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Note

Sampling method in capillary column gas–liquid chromatography allowing injections of up to 250 μl

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In gas chromatographic trace analysis, on the one hand we make great efforts to reduce detection limits to extreme levels, and on the other hand only a small amount of the isolated material is analysed, while most is usually wasted in capillary column gas–liquid chromatography. After splitting, only a fraction of a microlitre passes to the column and finally to the detector for quantification.

Various proposals have been made for overcoming this problem. The best known is the Grob and Grob-type splitless injection technique[1,2] and its modifications[3]. Another technique involves the use of a moving-needle system[4]. In general a maximal volume of 5 μl can be handled by these systems.

Because it is desirable to inject larger volumes, we have developed a split–splitless injector that allows the introduction of very large amounts of sample. Preliminary results of our studies are presented here.

EXPERIMENTAL

Injection system

The split–splitless injector was designed for a Varian 1440 gas chromatograph. The injection port together with the electronic control unit was removed and replaced by our injector, consisting of a thin-walled metal tube of very low thermal capacity, with a length similar to that of the original device. It can be heated rapidly by a heat-conducting coil (Philips Elektronik Industrie, Hamburg, G.F.R.) which is controlled by a thyristor circuit. For pre-heating, the carrier gas line was wound side by side with the heater coil. The glass insert was modified so as to obtain an optimal gas stream at the splitting point. Splitting was controlled by a vent-off valve. A 25-m SE-30 open-tubular glass capillary column (I.D. 0.27 mm) was used with nitrogen as the carrier gas. The inlet pressure was 1.0 bar and the flow-rate 1.2 ml/min.

Materials

The experiments were performed with test mixtures consisting of a homologous series of hydrocarbons (C_{18}–C_{30}) as proposed by Schomburg *et al.*[5], fatty acid methyl esters (C_{16}–C_{19}), and dimethylthiophosphinic esters of aromatic hydroxy acids[6].

RESULTS AND DISCUSSION

Like the moving-needle system, the proposed injector makes use of the different boiling points of the solvent and the sample constituents. However, its special construction enables us to apply far greater amounts of solutions.

The principles can be summarized as follows. Prior to the introduction of the sample, the injector is cooled to the appropriate temperature, which is preferably higher than the boiling point of the solvent used. Within approximately 40 sec up to 250 μl of the sample are slowly injected with the splitter valve fully open; the splitting ratio is 1:600. The solvent is thereby evaporated and flushed by the carrier gas through the vent-off valve. The sample constituents remain in the glass insert. After a few seconds, the splitter valve is closed and the interior of the injector heated immediately to the volatilization temperature of the sample (*e.g.*, 340°). The column is held at the starting temperature of the programme during this step. After a few minutes the temperature programme is run and the separation performed as usual.

The reproducibility of the technique was demonstrated by injecting different volumes of sample containing the same amounts of the compounds to be analysed. For example, a series of even-numbered alkanes (C_{18}–C_{30}) with alternating concentrations in carbon disulphide was analysed (Fig. 1). The peak areas from a 100-μl

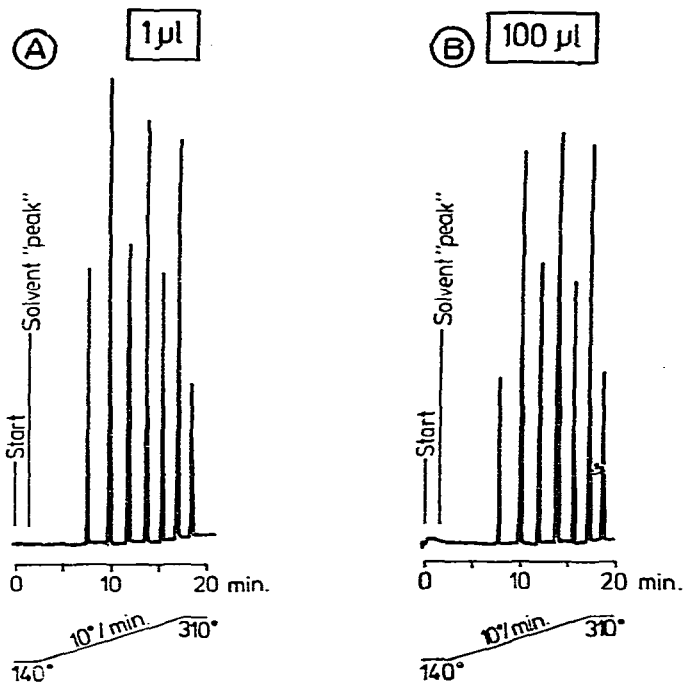

Fig. 1. Gas chromatograms from (A) a 1-μl and (B) a 100-μl injection of a series of even-numbered alkanes dissolved in carbon disulphide. The total amounts of the hydrocarbons were the same in each instance. The concentrations in solution A were C_{18}, C_{22}, C_{26} and C_{30} 250 ng/μl and C_{20}, C_{24} and C_{28} 500 ng/μl, and in solution B 2.5 and 5.0 ng/μl, respectively. The injector starting temperature was 50° and the vaporization temperature 320°. The column was 25 m × 0.27 mm I.D. SE-30, with nitrogen as carrier gas at a flow-rate of 1.2 ml/min, temperature programmed from 140° (4 min) to 310° at 10°/min. A flame-ionization detector was used, temperature 290°.

injection (Fig. 1A) agree well with those from a 1-μl injection (Fig. 1B), with the exception of the first (C_{18}). Similar results were achieved with other compounds, such as methyl esters of fatty acids or dimethylthiophosphinates. In addition, the retention times correspond well with each other. The peaks were sharp and showed no tailing. With carbon disulphide no solvent peak was observed at the expected retention time (Fig. 1), whereas only a small peak appeared when using hydrocarbons such as *n*-hexane. This solvent-free chromatography is an advantage over the common splitless injection techniques; the lifetime of the capillary column is prolonged and the chromatographic properties are enhanced.

A disadvantage of all large-volume injection systems is the relatively rapid contamination of the insert[7]. In some instances the glass insert has to be changed after each analysis. This effect has been considered in the mechanical construction of our device, and the replacement of the insert is rapid and simple.

In our opinion the proposed sampling technique increases decisively the overall sensitivity in gas chromatographic trace analysis.

REFERENCES

1 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 584.
2 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 587.
3 M. Novotny and A. Zlatkis, *J. Chromatogr. Sci.*, 8 (1970) 346.
4 P. M. J. van den Berg and Th. P. H. Cox, *Chromatographia*, 5 (1972) 301.
5 G. Schomburg, H. Behlau, R. Dielmann, F. Weeke and H. Husmann, *J. Chromatogr.*, 142 (1977) 87.
6 K. Jacob, E. Maier, G. Schwertfeger, W. Vogt and M. Knedel, *Biomed. Mass Spectrom.*, 5 (1978) 302.
7 F. J. Yang, A. C. Brown, III and S. P. Cram, *J. Chromatogr.*, 158 (1978) 91.