematically in Fig. 1. Sample (*e.g.*, directly from a reactor) is fed on to the column continuously in carrier gas at a concentration somewhat less than it will eventually leave the column in the displacement band. A number of heaters then pass along the column, and in front of each heater some concentration and then displacement separation takes place. The different components leaving the column can be collected by a valving sequence suitably timed in relation to the movement of the heaters. In this way most of the column can be utilised all the time, provided that, as is likely in practice, the process is used for a relatively close range of substances so that none of these elute ahead of the displacement bands.
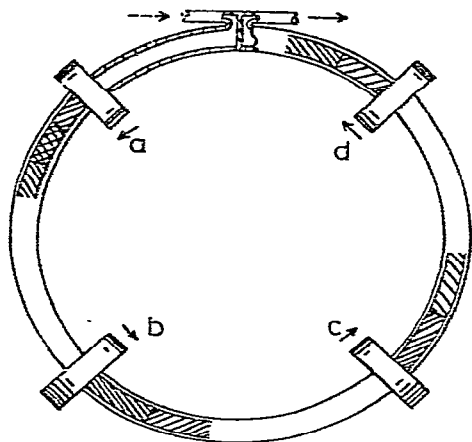

Fig. 1. Schematic heater-displacement apparatus with continuous operation. Sample is introduced continuously at top left and collects on column until it is displaced forward by one of the moving heaters, a, b, c, or d. Individual components are taken off at top right via valves suitably synchronised with the moving heaters.

The experiments which we have so far conducted have been limited to sample sizes not greater than 5 g leaving the column over a period of about 100 min. Reasonable increases in heater speed and carrier gas flow-rate and in particular increase in column diameter (say to 12.5 cm, which has proved entirely feasible in the ERAP-SRTI process) would lead to productive rates of a kilogram or more per hour per unit.

Examples of separation only

Figs. 2–4 illustrate the kinds of separation which have been achieved with the simple heater-displacement apparatus. Activated charcoal (as in Fig. 2) has a high sample capacity but is not as selective for alkane isomers as, *e.g.*, Al_2O_3 (Fig. 3). Terpenes have been found to be too strongly retained on charcoal and to undergo extensive reactions on unmodified Al_2O_3 or SiO_2 surfaces. They can, however, be separated satisfactorily with porous polymer (Fig. 4) as adsorbent. In this case undecane has been used as a "thermal buffer". It displaces the terpenes and thus protects them from reaction in the heater zone. Figs. 3 and 4 show the manner in which various impurities (so far unidentified in the case of the terpene samples) are concentrated in
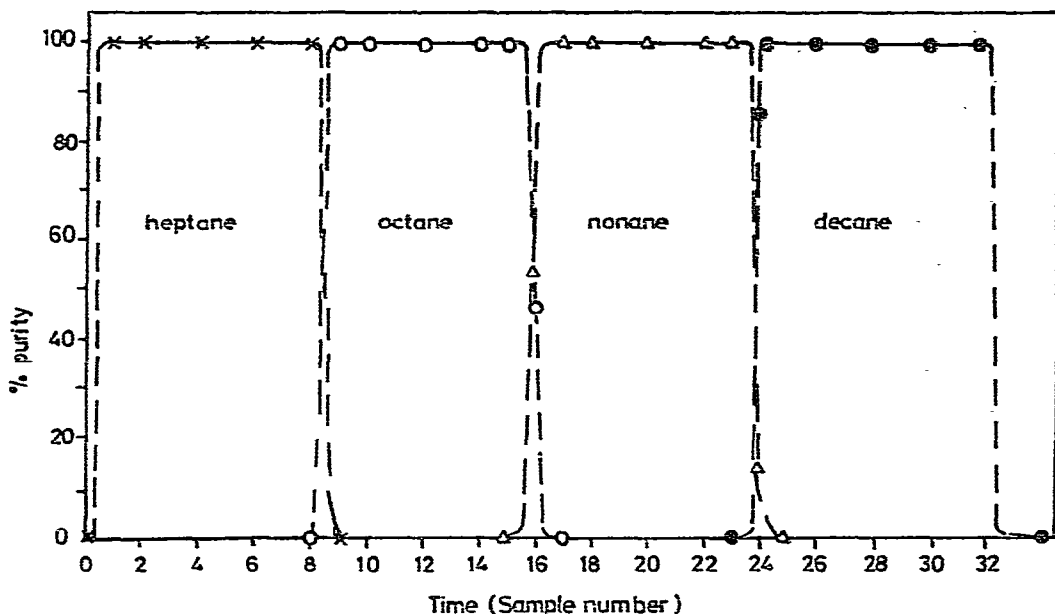
Fig. 2. Separation of a 4-g mixture of *n*-alkanes. Column, 90 × 1 cm I.D.; adsorbent, activated charcoal (Sutcliffe-Speakman 207C) at 100°; nitrogen flow-rate, 120 cm³ min⁻¹; heater temperature, 450°; heater speed, 20 cm h⁻¹. Samples taken for analysis every 5 min after a 2-h running time.
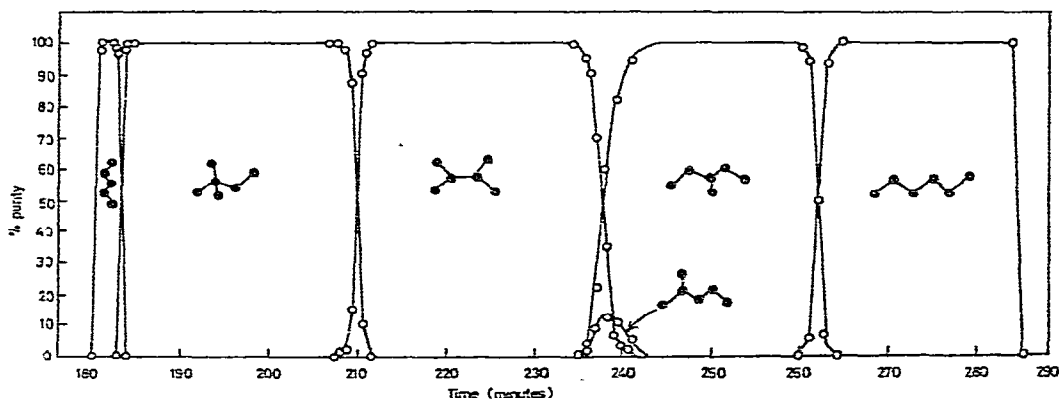

Fig. 3. Separation of a 2-g mixture of equal quantities of four isomeric hexanes (with *n*-pentane and 2-methylpentane impurities). Column, 100 × 1 cm I.D.; adsorbent, γ-Al₂O₃ (Phase Separations, Queensferry, Great Britain) at 18°; nitrogen flow-rate, 70 cm³ min⁻¹; heater temperature, 110°; heater speed, 21 cm h⁻¹.

front of or between the main displacement bands. It should be noted that increasing both the length of the column and the sample size will normally lead to broader bands without any increase in the width of the overlap zones. In general, gas flow-rates and heater speeds have to be adjusted to avoid elution (which will occur at high gas flow-rates and/or low heater speeds) on the one hand or condensation (which will occur at low gas flow-rates and/or high heater speeds) on the other.
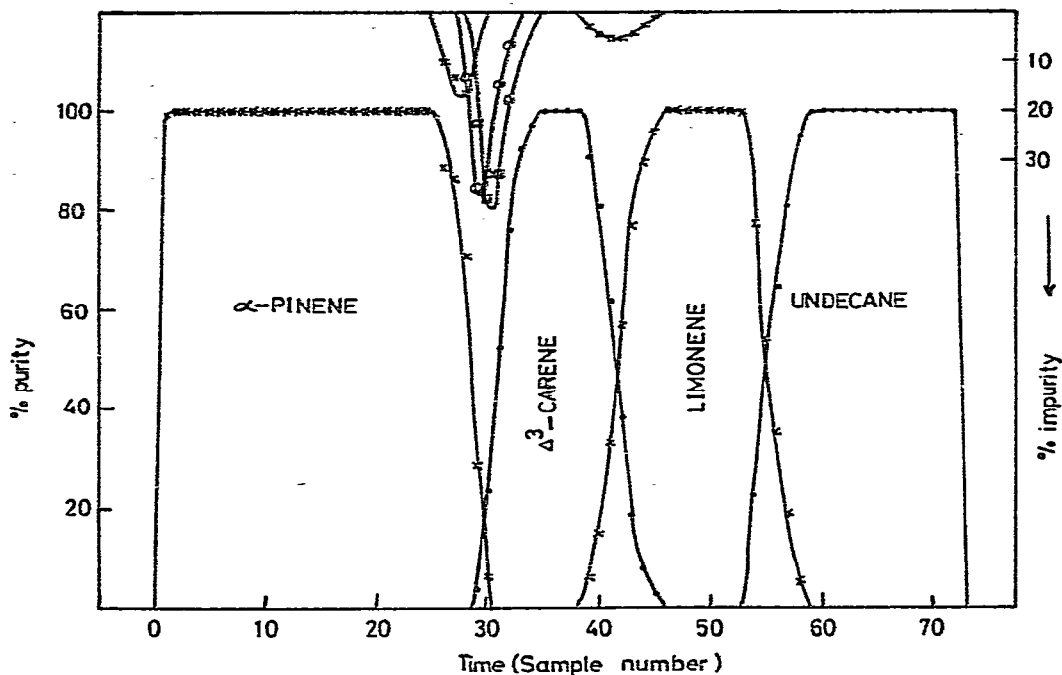
Fig. 4. Separation of a 1.5-g mixture of α-pinene, Δ³-carene, and limonene with concentration of four unidentified impurities. Undecane was added to act as "thermal buffer". Column, 50 × 1 cm I.D.; adsorbent, Porapak Q at 85°; nitrogen flow-rate, 200 cm³ min⁻¹; heater temperature, 300°; heater speed, 20 cm h⁻¹.

Reaction and separation

Further variations on the heater displacement principle are possible if the column adsorbent is a catalyst on which reactions take place at the temperature induced by the moving heater while only separation takes place ahead of the heater in the cooler parts of the column. It should thus be possible to carry out reaction and separation on the preparative scale in one single operation. We have as yet done relatively few experiments in this particular mode of operation, and it has become clear that in most cases a rather delicate choice of the conditions (thus the gas flow-rate, heater temperature, and heater speed markedly affect the amount of reaction occurring in the heater zone), and the catalyst and the adsorbent may be necessary to achieve optimum results. The general principles may, however, be illustrated by the chromatograms of Figs. 5–7.

Fig. 5. shows the results of a dehydrochlorination reaction on Al₂O₃ modified with KCl. The three olefins formed in the reaction in the heater are reasonably separated on the same material in the parts of the column ahead of the heater which were kept at room temperature. One interesting feature of this chromatogram is the combination of two of the products of the reaction, namely HCl and 1,1-dichloroethylene, to give 1,1,1-trichloroethane which emerges as a peak between the *cis-* and *trans-*1,2-dichloroethylene isomers. Fig. 6 shows the reaction of a sample of *n*-decane on a Ni–SiO₂ column under hydrogen carrier gas. Hydrocracking of the *n*-decane occurs
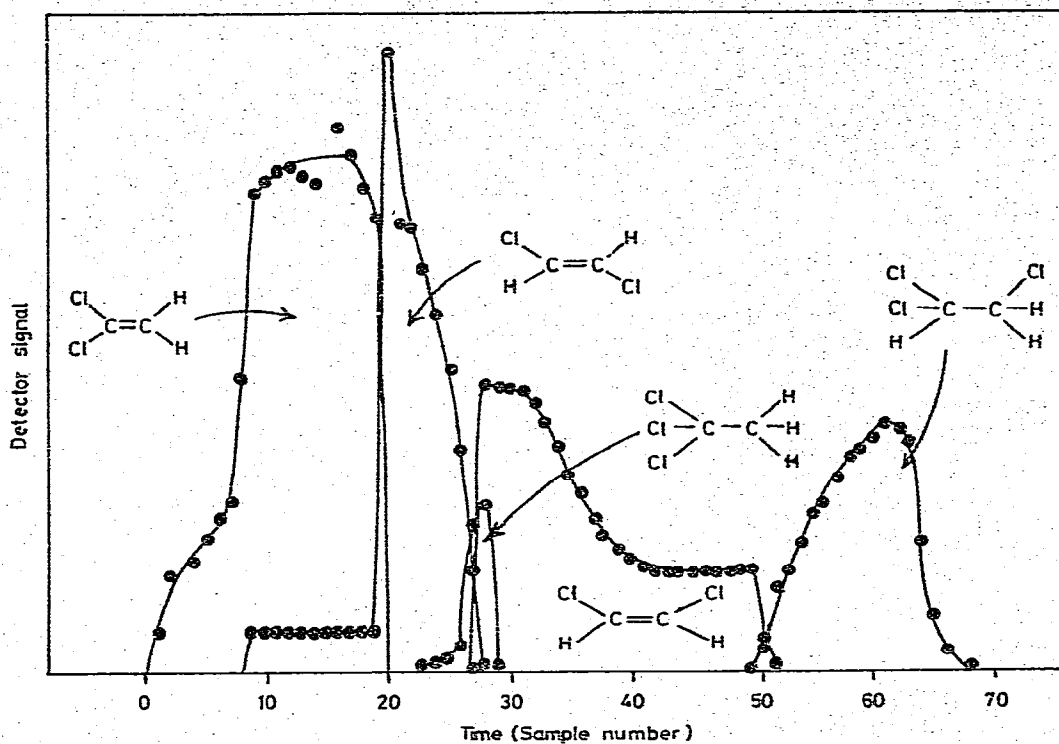
Fig. 5. Reaction (dehydrochlorination) of 1,1,2-trichloroethane (0.3 g) followed by partial separation of products on 5% KCl–Al₂O₃. Column, 30 × 1 cm I.D. at 18°; heater temperature, 500°.

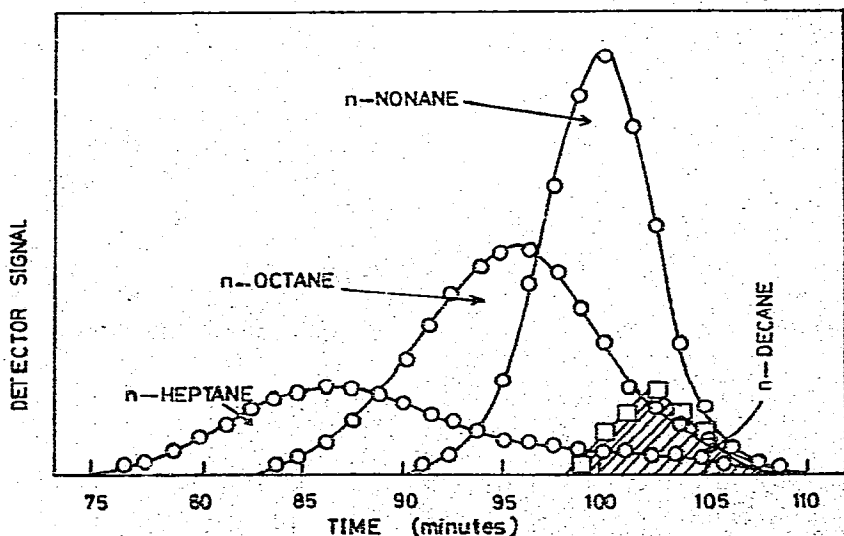Fig. 6. Reaction (hydrocracking) of *n*-decane (0.02 g) followed by partial separation of products on 2.3% Ni–SiO₂. Column, 33 × 1 cm I.D. at 125°; hydrogen flow-rate, 10 ml min⁻¹; heater temperature, 180°; heater speed, 20 cm h⁻¹.

largely by successive steps[6] to n-nonane, n-octane, etc., and these are then partially separated on the catalyst ahead of the heater. However, by packing the lower part of the column with a catalytically inactive adsorbent (which need not even be in the same oven as the catalyst) the reaction could be made to cease when the heater reaches the end of the Ni–SiO$_2$, so that only separation occurs in the last part of the column.

A particularly interesting possibility arises when the catalysed reaction involves an isomerisation, because the continuing sequence of reaction, separation, and re-reaction then offers the potential of driving the reaction beyond its thermodynamic equilibrium position and eventually to the production of only one isomer in high yield. The result of a preliminary experiment on the isomerisation of n-hexane is illustrated in Fig. 7. The original n-hexane is isomerised to a mixture of n-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane (there is also some hydrocracking to n-pentane, etc.) on the Pt–Al$_2$O$_3$ catalyst in the heater zone. The isomers then begin to separate ahead of the heater, but the n-hexane and the less branched isomers lie at the rear of the displacement sequence and thus come into
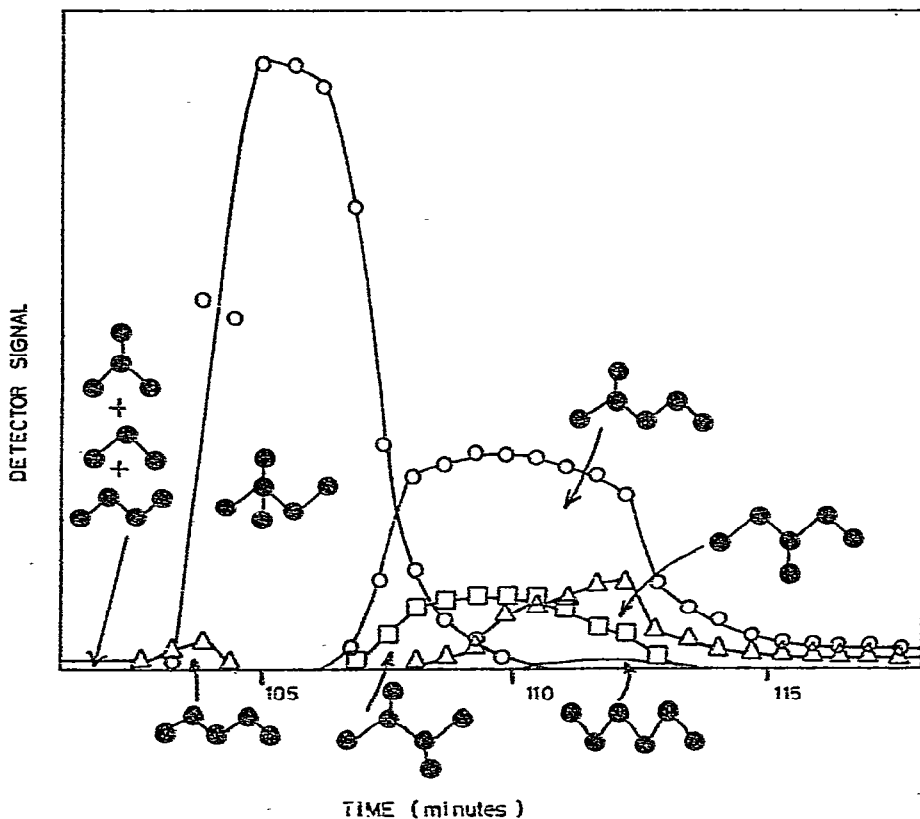

TIME (minutes)

Fig. 7. Continuous reaction (isomerisation) and partial separation of products from n-hexane (0.7 g) on Pt–Al$_2$O$_3$ (Engelhard RD-290C activated with CCl$_4$). Column, 100 × 1 cm I.D. at 18°; hydrogen flow-rate, 30 cm^3 min^{-1}; heater temperature, 120°; heater speed, 50 cm h^{-1}. Reaction has so far proceeded to 99.5% conversion of the n-hexane with a 46% yield of 2,2-dimethylbutane. 4.5% of the n-hexane has been hydrocracked to lighter material, eluting ahead of the displacement bands.

repeated contact with the active (hight-temperature) part of the catalyst, so that the doubly branched isomers are continuously increased at the expense of the less branched isomers. Eventually the reaction should give rise to 2,2-dimethylbutane as almost the only product. As the highly branched alkane isomers have much higher octane (anti-knock rating) values, this might be of some commercial application.

ACKNOWLEDGEMENTS

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