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A SAMPLE TRAPPING AND REINJECTION TECHNIQUE FOR USE WITH GAS CHROMATOGRAPHY

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SUMMARY

A technique for the collection and transfer of microgram or submicrogram quantities of gas chromatographic fractions is described. The technique has proved extremely useful for the examination of trapped components by combined carbon-skeleton gas chromatography–mass spectrometry.

INTRODUCTION

In the identification of trace components of volatile mixtures the chemist is often hampered by the limited amount of material available. Mass spectra can be obtained by combined gas chromatography–mass spectrometry (GC–MS), but with completely unknown samples positive identification based purely on mass spectral evidence can be difficult. The problem encountered in the isolation of sufficient pure material for examination by infrared and nuclear magnetic resonance spectroscopy often renders these techniques inapplicable as aids to identification. In such cases, valuable structural evidence can be obtained from retention time data and microchemical techniques such as carbon-skeleton gas chromatography[1,2] and on-line[3–5] or off-line[6] hydrogenation. For optimum performance, such techniques require the trapping and reinjection of microgram or submicrogram quantities of material without the use of solvents. Brownlee and Silverstein[7] have successfully trapped GC fractions in glass capillaries and reinjected them using a capillary breaker. Bierl *et al.*[8] have described a collection and transfer device using traps packed with coated support, but these authors reported a broadening of the trapped and reinjected peaks. Murray *et al.*[9] have developed a technique for reinvestigation of trapped components on capillary columns using an injector system built into the lid of a laboratory-built gas chromatograph. This technique has now been adapted for use with a conventional commercial gas chromatograph. It provides an efficient transfer of trapped components when used in conjunction with packed columns, and further has found useful application in the investigation of gas–liquid chromatographic fractions by hydrogenolysis and hydrogenation.

EXPERIMENTAL

Apparatus

The trap (Fig. 1A) was a thin-walled (0.42 mm) stainless-steel tube (102 × 3.2 mm

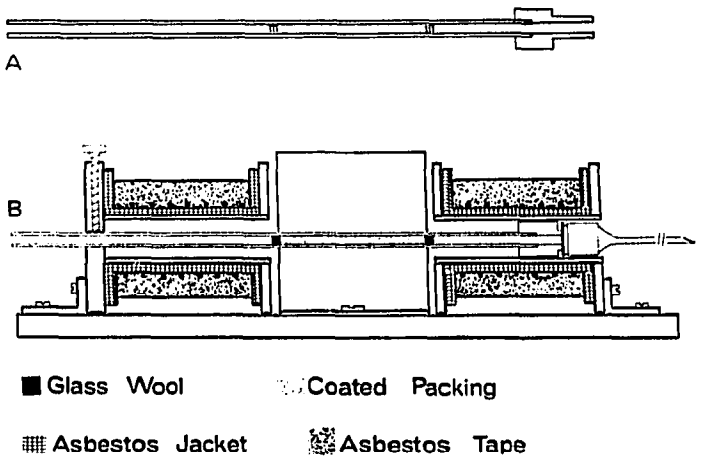

Fig. 1. (A) Stainless-steel collection tube; (B) cross section of the collection-tube heater with tube in position.

O.D.) with a male luer adaptor silver soldered to one end. A packing of glass wool or coated support was placed in the trap in the region which occupies the space between the two sections of the collection tube heater (Fig. 1B). The latter was constructed of brass. Each section consisted of two discs (31.75 mm diameter) attached to a tube (29 × 8 mm I.D.). An asbestos jacket was fitted to the two sections which were then wound with nichrome wire to yield a maximum temperature of 200° when used with a 32-V power supply. A layer of asbestos insulation tape was then applied and the two sections attached to a brass plate (114 × 38 × 4.8 mm) leaving a space in the centre (28 mm) to accommodate the hot and cold probes. A brass plate was fixed to the central section to support the two probes. The heater was mounted on a block of Syndanio board and attached to the gas chromatograph by means of two grooved right angle brackets (Fig. 2). The hot and cold probes were constructed according to Murray *et al.*[8].

Operation

Two gas chromatographs were used. Samples were collected from a Varian Aerograph 204 instrument fitted with a 5% SE-30, 1.5 m × 6.4 mm aluminium column. The collection tubes were attached to the exit port of the gas chromatograph using Swagelok fittings and Teflon ferrules and were cooled in the packed region with dry ice.

The injector device was attached to a Varian Aerograph 1740 instrument and the trapped samples reinjected onto a 1.5 m × 3.2 mm stainless-steel column packed with 3% SE-30 on 100–120 mesh Varaport. A miniature three port valve was installed to direct the carrier gas either to the GC column or to the front of the collection tube.

To reinject a collected sample, the collection tube is inserted partially into the heater from the rear and the syringe needle (19.05 mm, 26 gauge) attached.

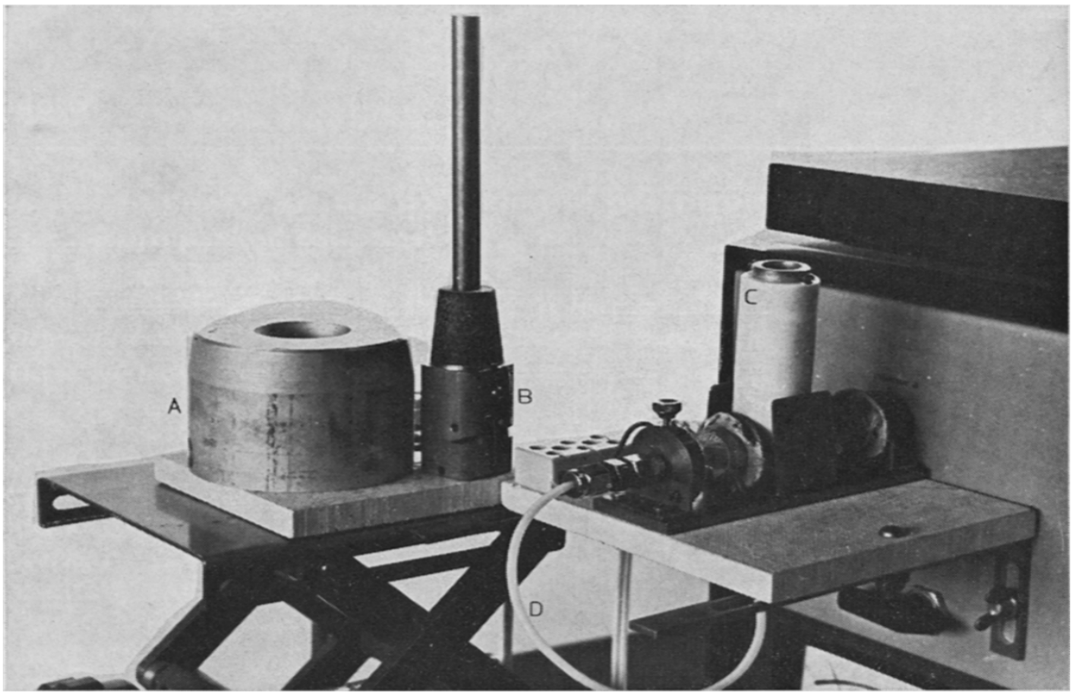

Fig. 2. Collection-tube heater attached to gas chromatograph. (A) Aluminium block heater for hot probe; (B) hot probe; (C) cold probe; (D) Teflon line for redirecting the carrier gas.

After insertion into the heater to the hilt of the needle the tube is held in position by tightening the thumb screw (Fig. 1B). The 3.2-mm Teflon line for the redirection of the carrier gas is attached to the front of the tube using a Swagelok union and Teflon ferrules. The packed section of the tube is now cooled by application of the cold probe, cooled with liquid nitrogen, and the carrier gas is diverted through the tube. The injection unit is pushed forward on the grooved brackets until the syringe needle penetrates the septum of the injection block. With the cold probe still in position, the low-voltage power supply to the two heating sections is switched on. When these reach a steady temperature, the sample is injected by removal of the cold probe and application of the hot probe pre-heated to a selected temperature in an aluminium block fitted with a cartridge heater. A tube cooled to $-110°$ attains a temperature of 150° in approximately 6–8 sec by application of the hot probe at 220°.

RESULTS

Fig. 3a shows the chromatogram obtained for a 1-μg sample of *n*-tridecane in methylene chloride injected by the conventional method using a syringe. Fig. 3b shows the chromatogram of 1 μg of the same sample after collection on 30–40 mesh Chromosorb A coated with 10% SF-96 and reinjected by the method described above. There is no loss in resolution of the column and no tailing of the peak although the sample is retarded slightly. There is a slight loss in sample some of which is

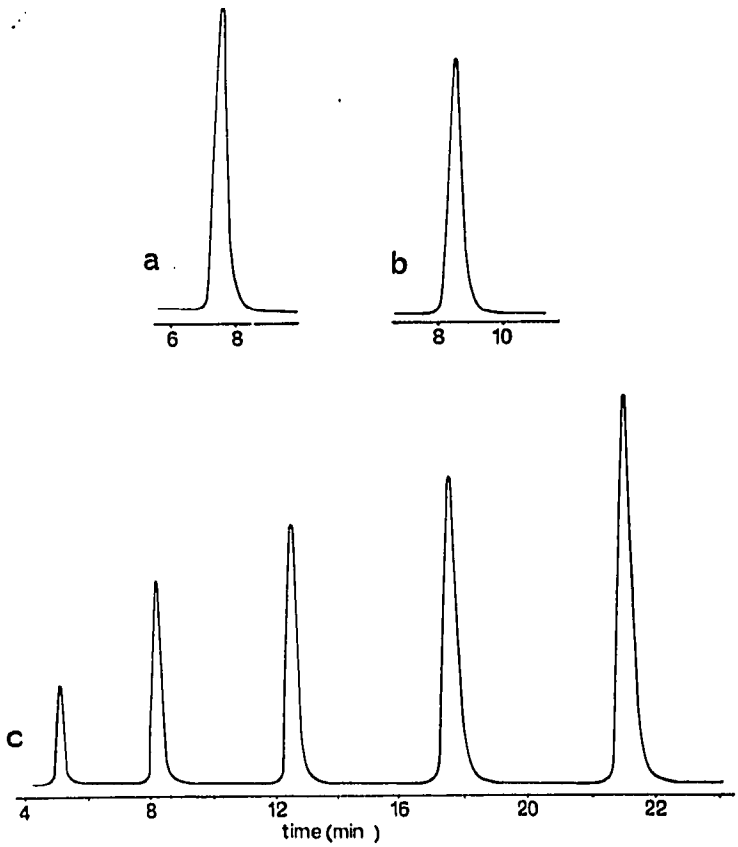

Fig. 3. (a) 1-μg sample of *n*-tridecane injected by conventional syringe method. Column, 1.55 m × 3.2 mm 3% SE-30; temperature, isothermal at 100 °. (b) 1-μg sample of *n*-tridecane after trapping and reinjection. Column as in (a). (c) *n*-C_{11}–C_{15} hydrocarbons injected by injector device. Column as in (a); temperature programmed from 100 ° at 2 °/min.

accounted for by the split ratio of the effluent splitter on the preparative instrument.

Fig. 3c shows the chromatogram for the series of *n*-alkanes C_{11}–C_{15} after trapping and reinjection. Again the peaks were as sharp as those obtained by conventional syringe injection under the same conditions. The technique thus provides an efficient method for the collection and reinjection of GC fractions on a second stationary phase or for investigation by combined GC–MS.

MS when used in conjunction with carbon-skeleton GC can provide a means of rapid analysis of the hydrogenolysis products. The device described above proved extremely useful in the examination of trapped components by combined carbon-skeleton GC–MS, a decided advantage being that microgram samples could be handled and injected without the use of solvents. Hydrogen was used as carrier gas and the catalyst, 500 mg of neutral 1% palladium on Chromosorb W (ref. 2), was contained in an injection port liner (a 140×6.4 mm O.D. stainless-steel tube). The hydrogenolysis products were investigated using a 1.5 m×3.2 mm stainless-steel column packed with 5% SE-30 on 80–100 mesh Chromosorb W. The gas

TABLE I
ANALYSIS OF HYDROGENOLYSIS PRODUCTS BY GC–MS
Catalyst, 1% Pd–Chromosorb W; temperature, 250°.

Compound	*Product*
Citral	2,6-Dimethylheptane
n-Decanal	Nonane
2-Methylcyclopentanone	No reaction
2-Methyl-5-ethylcyclopentanone	No reaction

chromatograph was connected to an AEI MS12 mass spectrometer via a single stage Llewellyn separator. Samples (10–50 μg) were trapped in collection tubes packed with glass wool and injected onto the catalyst as described above. Some preliminary results are summarised in Table I.

The two aldehydes citral and *n*-decanal were reduced almost quantitatively to the hydrocarbons 2,6-dimethylheptane and *n*-nonane whereas the two cyclopentanones passed over the catalyst unchanged.

The device has also been used successfully for the hydrogenation of olefins using the injection port hydrogenator described by Beroza and Sarmiento[4], the products were again analysed by combined GC–MS.

CONCLUSION

The injector device provides an efficient method for the trapping and injection of samples into a conventional gas chromatograph. It provides a means of handling and transferring microgram quantities of material without the use of solvent, which is an advantage in the investigation of compounds by carbon-skeleton GC. It offers a simple and effective means for the trapping of a minor component of a complex mixture for investigation by micro-chemical techniques and has been used successfully in this manner in this laboratory for the investigation of insect volatiles by combined carbon-skeleton GC–MS[10].

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REFERENCES

1 M. Beroza, *Anal. Chem.*, 34 (1962) 1801.
2 M. Beroza and R. Sarmiento, *Anal. Chem.*, 35 (1963) 1353.
3 T. L. Mounts and H. J. Dutton, *Anal. Chem.*, 37 (1965) 641.
4 M. Beroza and R. Sarmiento, *Anal. Chem.*, 38 (1966) 1042.
5 V. Koman, *J. Chromatogr.*, 45 (1969) 311.
6 G. Stanley and K. E. Murray, *J. Chromatogr.*, 60 (1971) 345; and references therein.
7 R. G. Brownlee and R. M. Silverstein, *Anal. Chem.*, 40 (1968) 2077.
8 B. A. Bierl, M. Beroza and J. M. Ruth, *J. Gas Chromatogr.*, 6 (1968) 286.
9 K. E. Murray, J. Shipton and F. B. Whitfield, *Aust. J. Chem.*, 25 (1972) 1921.
10 G. W. K. Cavill and E. Houghton, to be published.