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INTRODUCTION OF WATER AND WATER-CONTAINING SOLVENT MIXTURES IN CAPILLARY GAS CHROMATOGRAPHY

IV. PRINCIPLES OF CONCURRENT SOLVENT EVAPORATION WITH CO-SOLVENT TRAPPING

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SUMMARY

Concurrent solvent evaporation of aqueous solutions causes loss and broadening of peaks up to high elution temperatures. This deficiency is largely eliminated by using co-solvent trapping. A 5–20% concentration of a high-boiling co-solvent (butoxyethanol) is added to the water or mixture containing water (reversed-phase eluent). This co-solvent does not completely evaporate concurrently, retaining the solute material in the uncoated precolumn until evaporated some time after the end of the sample transfer. The concept and the required properties of the co-solvent are discussed and demonstrated for a 1-ml sample of methyl esters in aqueous solution, using 20% butoxyethanol as co-solvent.

INTRODUCTION

Injection or liquid chromatographic–gas chromatographic (LC–GC) transfer of samples containing high proportions of water is a serious problem owing to the poor wetting characteristics of water, the large volumes of vapour produced per unit volume of liquid, poor solvent effects, and also because of the high boiling point of water. Application of the retention gap techniques (with or without partially concurrent eluent evaporation) is restricted because of poor wetting of the uncoated precolumn[1] by water-containing solvent mixtures. Up to 28% of water can be introduced if 1-propanol is the main solvent or 16% with acetonitrile.

The tolerable proportion of water in the solvent mixture increases when high-boiling organic solvents with good wetting characteristics are applied. However, in that event, concurrent solvent evaporation with co-solvent trapping, to be described here, is a more attractive method. Despite the large volumes of liquid that can be introduced in this way, only a short, uncoated precolumn is required. Short precolumns are of particular interest when working with water, as no precolumn with water-resistant deactivation is yet available[2]. Precolumns used for the evaporation of aqueous solvent mixtures rapidly turn adsorptive, and their further use relies on the continuing introduction of water, as the water temporarily deactivates the surface

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again. This makeshift arrangement is the more critical the longer the precolumns are.

Concurrent solvent evaporation does not rely on wettability of the precolumn surface, but is of limited usefulness because of strong peak broadening or losses of solute material with high elution temperatures. The method was successfully applied to on-line sample enrichment by reversed-phase LC–GC of atrazine in water[3]. However, the minimum elution temperature for atrazine was 240°C.

For reasons discussed further below, concurrent eluent evaporation with co-solvent trapping appears to be the method of choice for coupled reversed-phase LC–GC involving water-containing eluents. This paper describes the concept of this technique. Directions on its experimental optimization for water, and also for water–methanol and water–acetonitrile mixtures, are published separately[4]. Optimized sets of co-solvent concentrations and transfer temperatures are fairly generally applicable, as the solvent evaporation system is more or less independent of the separation column used and the components to be analysed.

CONCURRENT ELUENT EVAPORATION

Concurrent solvent evaporation means evaporation of the solvent during its introduction into the GC system[5]. This permits the introduction of very large volumes of liquid (up to many millilitres) by the use of uncoated precolumns only 2–5 m long. In our hands, this has become the most important technique for on-line transfer of LC fractions to GC.

However, concurrent solvent evaporation has an inherent drawback: evaporation occurs under conditions ruling out solvent trapping[6]. As solvent evaporation takes place at the front of the flooded zone, no condensed solvent remains ahead of the evaporation site that would retain solute material. As a result, the first solute material starts to migrate into the separation column long before the last material follows. If there is a solvent vapour exit in an early part of the separation column, a substantial part of these solute materials is lost. The resulting band broadening or losses reach components with high boiling points.

Band broadening cannot be estimated by considering only the transfer time. The lead of the most advanced material must be calculated from the retention volumes, *i.e.*, from the volume of vapour that flushes the most advanced material forward until the last solute material enters the GC system.

Below, it will be shown that 1 ml of water containing 20% butoxyethanol could be transferred within 5.5 min. However, band broadening far exceeds these 5.5 min. The vapour volume produced by the mixture is about 2500 ml. Assuming a carrier gas flow-rate of 2.5 ml/min during analysis, this would correspond to a difference in retention times between the first and the last solute material, *i.e.*, to an initial band width, of 1000 min, which is 16.7 h!

In conventional concurrent eluent evaporation (without co-solvent trapping), broad initial bands are reconcentrated by cold trapping and phase soaking[7]. In practice, this means that the first sharp peaks can be expected to be eluted 60–100°C above the column temperature during sample introduction (assuming organic solvents and fraction volumes of 500–2000 μl).

Concurrent solvent evaporation with water

Water is a very difficult solvent for concurrent solvent evaporation. First, the volume of vapour produced per volume of liquid is extremely large (about six times that of hexane). These vapours act as carrier gas, intensively flush the solutes forward and cause correspondingly broad initial bands (see above). In addition, vapours must be discharged through an early vapour exit in order to avoid excessively broad solvent peaks. Second, the boiling point of water is relatively high, compelling us to use high GC oven temperatures during introduction (110–140°C, depending on the inlet pressure). The combination of these two factors, together with the fact that water does not produce any phase soaking (or rather a reversed-phase phase soaking[8]), causes the first sharp peaks to be eluted between 230 and 260°C.

Co-solvent trapping

Two years ago we started experimentation with concurrent solvent (LC eluent) evaporation with co-solvent trapping[9], hoping to overcome the drawback of the conventional concurrent solvent evaporation technique described above. Co-solvent trapping, obtained from a high-boiling co-solvent, added in modest concentrations to the main solvent, serves to retain volatile components during evaporation of the main solvent (Fig. 1). This prevents these components from starting to migrate prematurely into the separation column, or loss through a solvent vapour exit, if such an exit is located in the early part of the column. Fully trapped components are retained in the co-solvent until the last portion of the co-solvent evaporates. Solutes start to be chromatographed with a delay, but as sharp bands released within a short time and from a short section of the precolumn. In fact, sharp peaks of correct size could be obtained with elution temperatures near the column temperature during transfer.

The feasibility of this technique was demonstrated for the solvent system *n*-pentane–*n*-heptane[10]. A 500-μl volume of a highly dilute gasoline solution was introduced into a 4-m uncoated precolumn. The co-solvent (*n*-heptane) concentration

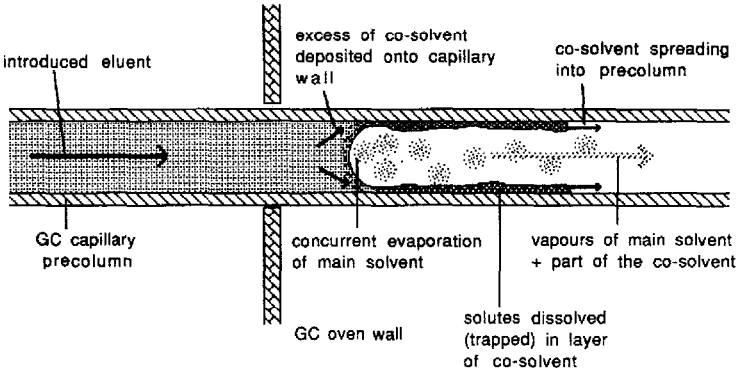

Fig. 1. Concurrent solvent evaporation with co-solvent trapping. The carrier gas pushes the sample into the oven-thermostated capillary precolumn. The oven temperature must be high enough to produce a vapour pressure, primarily of the main solvent, that stops the flow into the column. The main solvent evaporates, and just a small proportion of the liquid, consisting of a higher boiling mixture, primarily containing co-solvent, spreads along the walls into the uncoated precolumn. This layer retains the solutes and prevents volatile components from escaping prematurely through the solvent vapour exit (solvent trapping).

was 5%. The first perfect solute peaks were eluted before the xylenes. With the conventional concurrent solvent evaporation, almost all components of gasoline would have been lost through the solvent vapour exit. Previously, such a result could have been achieved only by the retention gap technique. Owing to the large volume of liquid introduced, partially concurrent solvent evaporation would have been presupposed in order to obviate the need for an excessively long uncoated precolumn.

Column temperature during transfer

Selection of a suitable column temperature during transfer is the most delicate point of the co-solvent trapping technique. The temperature must be within a range limited by the following aspects.

The lower end of the temperature range is determined by the fact that the concept involves concurrent solvent evaporation by the use of the loop-type interface[11]. Hence, the carrier gas pushes the sample liquid into the oven-thermostated precolumn (Fig. 1) against the vapour pressure of the sample (solvent). This means that the GC oven temperature must be high enough to produce a solvent vapour pressure exceeding the carrier gas inlet pressure. Hence, the minimum required oven temperature corresponds to the boiling point of the mixture of main solvent and co-solvent at the inlet pressure applied. At this temperature, primarily the main solvent evaporates, leaving behind a higher boiling mixture of main and co-solvent that is driven further into the precolumn by the vapours. This condensed main solvent–co-solvent mixture ahead of the main evaporation site is responsible for solvent trapping of the volatile solutes. The upper limit of the suitable temperature range is determined by the vapour pressure of the co-solvent. The vapour pressure of the co-solvent increases with temperature and thus increases the concentration of the co-solvent vapour in the gas phase. The concentration of the co-solvent vapour in the vapour mixture, discharged through the column, rapidly reaches that in the solvent mixture introduced. Hence, when the sample (LC fraction) is transferred at excessively high temperature, the co-solvent also completely evaporates, and the co-solvent trapping effect is lost again. In fact, the range of suitable oven temperatures during sample introduction is rather narrow (typically 5–10°C).

Terminology: partially concurrent solvent evaporation?

Partially concurrent solvent evaporation means that part of the solvent (LC eluent) evaporates during introduction while the non-evaporated part floods the GC precolumn[12]. Recently, Maris *et al.*[13] showed a nicely elaborated application of this technique for the LC–GC analysis of polychlorinated biphenyls (PCBs) in sediments.

It may be argued that concurrent solvent evaporation with co-solvent trapping should be classified as a partially concurrent solvent evaporation technique. Indeed, only part of the solvent evaporates during introduction, while another part, primarily co-solvent, pours into the GC precolumn. Nevertheless, classification as a concurrent solvent evaporation technique is preferred, because the co-solvent trapping technique is regarded as a sophisticated version of concurrent solvent evaporation. In fact, as long as the main solvent is considered, it still deserves the name (fully) concurrent solvent evaporation. In addition, instrumentation and working rules still very much resemble concurrent solvent evaporation, as a loop-type interface is applied, and the oven temperatures must be above the boiling point of the eluent.

REQUIREMENTS ON THE CO-SOLVENT

A co-solvent suitable for introducing water or water-containing solvent mixtures must fulfil a considerable number of requirements. Its selection should be made with care, also because a single co-solvent should be applicable to all kinds of samples, with the advantage that the co-solvent concentrations and GC conditions need to be optimized only once.

High boiling point

The optimum boiling point of the co-solvent is related to the required concentration of the co-solvent in the solvent. On the one hand, the required concentration of co-solvent should be small, as the co-solvent should be an additive, influencing the properties of the solvent mixture (*e.g.*, the eluent strength) as little as possible. Furthermore, work with short precolumns is easier when only small amounts of co-solvent are used (keeping the maximum volume of liquid flooding the precolumn small).

On the other hand, there is a minimum concentration of co-solvent required for a rapid build-up of a co-solvent film in front of the main evaporation site. Solvent evaporation tends to be a violent process. The front of the liquid often oscillates, *i.e.*, the liquid enters the oven-thermostated pre-column, *e.g.*, say 60 cm, evaporates and re-enters. Too small a co-solvent concentration would build up a layer of liquid that is periodically overrun by the liquid introduced for a long time, namely until a considerable part of the sample (LC fraction) has been introduced and the co-solvent layer has reached a sufficient length. Basically, this problem could be solved by a volume of pure co-solvent introduced ahead of the sample. However, this would complicate the system, particularly for automation, and experimentally we did not find any need for it as long as the co-solvent concentrations were not too low.

Work with low co-solvent concentrations presupposes that a high proportion of main solvent evaporates together with a small proportion of co-solvent, such that some condensed co-solvent remains in the precolumn, forming the layer required for solvent trapping. The boiling points of the two solvents must also be far apart to avoid the selection of the transfer conditions, primarily of the GC oven temperature, from becoming impractically critical (wide gap between the boiling and the condensation curves on the phase diagram).

The upper limit of the boiling point is determined by practical aspects. The evaporation rate must not be too low, as evaporation of the co-solvent at the end of the introduction process would otherwise become excessively time consuming (causing the solvent peak to become very broad). Even when added in small concentrations, the total amount of co-solvent to be evaporated easily reaches 50 μl. Further, the co-solvent should be minimally retained by the GC separation column, again to avoid an excessively broad solvent peak but also to prevent too many solute peaks from becoming obscured by the solvent peak.

Azeotropic mixture with water

Formation of an azeotropic mixture of the main solvent and the co-solvent, *i.e.*, with water in our case, has several advantages. First, evaporation occurs at a lower column temperature, allowing GC analyses to start at a relatively low temperature.

Second, the main solvent and the co-solvent co-evaporate in a well defined ratio, fairly independent of conditions. This is an important advantage over ideally evaporating solvent mixtures, such as the *n*-pentane–*n*-heptane mixture tested, where a small change in GC oven temperature or pressure has strong effects on co-solvent evaporation. With ideally evaporating mixtures, a change in the GC oven temperature by a few degrees causes a significant change in the volume of co-solvent–main solvent mixture flooding the precolumn, either in the direction of a full evaporation of the co-solvent or, *e.g.*, an extra 50 μl of liquid swamping the pre-column.

The stability of the main solvent–co-solvent ratio in the vapour phase is of particular importance when considering the effect of the pressure drop through the uncoated pre-column on the vapour composition, as discussed recently[10]. The pressure at the inlet of the precolumn corresponds to the carrier gas inlet pressure, whereas that at the outlet is only slightly above ambient pressure (depending on the pressure drop over the solvent vapour exit). If the solvents evaporate ideally, the concentration of the co-solvent in the vapour phase increases towards the outlet of the precolumn, because the vapour pressure of the co-solvent is constant (determined only by the temperature), whereas the total pressure decreases. If the pressure drop over the precolumn is large, the co-solvent is likely to evaporate completely at the front end of the flooded zone, releasing the volatile solutes (and causing their loss when an early solvent vapour exit is used). When the solvents evaporate as an azeotropic mixture (and as long as the composition of this mixture is fairly independent of pressure), such problems are eliminated. This allows us to apply increased inlet pressures (larger pressure drops through the precolumn), to accelerate the discharge of the eluent vapours.

Good wettability

The co-solvent spreading into the uncoated precolumn must wet the precolumn wall in order to form the film responsible for solvent trapping. A lack of wettability would cause an uncontrolled flow into the separation column or through the solvent vapour exit. Film formation is rendered more difficult by the fact that the co-solvent layer may contain a considerable concentration of water. Hence, to achieve wettability, the co-solvent must efficiently reduce the surface tension of water, an effect similar to that of detergents.

Chemical stability

The co-solvent must be chemically stable at the fairly high transfer temperatures usually required (100–130°C). Owing to the large amount of co-solvent introduced, a small concentration of a reaction (hydrolysis) product could seriously disturb the system.

LC compatibility

As the main application of the technique concerns coupled LC–GC, the co-solvent should be compatible with LC. Of course, the co-solvent could be added to the LC eluent only after the LC detector. However, this presupposes an additional LC pump, delivering the co-solvent into the LC effluent stream at a low flow-rate. Technically, it is simpler to add the co-solvent to the eluent, but this presupposes that the co-solvent does not excessively increase the viscosity of the eluent and that it does not interfere with UV detection.

Efficient solvent trapping

To obtain full solvent trapping, the co-solvent must be suitable for strongly retaining the solutes of interest. As the solutes amenable to GC analysis are of low to intermediate polarity, the maximum retention power is obtained with co-solvents of relatively low polarity. However, the co-solvent must be miscible with water, which requires some polar or polarizable functional groups.

BUTOXYETHANOL AS CO-SOLVENT

Among the high-boiling solvents tested, we found 2-butoxyethanol (ethyleneglycol monobutyl ether, butylcellosolve) to be best suited for our purpose. Its boiling point at ambient pressure is 171°C. At ambient temperature, butoxyethanol is miscible with water. However, the two solvents separate into two phases when heated to *ca.* 100°C (the GC temperatures during transfer).

Butoxyethanol of purum quality was obtained from Fluka (Buchs, Switzerland). This purity is insufficient for work with a flame ionization detector at higher sensitivity owing to interfering peaks (see the chromatogram in Fig. 4). In the near future, Fluka will offer a further purified butoxyethanol (Nr. 20398).

Phase diagram for butoxyethanol–water

For the mixture of butoxyethanol–water, data found in the literature[14] allowed us to draw the phase diagram shown in Fig. 2. This diagram shows an extremely flat boiling curve, indicating that a very large proportion of water evaporates within a narrow range of temperatures. This is important, as it causes efficient evaporation of the water within a few degrees above the boiling point of the sample mixture, leaving almost only butoxyethanol to flood the precolumn.

Ref. 14 does not give any indication about an azeotropic mixture, except that a mixture containing 20.8% butoxyethanol is mentioned to boil at 98.8°C. According to Horsley[15], the azeotropic mixture boils at 98.8°C and contains 27.1% (by weight)

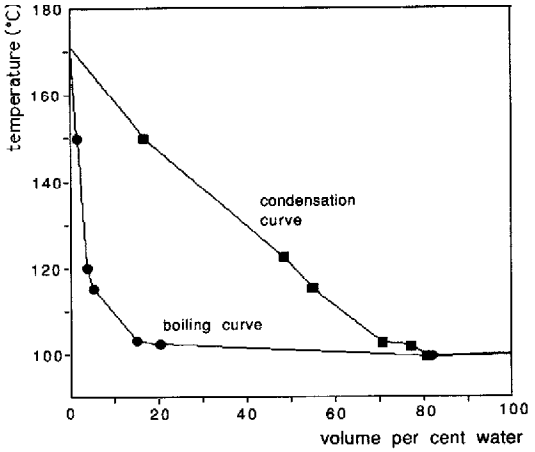

Fig. 2. Phase diagram of water–butoxyethanol after conversion of the commonly used mole fractions to volume percent.

of butoxyethanol. We distilled a water–butoxyethanol mixture, determining the composition of the distillate at various compositions of the boiling liquid. The compositions were analysed by measuring the refractive index of the liquid. With liquids containing 2.5–80% butoxyethanol (ten samples), the distillate always contained between 21.6 and 23.1% (by weight) butoxyethanol. Boiling points were at a minimum for mixtures containing 15–29% butoxyethanol (98.7°C).

Up to a pressure of at least 1 bar, the azeotropic mixture was found to be of constant composition, which is important regarding the pressure drop within the flooded zone. Neglecting possible problems with "shooting" liquid due to delayed evaporation, this allows us to work with both high and variable inlet pressures, but of course with the necessary corrections to the GC oven temperature.

Wettability characteristics

Wettability of a 0.32 mm I.D. phenyldimethylsilylated ("phesil") fused-silica capillary was tested, as described previously[16], by injecting increasing volumes of the solvent mixture to be tested until some liquid left the fused-silica capillary of interest and penetrated into the whitish glass capillary attached to it. Butoxyethanol was found to wet the "phesil" surface when it contained up to 30–35% of water.

INSTRUMENTAL

Concurrent solvent evaporation with co-solvent trapping was carried out with a device basically corresponding to the loop-type interface[11], although used for direct introduction by syringe. The design of the system is shown in Fig. 3. The test samples were drawn into the sample loop by a 10-ml plastic syringe. Steel capillary sample loops of 250 and 1000 μl were used.

Restriction instead of flow regulator

The pneumatic system for the carrier gas supply (located upstream of the carrier gas valve) differed from that of the standard loop-type interface. Instead of a flow regulator, as normally installed downstream of the pressure regulator, we mounted a restriction capillary (2 m × 0.25 mm I.D.), with a manometer ahead of and after the restriction. This arrangement served in the determination of the carrier gas flow-rate. During transfer, when almost no carrier gas flows, the two manometers show the same pressure. However, at the end of the transfer, the pressure measured on the second manometer drops to a level determined by the flow-rate of the gas passing the restriction. A more detailed description of the phenomena observed, and of their interpretation, will be given in a later paper[4].

T-Piece inside GC oven

In the standard loop-type interface, the T-piece, combining the sample supply line from the sample valve and the carrier gas line from the carrier gas valve, is located outside the GC oven. In this way, sample evaporation in the sample supply line before the T-piece can be ruled out (sample material deposited on the wall of the sample line is back-flushed as soon as the carrier gas valve is switched at the end of the transfer).

When working with co-solvents, two aspects differ from conventional concurrent eluent evaporation. First, there is no danger that sample material is lost in the

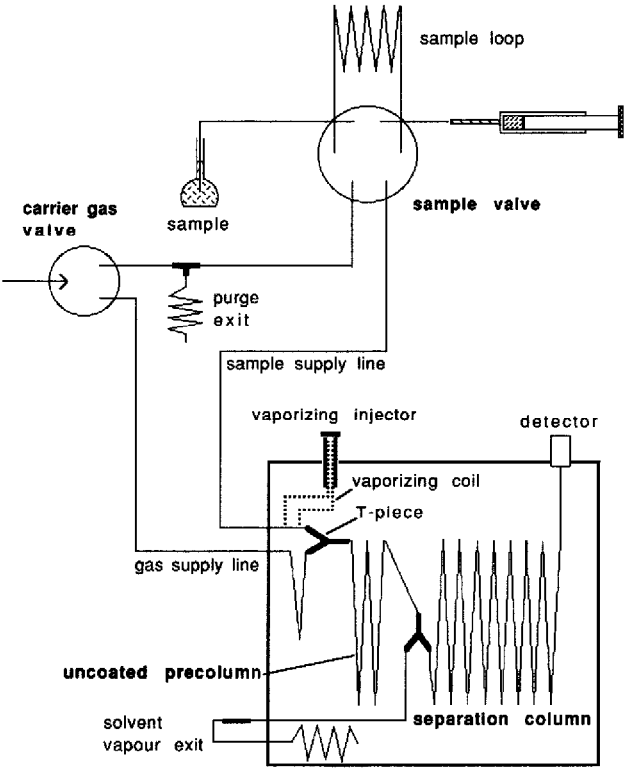

Fig. 3. Instrumental set-up used for the experiments described, basically involving a loop-type interface. However, the T-piece at the entrance of the uncoated precolumn and part of the carrier gas supply line are placed inside the GC oven. Further, there is no retaining precolumn ahead of the solvent vapour exit. The vaporizing coil entering the vaporizing injector was used for testing vaporization of the sample prior to introduction; an experiment to be described in a later paper.

sample supply line, even when the main evaporation takes place there (which is unlikely anyway with aqueous solvent mixtures, because the required heat of evaporation is large, and therefore the liquid penetrates relatively far into the oven-thermostated system). As there is a co-solvent–main solvent mixture pouring into the precolumn, solute material is carried safely through the T-piece under all conditions.

Second, the slow evaporation of the high-boiling co-solvent causes strongly broadened solvent peaks when the T-piece is kept outside the GC oven. At the end of the transfer, there is solvent within the T-piece and pushed backwards into the carrier gas line from the carrier gas valve. Switching the carrier gas valve causes the bulk of the liquid to be moved into the GC precolumn. However, there remains a film of liquid on the capillary wall that only can be transferred through evaporation. Although hardly 1 μl of liquid is involved, evaporation is disturbingly slow for high-boiling co-solvents.

For the loop-type interface used here, the T-piece and part of the carrier gas supply line were placed inside the GC oven. Both the carrier gas and the sample supply line consisted of 0.32 mm I.D. fused-silica capillaries, connected to a press-fit

T-piece. The oven-thermostated carrier gas supply line had a length of 50 cm; the remainder of the line outside the oven was *ca.* 40 cm long. The ratio of these two lengths must be chosen according to the pressure increase during transfer, as the extra pressure compresses the internal gas volume, pushing sample liquid into the line.

No retaining precolumn

Normally, concurrent solvent evaporation is carried out with two precolumns placed before the solvent vapour exit: an uncoated precolumn (2–4 m long) and a retaining precolumn about 3 m long, consisting of a piece of the separation column[17]. The retaining column is needed for retaining solute material of intermediate volatility, preventing their loss through the solvent vapour exit together with the solvent vapour. When working with co-solvent trapping, the retaining precolumn is not needed, as the co-solvent layer in the uncoated precolumn serves the same purpose (and retains volatile components far more efficiently than the stationary phase film in the retaining precolumn).

The solvent vapour exit was constructed of a press-fit T-piece and a 30 cm × 0.32 mm I.D. fused-silica capillary leaving the GC oven. To close this exit, a 1 m × 75 μm I.D. fused-silica capillary was attached to the outlet of the 0.32 mm I.D. capillary by a press-fit connector. For three reasons, this resistance capillary was re-introduced into the GC oven. First, recondensed, viscous solvent may completely block such a resistance for a long time, stopping the purge flow required to keep residual solvent vapour from the solvent vapour exit line away from the chromatographic path. Second, recondensation of solvent greatly reduces the volume, causing more vapour to be drawn into the solvent vapour exit (analogous to the recondensation effect in split and splitless injection[18]). This may have a strong impact on the (normally very small) proportion of the carrier gas–vapour mixture leaving through the solvent vapour exit, causing a loss of volatile solute material, co-evaporating with the co-solvent at the end of co-solvent evaporation. Finally, the resistance through the separation column increases with the oven temperature. To keep the proportion of the purge flow-rate with respect to the total carrier gas flow-rate constant, the resistance of the solvent vapour exit line must change with that of the separation column.

Wide-bore precolumn

In the interest of rapidly discharging the very large volume of vapour created by aqueous solvent mixtures, a wide-bore precolumn was used. In addition to the enhanced permeability, such precolumns offer an increased capacity for retaining liquid as a film on the precolumn wall. As this capacity increases proportionally with the inner diameter, a correspondingly shorter precolumn can be used, further reducing the resistance to the vapour flow.

There is probably an upper limit to the diameter of the precolumn; excessively wide precolumns used at excessively high flow-rates cause concurrent eluent evaporation to get out of control, as the liquid pushed into the precolumn by the carrier gas "shoots" too far. However, this limit has not been identified yet. The uncoated precolumn used here consisted of a 5 m × 0.53 mm I.D. fused-silica capillary deactivated with diphenyltetramethyldisilazane (DPTMDS), resulting in phenyldimethylsilylation.

RESULTS

Fig. 4 shows a chromatogram obtained from a 1-ml injection of water containing 20% of butoxyethanol. The sample components were C_{14}–C_{24} methyl esters; earlier peaks are obscured by the impurities in the butoxyethanol. Separation was 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. Transfer occurred at 114°C and 1 bar inlet pressure; during analysis, the inlet pressure increased with the oven temperature from 0.75 to 0.85 bar.

The solvent peak shown in the chromatogram has a width of 7.5 min. However, a closer analysis of the solvent peak observed at high attenuation and of the change of the inlet pressure during transfer (to be discussed in a later paper) makes it possible to explain this solvent peak width in more detail. Concurrent eluent evaporation took 5.5 min (starting about 1 min before the solvent peak began to be eluted). This means that the vapours passed through the solvent vapour exit at a remarkable rate of 440 ml/min. At the end of concurrent solvent evaporation, the solvent vapour exit was closed (connected to the high resistance). The additional 2 min of the solvent peak were due to evaporation of the small amount of co-solvent left in the precolumn, the vapour of which had to be discharged through the whole separation column and the GC detector. The last 1-min solvent peak width is due to impurities in the butoxyethanol.

Despite the fact that more than 100 ml of water passed through the system before the chromatogram shown was recorded, no tailing of the ester peaks was observed. This is worth noting after having experienced how rapidly precolumns become active when water is introduced.

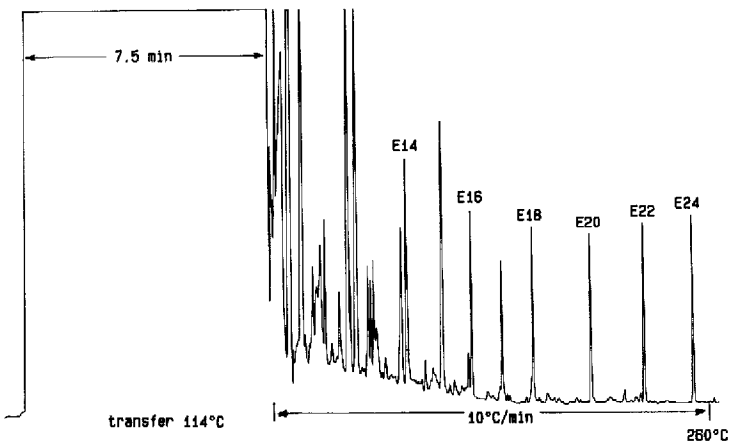

Fig. 4. Chromatogram resulting from the introduction of 1 ml of water containing 20% of co-solvent (butoxyethanol). Sample components, C_{14}–C_{24} methyl esters (E14–E24). With conventional concurrent eluent evaporation, all solute material was lost up to the last two peaks. More intensively purified butoxyethanol will be needed.

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