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SOLVENT TRAPPING IN CAPILLARY GAS CHROMATOGRAPHY

TWO-STEP CHROMATOGRAPHY

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SUMMARY

Solvent trapping is described as pre-chromatography of sample components on a layer of condensed solvent in the column inlet. As an approximation, the influence of sampling on the chromatography of components is determined by this pre-chromatography. This is the conclusion drawn for an experiment in which different sections of the material eluted from the layer of condensed solvent were analysed. It is therefore not necessary to take the stationary phase into consideration concerning solvent trapping effects.

INTRODUCTION

In a previous paper[1], solvent trapping effects were described as solvent effects occurring in the column inlet, *i.e.*, in the flooded inlet section of the column where condensed solvent or a dominating sample component is located. The term "solvent trapping" was chosen by analogy with "cold trapping", the other method used to retain sample components in the column inlet. The term "solvent effect" is considered to be more general, including all the ways in which the sample may influence its own chromatography, in particular the modification of the gas chromatography (GC) of a sample component by the presence of solvent or another component in the analytical part of the column.

Solvent trapping may occur whenever sampling creates condensed solvent in the column inlet, *i.e.*, in on-column sampling and in split or splitless injection under conditions leading to recondensation of the solvent (or dominating sample components). Solvent trapping may be useful; often it occurs without being noticed, but it may also be a source of trouble when retention times are disturbed or peaks are broadened and distorted owing to partial solvent trapping.

Solvent trapping may solve two problems. First, it may reconcentrate the broad initial bands originating from slow sample transfer from the injector to the column in splitless injection. Second, full solvent trapping releases the sample components within a very short time, so the latter start to be chromatographed as a short band. This is of interest also in cold on-column sampling. The evaporation of a 2-μl

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volume of liquid creates about 0.5 ml of vapour. Instantaneous and complete evaporation of such samples would (in addition to the problem of the removal of the vapour) create broad initial bands, *e.g.*, bands of 15 sec width at a carrier gas flow-rate of 2 ml/min. However, solvent trapping retains the fully trapped sample components in the condensed solvent. The solvent evaporates first from the rear to the front of the flooded zone and relases the components only at the very last moment of its evaporation, *i.e.*, within a short period of time.

Non-trapped components are negligibly retained in the condensed solvent. Their chromatography (retention and peak width) is not influenced by the solvent layer in the column inlet. In isothermal splitless sampling their peaks are broad and reflect the slow sample transfer from the injector to the column. In cold on-column injection non-trapped components form peaks with virtually no broadening because the sample transfer is rapid.

Partially trapped components form broadened and distorted peaks. Their initial band is broadened because of slow evaporation out of the condensed solvent. This evaporation may last as long as the evaporation of the solvent, which may range from seconds to several minutes. Partial solvent trapping is seen for components that are volatile at the column temperature during injection, especially if they are weakly retained (solvated) by the solvent. Partial solvent trapping of components eluted after the solvent is exceptional, whereas most peaks eluted before the solvent are distorted owing to partial solvent trapping.

This paper extends the description of solvent trapping. An experiment is described that supports the view that the common solvent effect is a solvent trapping effect and that the solvent trapping may be considered as pre-chromatography of the sample components on the condensed liquid. Thus, under solvent trapping conditions there are two chromatographic steps, which may be regarded as being independent of each other.

In the first step the sample components are chromatographed in the solvent layer. The stationary phase in the column inlet, if present, may be regarded as irrelevant because the thickness of the solvent layer exceeds many-fold the common film thicknesses of the regular stationary phase.

The second chromatographic step is carried out in the regular coating of the stationary phase, *i.e.*, in the major part of the column. Solvent effects occur during this step. In the experiments described in this paper, with commonly used test components and conditions, they may be noticed, but they do not have an important influence on the final results.

The chromatography of the sample in its own solvent is complex. First, the sample components do not start chromatography as a short band because they are spread out throughout the solvent as the solvent expands further into the column primarily by a flow of liquid. Second, the thickness of the solvent layer is irregular (there are visible waves) and this thickness is reduced as the liquid spreads out further into the column.

EXPERIMENTAL AND RESULTS

Chromatography on the solvent

We studied the elution of the sample components from the layer of condensed

solvent in the column inlet using a glass capillary column that consisted of two parts, representing the flooded inlet and the main analytical column. They were joined with a short piece of shrinkable PTFE tubing, allowing easy disconnection and reconnection inside the GC oven during a chromatographic run.

The first part of the column, mounted into a cold on-column injector (Model 4160, Carlo Erba, Milan, Italy), was 1 m long and Carbowax-deactivated but uncoated. This capillary tubing had a heavily etched inner wall, giving it a milky aspect. Condensed liquid rendered this surface transparent, allowing easy observation of where and for how long there was condensed solvent. The second part of the column consisted of an ordinary glass capillary, 20 m × 0.32 mm I.D., treated with barium carbonate and coated with a 0.18-μm thickness of Pluronic L61.

Fig. 1 shows the composition of the sample used for the experiment to be described. A. 1.7-μl volume of an *n*-hexane solution containing about 20 ppm of 2-propanol, benzene, *n*-octane and methyl butyrate was injected. The mixture was chosen to give a selection ranging from the sparingly trapped 2-propanol through the increasingly, but still only partially, trapped benzene and methyl butyrate to the fully trapped *n*-octane. At the low carrier gas flow-rate chosen (1.5 ml/min of hydrogen) and an oven temperature of 31°C, the evaporation time of the solvent in the column inlet was about 72 sec.

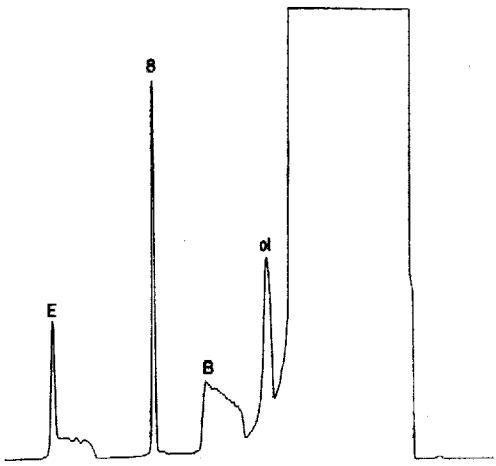

Fig. 1. Chromatogram of the mixture used to investigate the elution of sample components from the pre-chromatography on the condensed solvent in the column inlet: hardly trapped 2-propanol (ol), partially trapped benzene (B) and methyl butyrate (E) and fully trapped *n*-octane (8). Cold on-column injection of a 1.7-μl volume. Column, see text; 0.3 atm hydrogen as carrier gas.

For the first series of experiments the two parts of the column were joined during injection. The pre-chromatography of the sample components on the solvent was allowed to run for selected periods of time during which some solvent evaporated together with part of some sample constituents. This pre-chromatography was interrupted at various stages by taking the two column sections apart and allowing the carrier gas to flush the remaining material from the inlet part. After a few seconds the two parts were joined again to elute the transferred sample material from the analytical column.

The chromatograms in Fig. 2 show such sections of the pre-chromatography. A comparison with Fig. 1 allows the elution pattern of the sample components from the *n*-hexane to be reconstructed. Fig. 2a represents the material transferred during the first 12 sec after injection. The solvent peak is still small and reveals some non-trapped impurities which are obscured in Fig. 1. 2-Propanol eluted to about 15% of the amount injected. More detailed determinations have shown that it started to elute from the *n*-hexane layer about 8 sec after injection. Benzene started to elute after approximately 10 sec and is represented in Fig. 2a by less than 10% of the amount injected. The chromatogram contains a trace of methyl butyrate, but no *n*-octane.

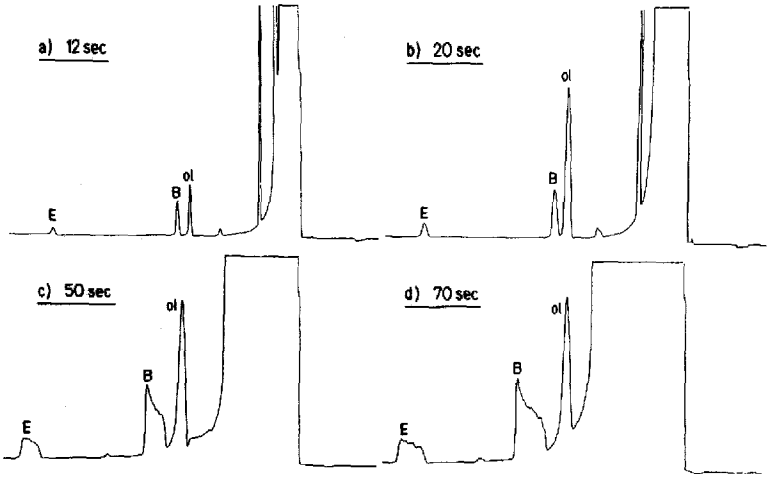

Fig. 2. Fractions of the chromatogram in Fig. 1. Material eluted from the column inlet section into the main analytical part of the column between the injection and a time selected before the solvent in the column inlet had fully evaporated (and released the final material of the sample components). Transfer time: (a) 12 sec; (b) 20 sec; (c) 50 sec; (d) 70 sec; solvent evaporation time, 72 sec. The sequence shows that the hardly trapped 2-propanol eluted early from the *n*-hexane layer, benzene and methyl butyrate were transferred during almost the entire transfer time, whereas *n*-octane and the sharp maximum of methyl butyrate remained in the final small portion of solvent left in the column after 70 sec. It is concluded that the major influence of sampling on the peak shapes (and the retention times) is due to solvent trapping, *i.e.*, pre-chromatography on the condensed solvent in the column inlet.

After a transfer time of 20 sec (Fig. 2b) more than 90% of the 2-propanol had left the condensed solvent. It is also apparent that the tail of the 2-propanol peak in Fig. 1 is not the result of adsorption in the column, but represents the small amount of material transferred only after a transfer time of more than 20 sec. Within the following 30 sec only benzene and methyl butyrate were transferred (Fig. 2c). Fig. 2d was obtained when the two columns were kept together up to a moment shortly before the condensed solvent had fully evaporated (transfer time about 70 sec). A wet section of about 3 cm length was left, coated with a relatively thin layer of condensed solvent as no waves were visible and its final evaporation was very rapid. The benzene peak in the resulting chromatogram resembles that in Fig. 1. The methyl butyrate peak consists only of the broad phase. Its sharp part is missing, as is the *n*-octane peak (the small shoulder near the expected retention of *n*-octane is an impurity). These must have been left in the last remaining portion of condensed solvent to be released within a short time at the very end of the trapping process.

Fig. 3 represents the material that is transferred from the inlet to the analytical part of the column during the last few seconds of the solvent evaporation. For this experiment, the inlet section was connected to another column serving as a restriction to allow a reasonable adjustment of the carrier gas flow-rate. When the injected

sample had nearly evaporated, the carrier gas supply was stopped, the injector opened to release the remaining pressure in the head of the capillary and the resistance column replaced by the analytical column. It took a further 5 sec to evaporate the remaining solvent in the inlet section.

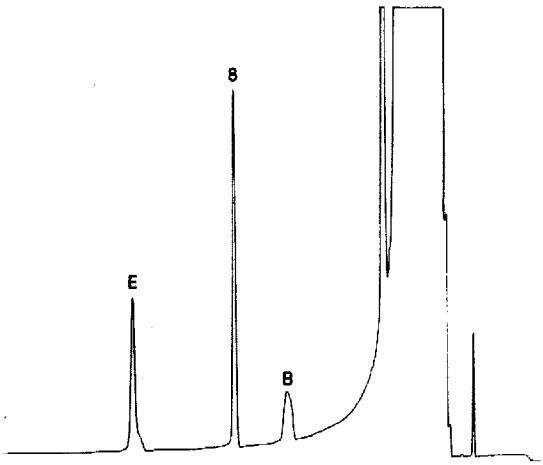

Fig. 3. Fraction of the chromatogram in Fig. 1. Material eluted from the column inlet into the main analytical column during the last 5 sec of the evaporation of the solvent. All of the 2-propanol had previously left the column inlet; there is a small final portion of benzene; the sharp maximum of the methyl butyrate and the complete *n*-octane are detected, the fully trapped materials, which were released only with evaporation of the last portion of condensed solvent.

The result shown in Fig. 3 corresponds to the expectations from Fig. 2. There is no 2-propanol and only a small, final portion of benzene. The missing sharp part of methyl butyrate and the *n*-octane were recovered.

These experiments confirmed that the deviations in the chromatography of the sample components due to the sampling are explained by the first chromatographic step in the condensed solvent, *i.e.*, that the deviations are the result of solvent trapping.

Other solvent effects

Even if the shape and the main retention behaviour of the peaks in Fig. 1 are determined by solvent trapping, a more detailed analysis of the chromatograms in Figs. 1–3 reveals some minor deviations of the experimental results from the predictions based exclusively on the solvent trapping mechanism.

Benzene started to elute from the layer of condensed solvent 10 sec after the injection. After a transfer time of 50 sec (Fig. 2c) the benzene peak had a width at its base of about 30 sec. After a transfer time of 70 sec (Fig. 2d) this width was increased to about 42 sec. Even if peak broadening due to the chromatography in the analytical part of the column is neglected, the elution from the pre-chromatography between 10 and 70 sec should have resulted in a base width of 60 sec. An analogous determination shows a similar reduction of the real from the predicted peak width for methyl butyrate. It is tempting to explain this observation with a solvent effect in the analytical column, *e.g.*, by the fact that the carrier gas is saturated with solvent vapour during the period of time condensed solvent is present in the column inlet. This solvent is partially retained in the stationary phase of the analytical part of the column and might increase its retention power.

The 2-propanol peak corresponded fairly well to the prediction based on pure

solvent trapping. Its base width in Fig. 2b is 13 sec, which is in agreement with the determined elution from the solvent between 8 and 20 sec. The retention time (determined at the maximum of the peak in Fig. 1) was increased by 17 sec compared with the retention of a peak obtained by an on-column injection of only about 0.1 μl (giving no solvent trapping). This is in a good agreement with the extra-retention in the solvent layer.

On the other hand, it may be noted that the 2-propanol and benzene peaks became shifted apart from each other the more *n*-hexane was transferred from the inlet to the analytical column (Figs. 2a and b and 1). This might again be explained by the extra-retention of the solvent containing stationary phase for benzene whereas 2-propanol was not affected by this solvent effect.

CONCLUSIONS

The experiments described above were carried out to provide a more solid background to our understanding of solvent trapping. At present the description of the solvent trapping is based on the following three types of information:

(a) Fully trapped components have an extra-retention time (compared with the retention time determined when no condensed liquid was present in the column inlet) that is directly related to the evaporation time of the solvent in the column inlet.

(b) The trapping behaviour of the sample components (non-, partial or full trapping) correlates with the expected retention of these components in the solvent. There was no influence of the stationary phase in the column inlet on the trapping characteristics[1].

(c) The retention and the shape of peaks of non-, partially or fully trapped components are correlated with the elution of materials from the flooded inlet section of the column.

We interprete our results as an indication that solvent trapping is the predominant solvent effect created by sampling that produces condensed sample in the column inlet. However, solvent effects in the analytical part of the column cannot be neglected.

Solvent trapping is independent of the regular stationary phase. Thus the stationary phase may be eliminated from the column inlet without affecting peak shapes. The elimination of the stationary phase is of interest in creating a retention gap[2,3] to reconcentrate bands broadened in space[4] and in reducing problems in everyday work caused by the column inlet such as phase stripping or contraction of the film coating due to contamination.

Our description of the solvent trapping should also rule out unnecessary complications in sampling techniques as introduced, *e.g.*, by Plotczyk[5] for the analysis of underivatized drugs. It is claimed (without supporting data or explanation) that the solvent used in splitless sampling must be soluble in the stationary phase because otherwise "ineffective reconcentration and poor ... solute peak shapes" would occur. For the described application it was concluded that mixed solvents or co-injections of two solvents are required.

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