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CONCURRENT ELUENT EVAPORATION WITH CO-SOLVENT TRAPPING FOR ON-LINE REVERSED-PHASE LIQUID CHROMATOGRAPHY GAS CHROMATOGRAPHY

OPTIMIZATION OF CONDITIONS

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SUMMARY

The pressure drop over a restriction built into the carrier gas supply line allows monitoring of the carrier gas flow-rate during transfer of a liquid chromatographic eluent into a gas chromatograph. A high inlet pressure indicates blockage of the gas flow by the plug of sample liquid; a layer of evaporating solvent still reduces the flow-rate owing to its vapour pressure, causing the inlet pressure to remain above that prior to transfer. The decrease in the inlet pressure at the end of the transfer provides the signal for closing the vapour exit, but also gives information for the optimization of the co-solvent concentration in the sample and of the column temperature during transfer. The co-solvent peak within the highly attenuated solvent peak indicates the amount of co-solvent left in the precolumn after the main solvent has been fully evaporated, helping to find the optimum co-solvent concentration in the sample.

PERSONAL COMMENT

G. Schomburg and the analysis of aqueous samples

Efforts to analyse aqueous samples can be traced through a large part of the work of G. Schomburg and his group. Two approaches were examined. In the early days, two-dimensional gas chromatography (GC) was applied to remove water from the sample by a first column packed with Tenax, followed by analysis of the sample by capillary GC[1–3]. On the other hand, aqueous samples were directly injected (by split or on-column injection)[4,5] to try to overcome the various types of peak distortion and shifts in retention times observed as soon as the amount of water entering the capillary column exceeds a certain level. Experiments between these two approaches involved a capillary column inlet thermostated separately in a double oven instrument[6]. Results showed that direct injection may be a very useful method, but also that it is limited to sample volumes of a small fraction of up to a few microlitres, depending on the precautions taken. For coupling reversed-phase liquid chromatography (LC) with capillary GC, the approach involving preseparation with a packed precolumn is more promising, and it remains the hope that this work will be continued.

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There is a long tradition in that Schomburg's group and ours are working on similar subjects but in different directions. In addition to the fact that this stimulates a thorough investigation of the various aspects, it also results in two alternative approaches being developed to a level that allows a deep evaluation. The subject of this paper is certainly such a case. It is not obvious whether direct transfer of water-containing LC eluents by the described technique, or the less direct transfer, *e.g.*, via a Tenax column, will be the superior method. Seen from the angle of retention powers, Tenax offers important advantages. It strongly retains the solute material while the retention power for water is minimal. In this respect, butoxyethanol, the co-solvent used in the work described here, can certainly not compete.

INTRODUCTION

What is concurrent eluent evaporation with co-solvent trapping?

Concurrent eluent evaporation[7] means evaporation of the LC eluent during its introduction into the GC system. No liquid penetrates into the GC precolumn. This allows the transfer of very large volumes of eluent (the maximum being 20 ml[8]), but early peaks are lost and/or broadened owing to co-evaporation with the eluent[9]. As a consequence, analysis may only start *ca.* 50–120°C above the column temperature during transfer. This restriction is particularly important if relatively high-boiling solvents (such as water) are involved, calling for high oven temperatures during transfer[10]. Further, highly polar solvents do not produce phase soaking[11], causing the temperature difference between introduction and elution of the first well shaped peaks to be particularly large.

Co-solvent trapping

Loss and/or broadening of early peaks, as observed with concurrent eluent evaporation, is due to the absence of solvent trapping[12]. This solvent effect causes volatile solute material to be retained in the inlet of the GC precolumn up to the end of solvent evaporation. Solvent trapping is ineffective because solvent evaporation takes place at the front, instead of at the rear of the liquid.

Co-solvent trapping strongly reduces this deficiency of concurrent eluent evaporation. As described in previous papers[13,14], a small proportion of a high-boiling co-solvent is added to the main solvent. While the main solvent evaporates concurrently, part of the co-solvent is left at the evaporation site. It forms a layer of liquid on the capillary wall and spreads into the uncoated precolumn as the transfer proceeds. This co-solvent, located ahead of the evaporation site, retains volatile solute material providing solvent trapping.

Co-solvent trapping versus partially concurrent solvent evaporation

In its principles, concurrent solvent evaporation with co-solvent trapping approaches partially concurrent solvent evaporation[15,16]. Both leave a layer of condensed solvent ahead of the main evaporation site and at the end of the transfer, both cause this residual solvent to evaporate from the rear to the front of the layer, which is the prerequisite for obtaining solvent trapping.

In their realization, however, the techniques strongly differ. Partially concurrent solvent evaporation leaves behind part of the main solvent. Introduction must

occur below the solvent boiling point and presupposes an on-column interface. As a first step in practical work, the solvent evaporation rate must be determined in order to derive a suitable eluent flow-rate (which also determines the flow-rate through the LC column at least during transfer of the LC fraction of interest). The GC conditions must remain stable during transfer, as changes affect the evaporation rate. This practically rules out a pressure increase during transfer for accelerating the discharge of the vapours.

The alternative technique leaves behind an additional solvent, the co-solvent. The volume of non-evaporating solvent is simply determined by the concentration of the co-solvent in the main solvent and, to some extent, by the column temperature during transfer. The properties of the co-solvent can be selected according to the needs of solvent trapping, which is important with water, which has poor wettability characteristics and is a poor solvent for retaining typical GC components. Introduction of the LC fraction into the GC system occurs by the carrier gas (loop-type interface), and thus does not influence the choice of the LC flow-rate. Adjustment of conditions does not require the determination of the solvent evaporation rate. It does, however, presuppose some experimentation to find a suitable co-solvent concentration and column temperature during transfer (as the choice of optimally suited co-solvents is limited, such data are rapidly compiled). Finally, the carrier gas inlet pressure during transfer can vary to some extent, facilitating accurate closure of the solvent vapour exit and simple automation of this and some other events (see below).

Butoxyethanol as co-solvent

We proposed the use of butoxyethanol as a co-solvent[14]. It boils at 171°C, is water-miscible but is nevertheless well suited for retaining the components of relatively low polarity analysed by GC. Butoxyethanol forms an azeotropic mixture with water of 22:78 (v/v) at 98.7°C.

Purpose of this paper

After having described the background of concurrent eluent evaporation with co-solvent trapping[14], this paper deals with practical subjects such as the recognition of the moment for closing the vapour exit and the optimization of the two key parameters, the co-solvent concentration and the column temperature during transfer. Experimental results obtained under non-optimum conditions are discussed in detail in order to facilitate the optimization process.

The detailed study of butoxyethanol as a co-solvent may be surprising. However, this co-solvent showed promising preliminary results, also with methanol and acetonitrile and their mixtures with water, suggesting that this co-solvent could serve for virtually all reversed-phase eluents. Hence it might be sufficient to know a few sets of well optimized conditions.

INSTRUMENTAL: THE GAS SUPPLY SYSTEM

Experiments were carried out on a Carlo Erba 4160 gas chromatograph equipped with a loop-type interface as described previously[14]. Samples were introduced into the sample loop with a syringe. The interface differed from the conventional loop-type interface in three respects. First, the (glass press-fit) T-piece required for

back-flushing the sample valve was positioned inside the GC oven. Second, the solvent vapour exit was not completely closed but equipped with a strong restriction, allowing for a small purge flow-rate. Third, there was just an uncoated, but no retaining, precolumn upstream of the vapour exit.

A 5 m × 0.53 mm I.D. fused-silica capillary deactivated by phenyldimethylsilylation (MEGA, Legnano, Italy) served as a precolumn at the front end, connected to the press-fit T-piece of the solvent vapour exit. Separations were carried out on a 12 m × 0.32 mm I.D. glass capillary column coated with PS-255 (a methylsilicone) of 0.3-μm film thickness. The co-solvent, butoxyethanol, was specially purified by Fluka (Buchs, Switzerland) and is available as Nr. 20398.

Closure of the vapour exit

Concurrent eluent evaporation with co-solvent trapping relies on closure of the solvent vapour exit before the co-solvent is fully evaporated, otherwise the volatile solute material trapped by the co-solvent is lost through the vapour exit together with the last portion of the co-solvent. On the other hand, premature closure is undesirable, because passage of large volumes of vapours through the separation column would considerably prolong the evaporation time, correspondingly broadening the solvent peak.

Closure of the exit at the correct moment is particularly critical if the co-solvent concentration only slightly exceeds that co-evaporating with the main solvent, *i.e.*, if trapping occurs with a small amount of co-solvent. Further, the flow-rate through the vapour exit is usually high (around 100 ml/min in our case), causing the evaporation of the residual co-solvent to be rapid. Therefore, a system is required that allows accurate recognition of the moment when evaporation of the main solvent is completed. At a later stage, this function must be amenable to automation.

Flow-regulated gas supply

The standard loop-type interface for conventional concurrent eluent evaporation includes a flow-regulated carrier gas supply[17]. The flow regulator automatically increases the carrier gas inlet pressure during eluent transfers. As the plug of eluent blocks the gas flow, the flow regulator increases the inlet pressure up to the level determined by the pressure regulator situated behind the flow regulator. In addition to accelerating the discharge of the eluent vapours (increasing the rate of eluent evaporation), this provides an easy means of detecting the end of eluent transfer. The inlet pressure remains high up to the disappearance of the plug of liquid and the eluent vapours blocking the gas flow. This can be exploited for manual or automatic regulation of events timed after completion of the transfer. For instance, the solvent vapour exit and the GC run are started (with a delay) after this moment. The Carlo Erba automated LC–GC instrument works on this principle[18].

Pressure drop over restriction

In this work, closure of the vapour exit occurred by the same concept. However, a simple restriction (2 m × 0.25 mm I.D. stainless-steel capillary tubing) was used, serving the same purpose as a flow regulator. This restriction was placed after a pressure regulator and a first manometer (see Fig. 1). A second manometer, placed downstream of the restriction, indicated the same pressure as the first manometer

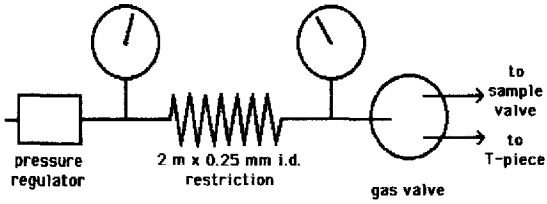

Fig. 1. Carrier gas supply system involving a restriction for accelerating eluent evaporation and for monitoring the carrier gas flow-rate during transfer.

when no gas flow passed the restriction (during transfer), while the pressure read on this second manometer was the lower the higher was the flow-rate through the restriction.

PATTERN OF THE PRESSURE DROP

The determination of the optimum co-solvent concentration in the LC eluent and of the most suitable column temperature during transfer is tedious when just based on the interpretation of chromatograms. Visual observation of the flooding liquid was not satisfactory because it was impossible to distinguish between the whole eluent and the co-solvent. However, two other techniques were used that are described below.

The pattern of the pressure drop towards the end of eluent evaporation, read from the second manometer, can be used as an interesting source of information about the evaporation process. Usually, pressure falls slowly and stepwise, indicating a gradual increase in the carrier gas flow-rate. The carrier gas flow-rate is still reduced owing to the vapours generated by the remaining solvent, this reduction depending on the vapour pressure of the liquid left in the column inlet (and the viscosities of the vapours and the carrier gas).

Fig. 2 illustrates this point by the course of the pressure observed on the second manometer during two transfers of 250-μl samples of water containing 22.5% of

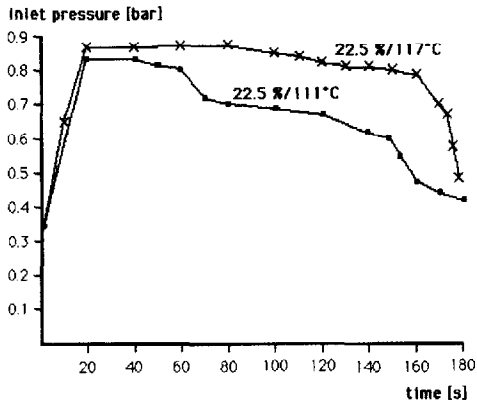

Fig. 2. Inlet pressure observed on the second manometer on transferring 250-μl volumes of water containing 22.5% of butoxyethanol at two different oven temperatures.

butoxyethanol. On starting the transfer, the pressure increased to the level of the first manometer, showing almost complete stoppage of the gas flow (there remains the small purge flow through the purge exit between the gas and the sample valve). The subsequent pressure changes depended on the eluent and the column temperature. At a moderately high temperature (the maximum is *ca.* 120°C, see below), the pressure remained at the maximum for about 90 s. Afterwards, the pressure fell slightly to a level maintained for another about 50 s, then decreased rapidly to *ca.* 0.45 bar. This level, about 0.1 bar above that before starting transfer (with an open vapour exit), would have been maintained for another 15 s, but closure of the vapour exit occurred as soon as the pressure dropped below 0.5 bar. As closure of this exit caused a reduction in the flow-rate, the pressure increased again to 0.65 bar (and further increased to 0.75 bar during temperature programming).

Blockage of the carrier gas flow obviously occurs through an eluent plug reaching into the entrance of the oven-thermostated precolumn (see Fig. 3A). The first decrease in inlet pressure was accompanied by a small gas flow leaving the vapour exit. The eluent plug must have disappeared at this time; the remaining eluent formed a thick layer on the wall of the precolumn (Fig. 3B). As the vapour pressure was still nearly as high as the carrier gas inlet pressure, the gas phase flowing through the precolumn consisted almost exclusively of eluent vapour, which explains the small carrier gas flow-rate. However, evaporation of the azeotropic butoxyethanol–water mixture caused the boiling point of the residual solvent mixture to increase and the vapour pressure to decrease. As a consequence, the carrier gas flow-rate slowly increased and the pressure read on the manometer decreased. At a late stage of the evaporation, the water was evaporated, leaving behind the excess of butoxyethanol (Fig. 3C). As the boiling point of butoxyethanol is high, the vapour pressure de-

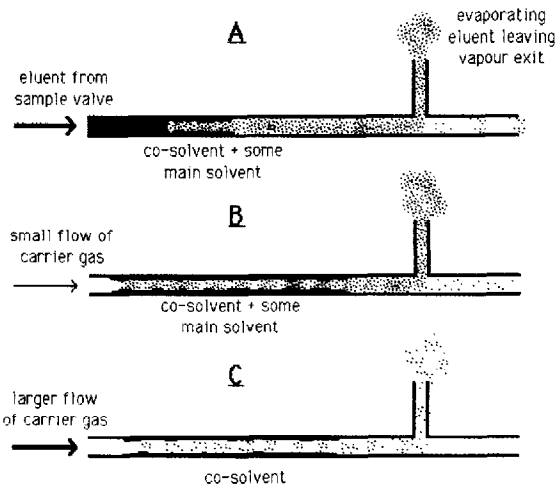

Fig. 3. Transfer by concurrent eluent evaporation with co-solvent trapping. (A) The eluent plug completely blocks the carrier gas; only eluent vapour flows through the uncoated precolumn, most of it leaving through the vapour exit. (B) The plug of liquid has disappeared; the thick layer of co-solvent and main solvent on the capillary wall exhibits a vapour pressure that allows a small flow-rate of carrier gas to pass. This flow-rate increases as water evaporates. (C) Only co-solvent is left in the uncoated precolumn, with a low vapour pressure that allows a large carrier gas flow-rate to pass. Now the vapour exit must be closed.

creased considerably, the carrier gas flow-rate increased and the inlet pressure fell to the 0.45 bar observed at the end. The evaporation of butoxyethanol at 117°C is relatively slow, but it was nevertheless advisable to close the vapour exit rapidly at this stage, because the volume of residual co-solvent only amounted to a few microlitres.

Transfers at higher temperatures

Transfer at temperatures exceeding 117°C caused the inlet pressure to remain at the maximum for longer times, *i.e.*, for 150 s at 119°C and for 185 s at 121°C. This extra time was mainly at the cost of the subsequent period with the slightly lower pressure (although the total evaporation time also slightly increased). Towards the end of solvent evaporation, the pressure decreased more rapidly. At 125°C, it fell straight back to 0.35 bar. This pressure corresponded to that prior to transfer and indicates that no co-solvent was left in the pre-column after disappearance of the eluent plug, *i.e.*, that no noticeable co-solvent layer was formed. Apparently, the oven temperature of 125°C was too high for obtaining co-solvent trapping under the conditions used.

Transfers at relatively low temperatures

On transferring the same sample at 111°C (Fig. 2), the pressure remained at the maximum only for *ca.* 40 s, then decreased to a level where it remained more or less stable for *ca.* 90 s. The rapid disappearance of the plug of liquid is explained by its deep penetration into the uncoated precolumn (to a point where the reduced pressure corresponded to its vapour pressure). As soon as no further liquid was supplied from the rear, the carrier gas opened a channel through the plug; the remaining fairly large volume of liquid was spread on the wall of the precolumn. During the subsequent 90 s, water and butoxyethanol evaporated azeotropically, leaving behind the excess of butoxyethanol. Butyloxyethanol has a low vapour pressure, causing the carrier gas flow to increase and the inlet pressure to decrease to about 0.45 bar.

At column temperatures below 110°C, the pressure hardly reached the maximum. The temperature must have been too low to produce a vapour pressure resisting the inlet pressure; more or less the whole volume of liquid rushed into the precolumn. Of course, the temperature was still above the boiling point of the solvent mixture at ambient pressure and, as the pressure at the vapour exit is not far above ambient, one would expect the liquid to be stopped within the precolumn. However, as evaporation is a violent process, some liquid left the precolumn (as observed in the resulting chromatograms; see below).

The lower temperature limit depends on the capacity of the uncoated precolumn and the sample volume introduced. If the capacity is small, only a small proportion of the liquid may spread into the precolumn. For the pressure diagram, this means that the pressure must remain at the maximum for a long period, which is achieved by a relatively high column temperature during transfer.

Speed of solvent evaporation

The pressure profile also provides some information about the speed of solvent evaporation. At 117°C, nearly all the solvent evaporated during about 170 s. As the total volume of vapour generated by the 250-μl sample volume was *ca.* 300 ml, the gas and vapour flow-rate within the precolumn was just above 100 ml/min.

CO-SOLVENT PEAK

The shape of the highly attenuated solvent peak is another useful source of information about co-solvent evaporation. Fig. 4 shows a chromatogram for a 250-μl sample of esters in water containing 22.5% of butoxyethanol. The solvent peak with a total width of 3.7 min is strongly attenuated (2^{21}). During the first part, the vapour exit was open; the flow-rate through the separation column was very small (low pressure at the T-piece), causing some delay on the first appearance of the solvent peak and a very low response due to small amounts of vapour carried through the separation column. After a first "hill", small "peaks" are observed. These "peaks" cannot represent individual substances, but show thrusts of violent evaporation (delayed evaporation), causing portions of vapour to be pushed into the separation column.

The vapour exit was closed 160 s after starting transfer (*i.e.*, in the centre of the solvent peak). With a delay corresponding to the gas hold-up time of the separation column, the pen started to rise. If closure of the exit occurred early (prematurely), the pen rose slowly or even produced a low shoulder (as is shown in the centre chromatogram of Fig. 7). This indicated that primarily water vapour passed through the column; the detector (flame ionization) shows only the butoxyethanol. Finally, the pen rose to a broad peak (shown in black in all chromatograms), representing butoxyethanol. The height of this peak depended on the column temperature (determining the vapour pressure of the co-solvent).

The size of the co-solvent peak indicates the amount of co-solvent left in the pre-column on closing the vapour exit and can be used for optimizing the co-solvent concentration, as will be shown by the following examples.

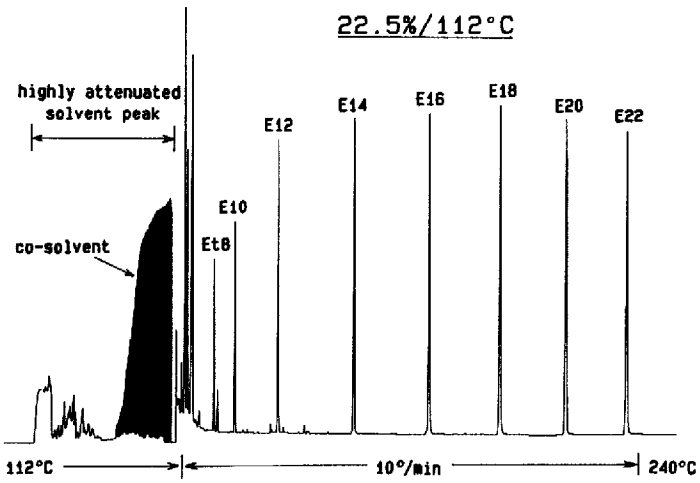

Fig. 4. Successful concurrent eluent evaporation with co-solvent trapping. Methyl esters of C_{10}–C_{22} acids (E10-E22) and ethyl octanoate (Et8), 0.1 ppm in water containing 22.5% of butoxyethanol (co-solvent). Transfer of a 250-μl volume at 112°C; inlet pressure behind the restriction, 0.9 bar (H_2). The solvent peak is highly attenuated to show its shape. The black peak indicates the amount of co-solvent left in the precolumn after complete evaporation of the main solvent.

Optimum conditions

The chromatogram in Fig. 4 shows successful co-solvent trapping. The loss of volatile solute materials is small. Methyl ester peaks down to methyl tetradecanoate (E14) are perfect in shape and size, indicating complete solvent trapping (without co-solvent trapping, even a large proportion of the E22 is lost). The methyl dodecanoate peak (E12) is *ca.* 10% too small; methyl decanoate (E10) is lost to the extent of *ca.* 50%, and 70% of the ethyl octanoate (Et8) is missing. The three first eluted peaks must be considered to be partially trapped[19]; part of this material co-evaporated with the solvent and was lost through the vapour exit. Losses do not depend on the elution temperatures from the separation column but on retention by the co-solvent layer.

From the fact that the pressure remained at the maximum only for *ca.* 60 s, we concluded that intense flooding of the pre-column had occurred (see above). The size of the co-solvent peak (black) is near the optimum (see below).

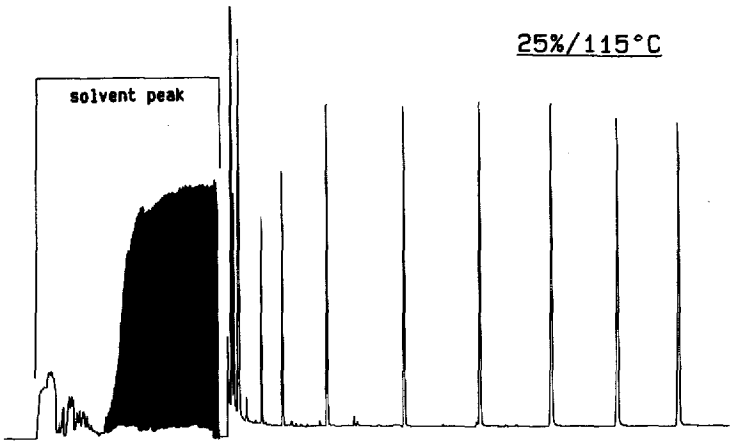

Fig. 5. Same as Fig. 4, but with a slightly increased concentration of butoxyethanol.

Fig. 5 shows a chromatogram resulting from a sample containing 25% of co-solvent. Losses of early ester peaks are reduced; the E12 peak is now of the correct size. On the other hand, the co-solvent peak is much broader (*ca.* 2.8 min compared with *ca.* 1.4 min in Fig. 4), indicating that the extra 2.5% of co-solvent resulted in more than double the amount of co-solvent being left behind on the precolumn wall at the end of solvent evaporation. Using a 30% co-solvent concentration, the co-solvent peak was more than doubled in width compared with Fig. 5, without noticeably improving the recovery of the two earliest peaks. The total solvent peak width was now just above 8 min. If this is of no concern for the 250-μl volume introduced, the unnecessary extra width of the solvent peak would hardly be tolerated any longer on increasing the sample volume, *e.g.*, to 1 ml. Considering the optimum trapping efficiency and minimal solvent peak width, we conclude that the optimum co-solvent concentration is 22.5–25%.

Insufficient co-solvent concentration

Fig. 6 shows two chromatograms of samples containing only 20% of co-solvent, a concentration clearly below that in the azeotropic mixture. The results depended on the transfer temperature, but were always unsatisfactory. At 117°C, there is a clearly visible co-solvent peak. However, even methyl tetradecanoate (E14) was partially lost. The co-solvent layer responsible for trapping the volatile solutes might have been built up only after a considerable part of the sample had evaporated, causing large losses during the first period of the transfer. At a transfer temperature of 114°C, the co-solvent peak was very small and the losses even affected the last peak (E22).

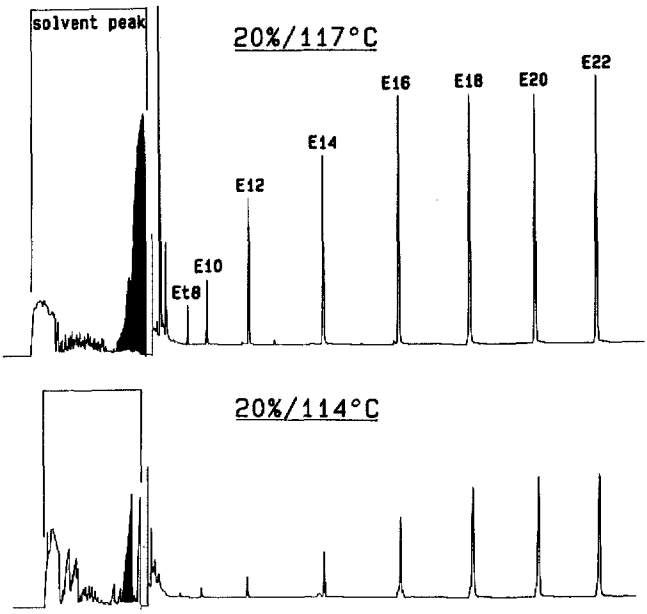

Fig. 6. Increased losses of solute material on reducing the co-solvent concentration to 20%.

It was surprising to observe co-solvent trapping effects when using co-solvent concentrations below that in the azeotropic mixture (*ca.* 22%). One would expect that a layer of water is left behind after complete azeotropic evaporation of the co-solvent. However, the presence of a co-solvent peak in the chromatograms contradicts this expectation. In this context it was interesting that clearly higher co-solvent concentrations (at least 25% butoxyethanol in water) were required when heating a short section of the precolumn inlet inside a vaporizing injector (280°C), as suggested by Noij *et al.*[20]. For this experiment, a 0.32 mm I.D. fused-silica capillary, inserted into the inlet of the 0.53 mm I.D. precolumn, passed from the oven to the top of the vaporizing injector and back into the oven again (indicated in Fig. 3 in ref. 14). The very narrow curve at the top of the injector was prepared by a correspondingly deformed press-fit connector. After complete evaporation of the sample in this vaporization loop, part of the solvent recondensed in the oven-thermostated precolumn.

Basically, the same equilibrium between the condensed phase and the gas phase should result as when starting out from evaporation in the oven-thermostated precolumn. However, this is obviously not completely true, showing that we have not yet fully explained solvent evaporation.

Excessive transfer temperature

The chromatograms in Fig. 7 show the consequences of an excessively high oven temperature during transfer for the sample containing 22.5% of butoxyethanol. At 121°C, the co-solvent peak was still fairly large. However, losses of component material reached up to E14. This temperature was right at the limit, because with transfer at 120°C the E14 peak was still of perfect size and the loss of E12 hardly exceeded that at 112°C (Fig. 4). An increase in the transfer temperature by another 1°C (to 122°C, centre chromatogram) caused the losses to extend up to the last peak. There is still a substantial co-solvent peak, but the co-solvent layer was probably formed only after a substantial proportion of the sample had been transferred. As mentioned above, the early eluted shoulder of the co-solvent peak indicates premature closure of the vapour exit. Finally, at 125°C, losses of solute material were severe. No co-solvent peak was observed and, after concurrent evaporation of the main solvent, the pressure dropped directly to 0.35 bar, confirming the absence of co-solvent in the precolumn at the end of the water evaporation.

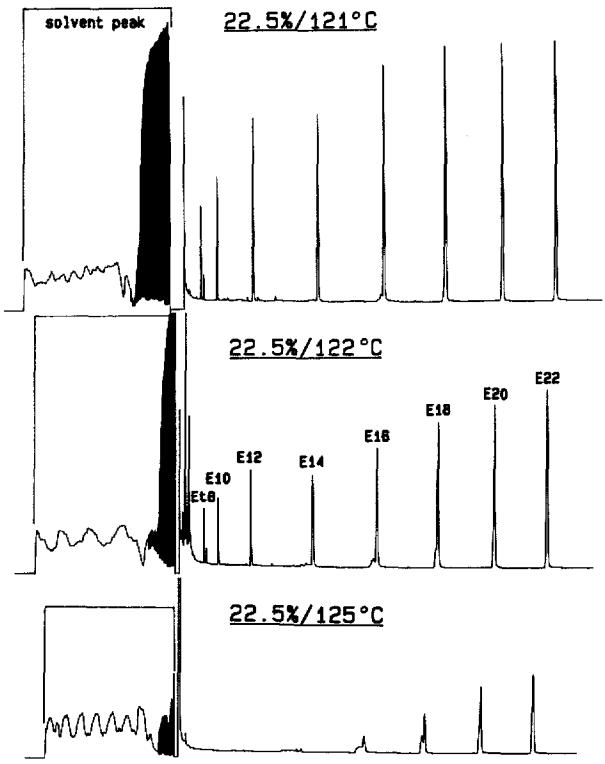

Fig. 7. Results observed with a column temperature during transfer slightly exceeding the optimum, using 22.5% of co-solvent.

Insufficient transfer temperature

Fig. 8 shows the result of a transfer carried out at an excessively low column temperature. The pressure hardly reached the maximum, indicating that the plug of liquid passed almost unhindered into the precolumn (although, as mentioned above, the pressure drop within the precolumn should have stopped the flow of liquid in the second half of the precolumn). As deduced from the peak sizes, *ca.* 20% of the sample must have penetrated into the T-piece of the vapour exit, presumably owing to "shooting" liquid, the result of irregular and violent evaporation. There, a major portion of the liquid left through the vapour exit, while a smaller part entered the separation column. In the separation column, the liquid was spread by the flow of gas and vapours, resulting in band broadening in space. As the corresponding solute material is ahead of the material chromatographed normally, it elutes prematurely (black peaks indicated by arrows in Fig. 8).

The lower temperature limit for the transfer was *ca.* 110°C, as also deduced from the rapid decrease in the time the pressure remained at the maximum. At 110°C, some chromatograms showed peak distortion such as that shown in Fig. 8, whereas the peaks in others were of perfect shape and height. As the evaporation is violent, the lower temperature limit is not very reproducible.

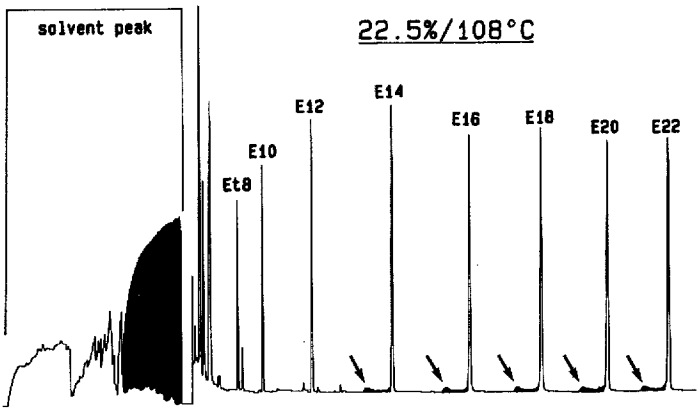

Fig. 8. Lower limit of the column temperature during transfer: the flow of liquid exceeds the T-piece of the solvent vapour exit; part of the sample flows into the separation column, producing the low pre-peaks shown in black and indicated by arrows.

Delayed closure of the vapour exit

Fig. 9 shows the result of closing the vapour exit with a delay of *ca.* 40 s. At closure, the pressure had decreased to 0.35 bar, the pressure observed before starting transfer, which signifies that no co-solvent was left in the precolumn. On the other hand, some co-solvent is still visible on the chromatogram. The esters were nearly completely lost up to E20; the small peaks of the earlier eluted esters indicate the splitting ratio at the vapour exit T-piece.

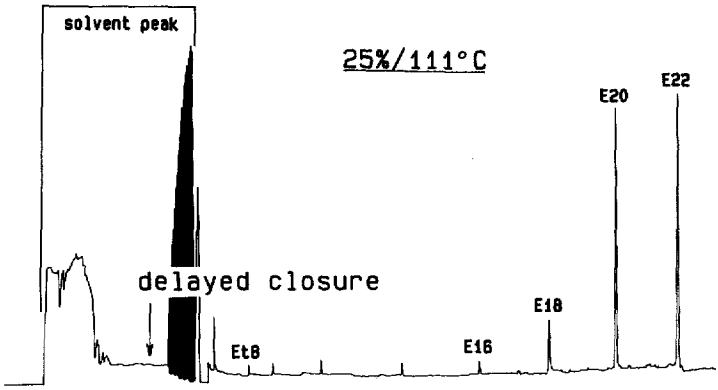

Fig. 9. Nearly complete loss of the volatile solutes on closing the vapour exit with a delay of *ca.* 40 s (conditions otherwise producing efficient co-solvent trapping).

SUMMARIZING GUIDELINES

Column temperatures during transfer are most rapidly optimized through the course of the pressure drop towards the end of the transfer, introducing the solvent mixture without any solute material. The pressure should remain at the maximum for a considerable part of the transfer time (limit towards lower temperature); on the other hand, it must not decrease rapidly at the end of the transfer (limit towards high temperature). During these transfers, the recorder runs at high attenuation, allowing the optimization of the co-solvent concentration by the size of the co-solvent peak.

Table I gives some preliminary guidelines on optimum butoxyethanol concentrations in different reversed-phase eluents and optimum column temperatures for transfer at an inlet pressure of 0.9 bar. Results were obtained from two similar experimental set-ups. Nevertheless, it was observed that the optimum temperatures differed by up to 7°C and the optimum butoxyethanol concentrations differed by up to 2% (absolute). The reason for these deviations is unknown. However, as the evaporation of water-containing liquids on hardly wetted surfaces is an irregular process, they are not really surprising.

TABLE I

APPROXIMATE OPTIMUM BUTOXYETHANOL CONCENTRATIONS AND COLUMN TEMPERATURES DURING TRANSFER (0.9 BAR INLET PRESSURE)

Main solvent	*% Butoxyethanol*	*Transfer temperature (°C)*
Water	23	110–120
50% Methanol	15	105–110
75% Methanol	8	96–103
Methanol	4.5	85– 93
50% Acetonitrile	15	107–115
75% Acetonitrile	10	102–110

REFERENCES

1 G. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 112 (1975) 205.
2 G. Schomburg, *Separation*, 1 (1987) 3.
3 G. Schomburg, in P. Sandra (Editor), *Sample Introduction in Capillary GC, Vol. 1*, Hüthig, Heidelberg, 1985, p. 235.
4 E. Bastian, H. Behlau, H. Husmann, F. Weeke and G. Schomburg, in R. E. Kaiser (Editor), *Proceedings of the Fourth International Symposium on Capillary Chromatography, Hindelang, 1981*, Hüthig, Heidelberg, 1981, p. 465.
5 G. Schomburg, E. Bastian, H. Behlau, H. Husmann, F. Weeke, M. Oreans and F. Müller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 4.
6 G. Schomburg, in P. Sandra (Editor), *Proceedings of the Seventh International Symposium on Capillary Chromatography, Gifu, 1986*, Hüthig, Heidelberg, 1986, p. 27.
7 K. Grob, B. Schilling and Ch. Walder, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 95.
8 K. Grob, H.-G. Schmarr and A. Mosandl, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, in press.
9 K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 297.
10 K. Grob and Z. Li, *J. Chromatogr.*, 473 (1989) 423.
11 K. Grob and B. Schilling, *J. Chromatogr.*, 259 (1983) 37.
12 K. Grob, *J. Chromatogr.*, 279 (1983) 225.
13 K. Grob and E. Müller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 388 and 560.
14 K. Grob and Z. Li, *J. Chromatogr.*, 473 (1989) 411.
15 F. Munari, A. Trisciani, G. Mapelli, S. Trestianu, K. Grob and J. M. Colin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 601.
16 E. Noroozian, F. A. Maris, M. W. F. Nielen, R. W. Frei, G. J. de Jong and U. A. Th. Brinkman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 17.
17 K. Grob and J.-M. Stoll, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 518.
18 F. Munari and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 172.
19 K. Grob, *J. Chromatogr.*, 251 (1982) 235.
20 Th. Noy, E. Weiss, T. Herps, H. Van Cruchten and J. Rijks, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 181.