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EXPERIMENTS IN SOLID SAMPLING GAS CHROMATOGRAPHY

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SUMMARY

The influence of probe material on the total evaporation time of compounds injected into the gas chromatograph by solid sampling has been investigated. A quartz needle was found to give the shortest evaporation time. The type of analysis will, however, to some extent determine the probe material to be chosen. A comparison of solid sampling with liquid sampling showed that the former has a higher degree of reproducibility.

INTRODUCTION

Recent publications in which numerous types of solid sampling devices and a wide range of applications were described indicate that solid sampling gas chromatography is becoming increasingly common. Applications have been reported in the fields of pharmaceutical and biological analysis[1–10] and in the analysis of technical products[11–13]. Solid sampling may be a valuable addition to the ancillary techniques of gas chromatography.

Many solid sampling analyses are carried out with the solid deposited on some sort of carrier material, such as metal, glass-wool, quartz and filter-paper[14–18]. The evaporation time of the sample is of vital importance to the quality of the analysis. The sample must be converted into vapour in a small volume in a short time in order to obtain sharp, symmetrical peaks. The evaporation time depends on the properties of the carrier material and of the substances to be analyzed.

This paper describes the results of solid and liquid injections carried out on two substances that differ considerably in their polarity, *viz.* warfarin and a normal hydrocarbon, *n*-octadecane (C_{18}). *n*-Octadecane was chosen because it is suitable for GLC analysis, and the more polar compound, warfarin, was chosen because it represents a typical drug molecule in polarity. Warfarin gives a low response to the flame ionization detector, it easily gives tailing and is usually analysed as a derivative[19,20]. The purpose of this paper is to report some aspects of solid sampling. We have studied the evaporation rates of the two substances when different carrier

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materials were used and the reproducibility of injections carried out by liquid and solid injection.

EXPERIMENTAL

Apparatus

The gas chromatograph was a Becker Model 409 (Becker, Delft, The Netherlands), with a flame ionization detector. The column was a 2-m long glass coil, I.D. 2 mm, with 3% OV-17 on Chromosorb W (acid washed and dimethyldichlorosilane treated), 60–80 mesh, as the stationary phase and a carrier gas (nitrogen) flow-rate of 30 ml/min. The temperatures used were: flash heater, 280°; column, 170°; and detector, 280°. The sensitivity setting was 4×10. The integrator used was a Kent Chromalog 2 (Kent Instruments Ltd.) and the syringe was a Hamilton 701 N. The solid sampler has been described elsewhere[17].

Carrier materials

The filter-paper was Selecta No. 595 (Schleicher & Schüll, Dassel, G.F.R.), and Whatman glass-fibre paper was used. The following metal spirals were used: platinum, 0.1 mm diameter; nickel–titanium–chromium alloy, 0.1 mm diameter (Kanthal); nickel–copper alloy, 0.3 mm diameter; nickel–chromium alloy, 0.2 mm diameter (Nichrome). The quartz needle was 1.5 cm long and 0.2–0.3 mm diameter.

The filter-paper and the glass-fibre paper (20×2 mm) were mounted directly on a basket screwed to the stainless-steel rod of the injector. The metal spirals and the quartz needle were fastened to a separate screw mounting, which also could be fitted to the stainless-steel rod. By means of the rod, the probe materials with the sample could be moved into the flash heater of the gas chromatograph.

Evaporation rate analyses

With the syringe, 1 μl of a solution of warfarin or *n*-octadecane in chloroform (1 μg/μl and 50 ng/μl, respectively) were applied on to the carrier material. The solvent was allowed to evaporate at room temperature and the injector was then mounted on the gas chromatograph. The sample was pushed into the flash heater of the gas chromatograph, retained there for a certain time interval and then removed. A second and then a third injection were carried out on the same sample until the evaporation was complete. The detector signals were registered by the electronic integrator and the amount of the test substance that evaporated during the first injection was calculated.

Reproducibility

Twenty-six single liquid and solid injections were carried out with *n*-octadecane. A 1-μl volume was injected by the syringe and 1 μl *n*-octadecane solution (20 ng/μl) was applied on a quartz needle. The injections were carried out as described above. The detector signals were measured by the integrator and the coefficient of variation was calculated.

RESULTS

Evaporation of n-octadecane

With all of the investigated carrier materials, complete evaporation was achieved within 5 sec.

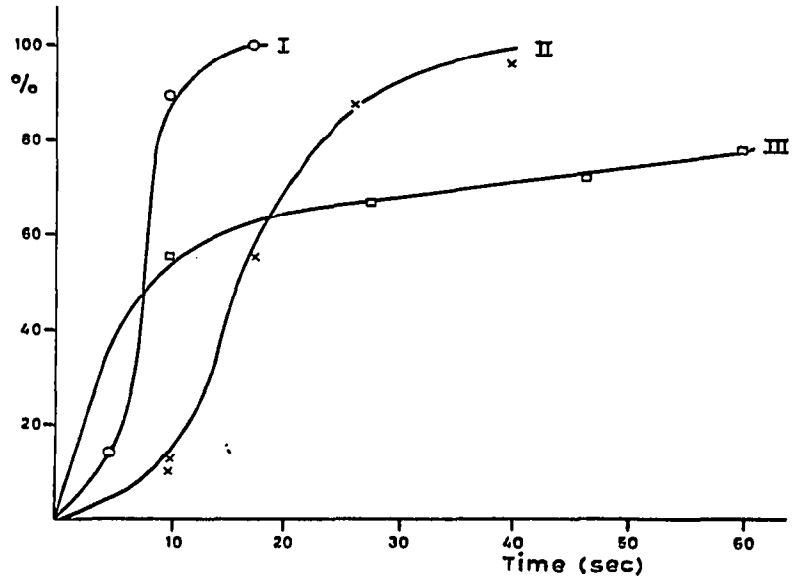

Fig. 1. Percentage of warfarin evaporated as a function of the injection time. I = quartz needle; II = nickel–copper alloy; III = glass-fibre paper.

Evaporation of warfarin

Quartz needle. The evaporation of warfarin from the quartz needle is shown in Fig. 1. Total evaporation was effected within 20 sec.

Filter-paper. On filter-paper 50% of the sample evaporated within 5 sec, but the remaining solid evaporated more slowly. Silylation or covering the paper with stationary phase (OV-17) did not influence the evaporation rate.

Filter-paper also contains components that evaporate when introduced into a gas chromatograph. Most of these components are removed before the analysis by heating the filter-paper in a stream of nitrogen at the flash heater temperature. The volatile components are not, however, completely evaporated, but the paper is sufficiently cleaned to allow the analysis of larger samples (1–10 μg). The residual volatile substances in the filter-paper will adversely affect an analysis if it has to be carried out near the detection limit of the substances being analyzed.

Glass-fibre paper. Surprisingly, the evaporation of warfarin from this material took place slowly. Silylation or covering the paper with stationary phase did not shorten the evaporation time. It is, however, well known that the presence of a plug of glass-wool in the column may result in tailing of semi-polar components, and this effect is clearly demonstrated here.

Metal spirals. The evaporation of warfarin from the nickel–copper alloy is shown in Fig. 1. More than 40 sec were necessary in order to ensure the evaporation of at least 90% of the solid. The evaporation pattern of the other alloys lies between those of the nickel–copper alloy and the quartz needle. The total evaporation time for the metal alloys could be reduced by using a thinner metal spiral.

Reproducibility

Repeated injections of 20 ng of *n*-octadecane gave a coefficient of variation of 3.3% for solid injection and 6.0% for syringe injection.

DISCUSSION

The evaporation of *n*-octadecane showed that the nature of the carrier material gave rise to no problems with a non-polar substance, but this was not so for the more polar compound, warfarin. We considered the quartz needle to be the best choice of material. Warfarin evaporated rapidly and the change of interactions with the probe material seemed to be minimal. Filter-paper, however, was not suitable for the analysis of nanogram amounts of warfarin, but its properties are useful for other types of analyses.

Fig. 2 shows chromatograms of warfarin and *n*-octadecane introduced into the gas chromatograph as a solid, a chloroform solution and a carbon disulphide solution. Volumes of 1 μl of the standard solutions corresponding to 400 ng of warfarin and 20 ng of *n*-octadecane were injected. Fig. 2 shows the advantages of the solid sampling technique: sharp, symmetrical peaks are obtained for both components, and no time lag is necessary for the detector to reach a zero-base line. Because of its low response to the flame ionization detector, carbon disulphide must be used as a solvent in order to obtain reliable chromatograms with syringe injection.

In order to investigate the reproducibility of the injection of the compounds by solid and liquid sampling, *n*-octadecane was chosen as the test substance, as no loss

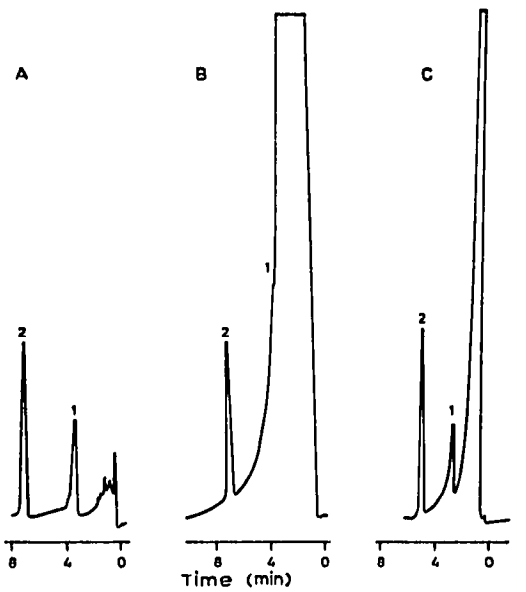

Fig. 2. Chromatograms of warfarin and *n*-octadecane introduced into the gas chromatograph as a solid on the quartz needle (A), in chloroform solution (B) and in carbon disulphide solution (C). Peaks: 1 = 400 ng of warfarin; 2 = 20 ng of *n*-octadecane.

of this compound due to adsorption in the column or thermolability was anticipated, and a good comparison of the two techniques could be expected. For the conditions chosen, solid sampling seemed to be preferable as the method of introduction.

CONCLUSIONS

No problems regarding the choice of probe material were encountered in solid sampling GLC of a non-polar substance such as *n*-octadecane. However, for a more polar compound, such as warfarin, the success of solid sampling GLC depended upon the construction of the probe. With regard to the reproducibility and the gain in analysis time, we believe that solid sampling GLC is advantageous when the GLC of semi-polar compounds in biological materials is to be carried out.

One of the advantages of solid sampling is the elimination of the need to use a solvent to transfer compounds isolated from biological materials into the carrier gas stream of a gas chromatograph. As it is not practical to concentrate a biological extract to a few microlitres in order to transfer the compounds quantitatively into the gas chromatograph, only a fraction of the compounds present can be analyzed. Solid sampling allows diluted solutions to be concentrated on the carrier material, thereby increasing the sensitivity of GLC analysis.

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