CHREV. 158

PARTIAL SOLVENT TRAPPING IN CAPILLARY GAS CHROMATOGRAPHY

DESCRIPTION OF A SOLVENT EFFECT

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CONTENTS

1. INTRODUCTION

I find it amazing that, more than 20 years after its introduction and with tens of thousands of users, there are still fundamental phenomena in capillary gas chromatography which are unexplored. One such phenomenon is described in this review.

According to the classical concept, the "solvent effect" sharpens the peaks eluted after the solvent peak (used for splitless and cold on-column sampling). Occasionally, however, broadened peaks are seen. The surprised chromatographer might assume that the cause of this problem is insufficient recondensation of the solvent in the column inlet (splitless injection). Accordingly, he might lower the column temperature or increase the sample size (if possible). As a result, the peaks might become even broader. Another disturbing feature would be the presence of perfectly shaped peaks just beside the "patients". This review describes the characteristics of this peak distortion and the source of the problem.

There are several solvent effects. Common to all is that the sample influences its own chromatography, usually via the solvent but perhaps also via a component[1]. The classical "solvent effect" is due to condensed solvent in the column inlet[2–6]. The condensed solvent behaves like a temporary stationary phase. The average thickness of this layer is of the order of 10 μm, and thus exceeds the film thickness of the regular stationary phase by a factor of 10–100. Therefore it is not surprising that such a layer of solvent influences the chromatography of certain sample components, sharpening some peaks, but broadening and distorting others.

The "solvent effect" was first utilized in splitless injection[7]. The solvent re-

condenses partially in the column inlet when the column is kept at a temperature at least 20°C below the boiling point of the solvent. This layer of solvent was found useful in trapping the sample components. As the splitless transfer of the sample vapours from the injector into the column requires 30–80 sec[8], the initial bands tend to be broad ("band broadening in time"[9,10]). This broadening is avoided if the recondensed solvent retains (traps) the transferred sample until the last portion of the sample has entered the column. All the sample is then collected in the condensed solvent. This "solvent trapping effect" requires that the layer of recondensed solvent remains in the column inlet at least until the sample transfer is completed. Afterwards, the solvent evaporates, thus allowing the trapped material to be chromatographed normally.

I propose to use the term "solvent trapping effect" in analogy to the "cold trapping effect", where the sample components are trapped in the column inlet by a low column temperature. The two effects are closely related since both create a zone of high retention in the column inlet.

Cold on-column sampling is always associated with condensed solvent in the column inlet. The liquid sample must be introduced into a column kept at a temperature below the boiling point of the solvent to avoid an excessively rapid evaporation of the sample (which would create a larger vapour volume than could be carried away by the carrier gas)[11]. The condensed solvent is again the source of solvent effects.

Cold on-column injection does not result in broadened bands due to a slow sample transfer as in splitless sampling. Accordingly, the related aspect of solvent trapping is not important. However, there is a second aspect of the solvent trapping effect which is relevant for the initial band width in cold on-column as well as splitless sampling. This requires careful attention as it is directly related to the subject of this review, the "partial solvent trapping".

The evaporation of the solvent in the column inlet requires a relatively long period of time —up to several minutes (which is in fact used for the trapping in splitless sampling). The sample components of interest must be released from this solvent layer within a fraction of a second to give them a short initial band width. Successful solvent trapping achieves this by a retention of the components until the last portion of the solvent is evaporated.

Visual observation of certain glass capillaries is a great help in understanding how the solvent retains the sample components until the very last moment of its evaporation. First the liquid flows into the column until a mechanically stable layer "coats" the column inlet —commonly over a column length of several tens of centimetres. During this flow of liquid the solvent starts to evaporate. The important point is that evaporation takes place exclusively at the rear (injector oriented) end of the wet (solvent coated) zone of the column. The carrier gas is rapidly saturated with solvent vapour when passing this area. Thus it is unable to take up further amounts of vapour from the forward part of the wet zone. As a consequence, the solvent does not evaporate simultaneously from the whole length of the wet zone. The rear of the solvent zone seems to move towards the front. The solvent does not disappear gradually but there is a clear moment when the rear reaches the front of the wet zone.

The movements of the volatile and the high boiling sample components have to described separately. The components which are non-volatile at the column temperature during sampling remain on the spot where they were left by the evaporating

solvent. Hence they are spread out over the whole length of the previously wet zone. This is the source of the "band broadening in space"[9,10,12,13]. The volatile components follow the rear of the wet zone. As soon as the solvent is evaporated at a given spot, these components start migrating. However, they only move as far as the rear of the wet zone, where they are trapped again. Finally, they are concentrated at the spot where the last portion of the solvent evaporates and are released within a very short period of time. This sudden release of the sample components, the second aspect of the solvent trapping effect, is a prerequisite for splitless and on-column sampling. Although the sample transfer in on-column sampling is rapid, peaks would be broad due to slow evaporation if the components were not trapped by the solvent.

2. SOLVENT TRAPPING

If the condensed solvent in the column inlet is regarded as a temporary stationary phase, it may be characterized by its ability to retain given compounds. A solvent trapping effect requires a very high —ideally infinite— retention of the sample components of interest, first to confine the introduced vapours to a short initial band (splitless sampling) and secondly to prevent release of sample material before the solvent is completely evaporated. The retention power of the solvent is usually high due to the enormous thickness of the layer —provided the solvent and the sample components do not differ greatly in polarity.

To summarize, there are two requirements for a successful solvent trapping effect:

(a) In splitless sampling the solvent must recondense in the column inlet and remain there at least until the sample transfer from the injector to the column is complete.

(b) The solvent must retain the sample components of interest.

These requirements apply to sample components eluted after the solvent peak. The situation is more complex for components eluted before the solvent peak, but will not be considered in this review.

3. NON-TRAPPED COMPONENTS

Very rarely, peaks are observed which are not influenced by the condensed solvent, although eluted in the early part of the chromatogram. Their retention is the same as in split injection. Thus, these components are not trapped at all. Considering only peaks after the solvent peak, such non-trapped components must be both volatile and poorly retained by the solvent. Also they must be more retained in the (thin) film of the regular stationary phase than in the (thick) solvent layer. Fig. 1 illustrates such a situation. A mixture containing two alkanes (n-decane and n-undecane) and ethanol, diluted $ca.$ 1:500,000 in n-pentane or n-hexane, was injected in splitless mode and by cold on-column sampling. The column temperature was 30°C, which caused a strong recondensation of the n-hexane in the column inlet in splitless mode. Fig. 1a and b show splitless injections. Perfect peaks for the two alkanes are seen in Fig. 1a. The solvent trapping effect reconcentrated them at the head of the column. The ethanol peak, however, is badly deformed, as in Fig. 1b where the solvent was n-pentane instead of n-hexane. As n-pentane did not recondense
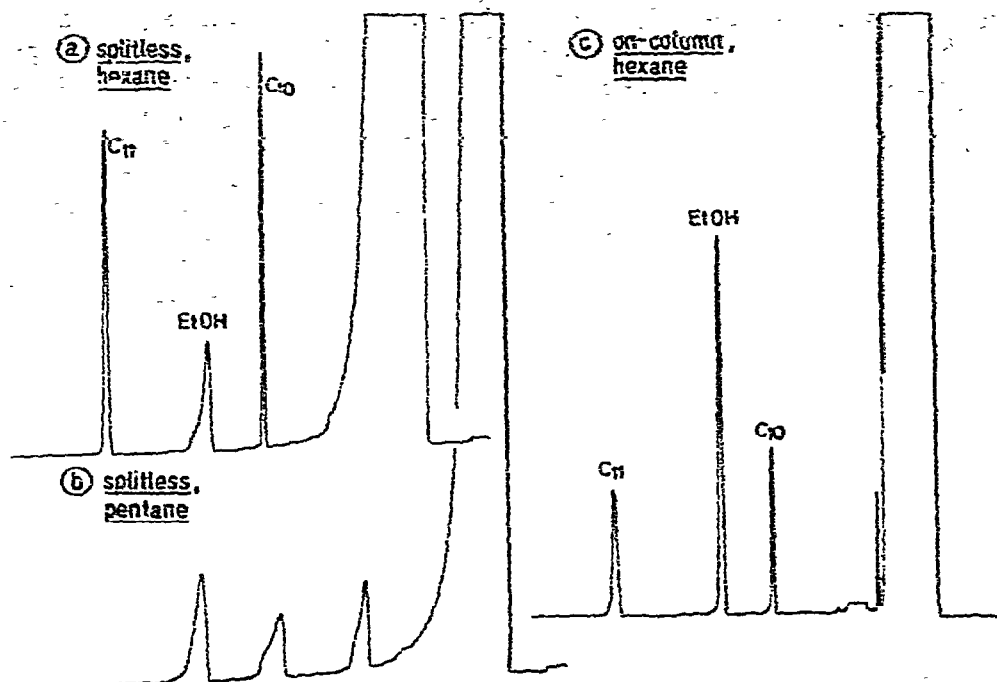
Fig. 1. Ethanol (EtOH) as a non-trapped component when injected with an alkane as the solvent; *n*-decane and *n*-undecane are reference peaks which are solvent trapped in Fig. 1a and c. Column: 25 m × 0.32 mm, coated with 0.16 μm of Carbowax 400; 0.4 atm H₂ as carrier gas; temperature, 30°C. 1a, splitless injection of 2 μl of a *n*-hexane solution; splitless period, 25 sec. The non-trapped ethanol peak reflects the sample transfer from the injector to the column. 1b, Splitless injection of 2 μl of a *n*-pentane solution as in 1a. Since *n*-pentane did not recondense in the column inlet there is no solvent trapping even for the alkane peaks. The peak shapes resemble the shape of the ethanol peak in 1a, but the latter peak is sharper due to the accelerated sample transfer caused by the recondensation of the solvent*. 1c, Cold on-column injection of the *n*-hexane solution (sample volume 2 μl). The ethanol peak is not broadened notably because the sample transfer is rapid and ethanol is not trapped in *n*-hexane and is therefore released from the condensed solvent immediately upon injection. Note the shift in relative retention times as compared to 1b. The alkane peaks are retarded due to the solvent trapping effect whereas ethanol is eluted at the same retention time as in 1b.

in the column inlet, there was no solvent trapping effect —even for the alkanes. The shape of these deformed peaks is a result of the transfer from the injector to the column. The deflexion of the chart pen was rapid when rising, indicating an abrupt arrival of the sample vapours in the column. During the transfer, the vapours in the injector became increasingly diluted by carrier gas. Thus less material was transferred per volume of gas or per unit of time. Accordingly, the pen slowly returned toward the baseline. After 25 sec the splitting valve was opened to purge the injector. As this stopped the sample transfer, the pen dropped back onto the baseline. (For demonstration purposes the splitless period was chosen to be short. Under the conditions used, there was no satisfactory —95% or more— sample transfer.)

In splitless sampling the width of a non-trapped peak is equal to the splitless period plus the peak broadening due to the chromatography. The peak shows a broad tailing, the end of the tail being cut off.

Fig. 1c shows the result of a cold on-column injection of the same mixture, all other conditions being identical. The two alkane peaks are as in Fig. 1a, but the ethanol peak is not broadened notably.

The shape of the ethanol peak may be discussed on the basis of the two aspects of the solvent trapping effect discussed in the Introduction. The broad inlet band of ethanol in Fig. 1a, the result of the slow sample transfer in splitless injection, was not reconcentrated as ethanol was not trapped in n-hexane. This kind of band broadening was not important for cold on-column sampling, because the sample transfer time is negligible. This explains the difference between Fig. 1a and c. However, it does not explain other details of the chromatograms. The second aspect of the solvent trapping effect, the release of the sample components, must now be considered.

The release of the alkanes and the ethanol from the head of the column occurred at different times. As is typical of a solvent trapping effect, the alkanes were retained until the last portion of the solvent evaporated. Their chromatography did not start until nearly 1 min after the injection. The ethanol, however, was not trapped and started to be chromatographed immediately after the injection. This has some consequences for the relative retention times of the peaks in Fig. 1b and c. In Fig. 1b (without a solvent trapping effect) the ethanol peak is slightly closer to the n-undecane than to the n-decane peak (which is exclusively the result of the selectivity of the regular stationary phase of the column, Carbowax 400). In Fig. 1c, however, the ethanol peak is shifted toward the n-decane peak.

The alkane peaks in Fig. 1c are sharp because these components were released at the moment when the last portion of the solvent evaporated. The ethanol peak is sharp because this component left the solvent layer immediately after the injection. As a first approximation, the ethanol was not retained in the n-hexane layer at all.

A precise determination of the width of the ethanol peak in Fig. 1c reveals a minute broadening as compared to that obtained in a split injection. Under more extreme conditions, using methanol and a shorter column to give a shorter retention time, this peak broadening was confirmed. It is partly due to the fact that there is no truly non-trapped component. Another reason for the broadening might be the time needed for some molecules to migrate through the solvent to the surface of the liquid before their evaporation. In the first moments after the injection the thickness of the solvent layer is still enormous (before being reduced by liquid flowing into the column). Nevertheless, in practice for gas chromatography (GC) this broadening may be neglected.

To summarize, non-trapped components introduced by the cold on-column technique produce (nearly) perfect peaks with a relative retention time which depends on the injection conditions (sample size, column temperature). For some applications it might be advantageous to use cold on-column sampling instead of the splitless method to avoid peak broadening.

4. PARTIAL SOLVENT TRAPPING

The phenomena of partial solvent trapping are more frequently observed than those of non-trapping. Partial solvent trapping occurs if a component is neither fully trapped (normal solvent trapping effect) nor so weakly retained, e.g., ethanol in hexane, that the component is liberated immediately after the injection. A partially

trapped component is retained to some extent in the solvent, but not sufficiently to create a trap —the trap "leaks".

Partially trapped components form broadened peaks. In contrast to non-trapped components, their peak widths are not dependent on the splitless period. Their initial band widths are determined by the time at which each component evaporates from the solvent layer. Very often this time is equal to the evaporation time of the solvent —the time during which condensed solvent is present in the column inlet. The evaporation time of a solvent may be determined visually in certain glass capillaries. Some values for different solvents and different sample volumes are given in ref. 9. They range from less than 10 sec to more than 3 min, most often being between 30 and 60 sec, and are dependent on the solvent, the column temperature and the quantity injected. Polar solvents require longer evaporation times (higher evaporation energies) than apolar solvents. Water may remain in the column inlet for 10 min. Accordingly, peak broadening due to partial solvent trapping becomes more drastic with larger sample volumes, more highly polar solvents and increasing difference between the column temperature and the boiling point of the solvent. This explains, why an operator, trying to eliminate peak broadening by a reinforced recondensation of the solvent, may worsen the results instead of improving them.

Fig. 2 shows some peaks of partially trapped components. The mixture used for all of the four chromatograms contained benzene, methyl butyrate, trichloroethene and chloroform diluted in n-hexane. The column was coated with 0.13 μm of Carbowax 400. Fig. 2d shows the normal, perfectly shaped peaks obtained by a split injection. Fig. 2a depicts the result of a splitless injection of a more dilute solution (about 1:100,000). As the sample size was increased from 2 to 3.5 μl (including the content of the syringe needle), Fig. 2b was obtained —a chromatogram which cannot be interpreted.

For the interpretation of Fig. 2a it is helpful to know the evaporation time of the solvent, 56 sec. The width of the benzene peak at half-height was 60 sec. The peak started to elute at the retention time observed for benzene in Fig. 2d (split injection). Thus the first part of the benzene started to chromatograph as soon as it entered the column without being trapped. But the majority of the benzene was trapped and released from the solvent layer until the condensed solvent had evaporated. Thus the peak width of 60 sec is the sum of the evaporation time of the solvent and the broadening effect in the column (determined in Fig. 2d).

The peak broadening due to partial solvent trapping is related to the second aspect of the solvent trapping effect, the release of the sample from the solvent layer. Therefore it does not depend on how the condensed solvent was introduced. Splitless and cold on-column sampling produce nearly the same results. There may be some difference due to a different evaporation time of the solvent. In splitless sampling only a limited proportion of the sample is recondensed if the column temperature is fairly close to the boiling point of the solvent. Thus there may be less solvent to be evaporated if the same quantity is introduced by splitless injection instead of by the cold on-column technique.

There is no difference in the partial solvent trapping effect when comparing Fig. 2a and c. which show a splitless and a cold on-column injection of the same sample size. At the column temperature used (28°C) the recondensation of n-hexane after the splitless injection was virtually complete, resulting in the same evaporation time of the solvent as for the cold on-column injection.
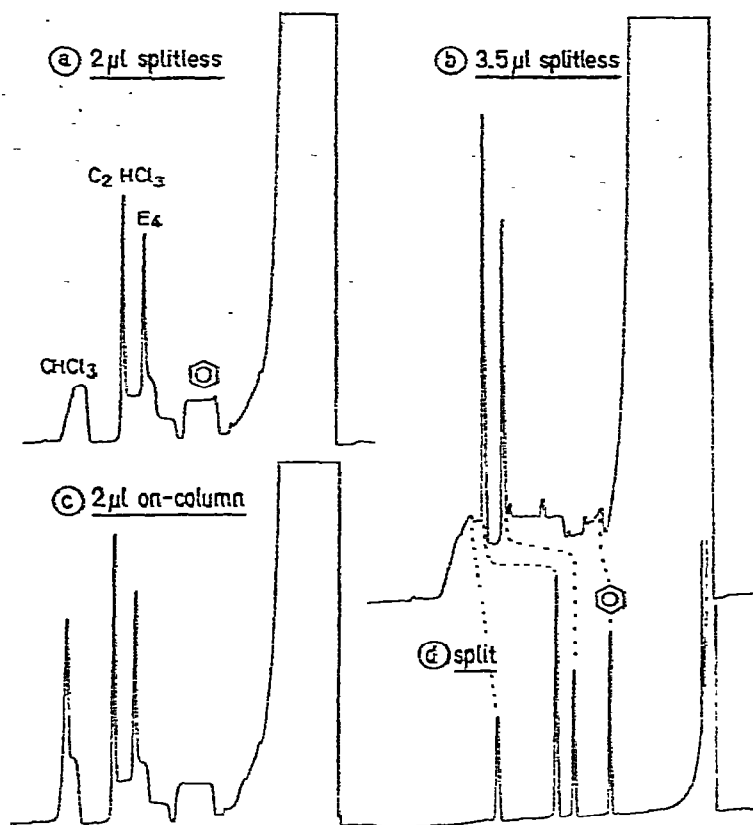
Fig. 2. Partially solvent trapped components dissolved in *n*-hexane: benzene, methyl butyrate (E₄), tri- chloroethene and chloroform. Column: 30 m × 0.31 mm, glass capillary, coated with 0.13 μm of Carbowax 400; 0.4 atm H₂ as carrier gas; temperature, 27°C. The peak shapes reflect the evaporation of the com- ponents from the layer of condensed solvent in the column inlet. Benzene evaporated continuously during the time condensed solvent was present in the column inlet. Chloroform evaporated rapidly and should be classified as intermediate between non-trapped and partially trapped. The two other peaks overlap in 2a and c. Parts of them were fully trapped and released only when the solvent was completely evaporated.

Comparing Fig. 2a and c, there is a difference in the shapes of the chloroform peak. Chloroform is only slightly trapped in *n*-hexane and may be considered as an intermediate case between non-trapping and partial trapping. The shape of the chlo- roform peak in Fig. 2a is mainly determined by the splitless sample transfer (compare with Fig. 1a). However, the perfect peak shape expected for a non-trapped peak in an on-column injection is not observed, confirming that there still is partial, although weak solvent trapping.

Partial solvent trapping effects are most often seen either for non-polar or for polar solvents when analysing components with strongly differing polarities. These two cases are considered below for two typical test samples.

5. NON-POLAR SOLVENTS

Non-polar solvents have little ability to solvate sample components. Intermolecular forces between the molecules of the solvent and the sample are small, hence their retention power is poor. Accordingly, there is a wide range of relatively volatile compounds which are partially trapped in solvents like n-hexane.

Fig. 3 shows a selection of compounds which form distorted peaks when injected splitless or on-column with n-hexane as the solvent. Fig. 3a, obtained by a splitless injection, should be compared with Fig. 3b, the result of a split injection which did not create condensed solvent in the column inlet. Two components, n-
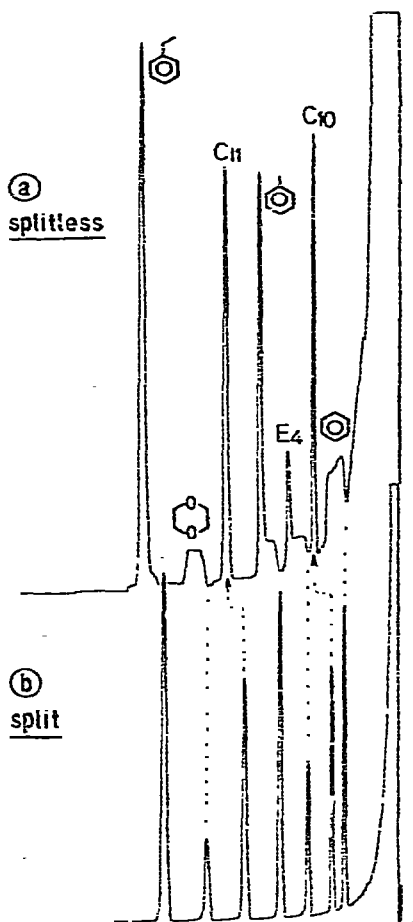

Fig. 3. The trapping behaviour of some apolar to medium polar components in n-hexane as solvent. Column: 18 m × 0.32 mm, glass capillary, coated with 0.09 μm Carbowax 400; 0.3 atm H₂ as carrier gas; temperature, 28°C. a, Splitless injection of 2.5 μl of sample; b, split injection of 1 μl at a pre-set splitting ratio of 30:1. n-Decane and n-undecane are fully trapped. Benzene, methylbutyrate (E₄), toluene, 1,4-dioxane and ethylbenzene are partially trapped with various trapping efficiencies. Nearly all of the common solvents except the alkanes are partially trapped in alkane solvents. Note the shifts in retention times between the split and splitless injections.

decane and *n*-undecane, form perfect peaks in Fig. 3a. Their retention is prolonged by 45 sec as compared to Fig. 3b. The evaporation time of the solvent was 47 sec. All peaks other than the alkanes are distorted. The benzene peak shows a similar shape to that in Fig. 2a. Its width at half-height was 50 sec. 1,4-Dioxane behaved like benzene. In an alkane environment the two oxygen atoms are of little relevance to the volatility of the compound.

The comparison of the peaks corresponding to benzene, toluene and ethylbenzene reflects increasing trapping efficiency. The toluene peak may be regarded as composed of a broad base as seen for benzene topped by a sharp peak. The sharp peak was produced by the material which did not evaporate until the last portion of the solvent had evaporated, *i.e.*, by the fully trapped toluene. The first part of the toluene started to elute at the retention time in Fig. 3b. The sharp main peak had an extra retention of 46 sec, similar to the value for the alkane peaks. The peak of ethylbenzene had a nearly perfect shape. However, there is still somewhat of a tail on the initial side of the peak, produced by a small proportion of material evaporated prematurely from the trap —a small leak of the trap. The improvement of the peak shape from benzene to ethylbenzene is the result of decreasing volatility.

The peak of methyl butyrate shows a partial solvent trapping with a trapping efficiency between those of benzene and toluene. The same peak is also present in Fig. 2, although overlapped by the trichloroethene peak (see Fig. 2b).

The compounds in Figs. 2 and 3 show that the range of compounds which are partially solvent trapped in alkanes is broad. Weakly polar compounds such as aromatics are badly affected. More polar substances of similar volatility all form distorted peaks unless their retention in the aliphatic solvent is negligible (ethanol) and cold on-column sampling is used. The range of problematic sample components includes most of the common solvents but also compounds like N-nitrosodimethylamine.

Solvents more polar than the alkanes have far higher trapping efficiencies than alkanes. Ethers, benzene, dichloromethane or carbon tetrachloride exhibit normal solvent trapping effects for all components ranging from non-polar to medium polar. However, they fail to trap polar compounds like methanol and ethanol.

It must be concluded that alkanes, primarily pentane, hexane and petroleum ether, should be avoided if volatile components other than alkanes are analysed by a method which creates condensed solvent in the column inlet. In practice, however, it is often difficult to avoid using these solvents, either because of the requirements of the sample preparation procedure or because of the separation of the components of interest from the solvent peak. As problematic compounds elute in the early part of a chromatogram, the choice of the chromatographic conditions is usually limited. The best stationary phases to separate moderately polar compounds like the common solvents are moderately to strongly polar like polyethylen- or the polypropylene glycols (Carbowaxes, Pluronics, Ucons). It is difficult to find solvents which exhibit retention times as short as the alkanes on these phases. Columns of extremely thick films with apolar phases are rarely preferable. Again the solvent peaks tend to be very broad and to obscure important sample components.

If the use of an alkane solvent cannot be avoided, the peak broadening caused by the partial solvent trapping effect can only be minimized by the choice of conditions which reduce the solvent evaporation time.

6. POLAR SOLVENTS

Some chromatograms exhibiting "strange solvent effects" associated with polar solvents were reported by Jenkins[14]. These phenomena are the result of the partial solvent trapping effect.

Non-polar sample components are squeezed out of polar solvents and are therefore poorly retained. The use of polar solvents and apolar to slightly polar sample components results in analogous effects as described for non-polar solvents.

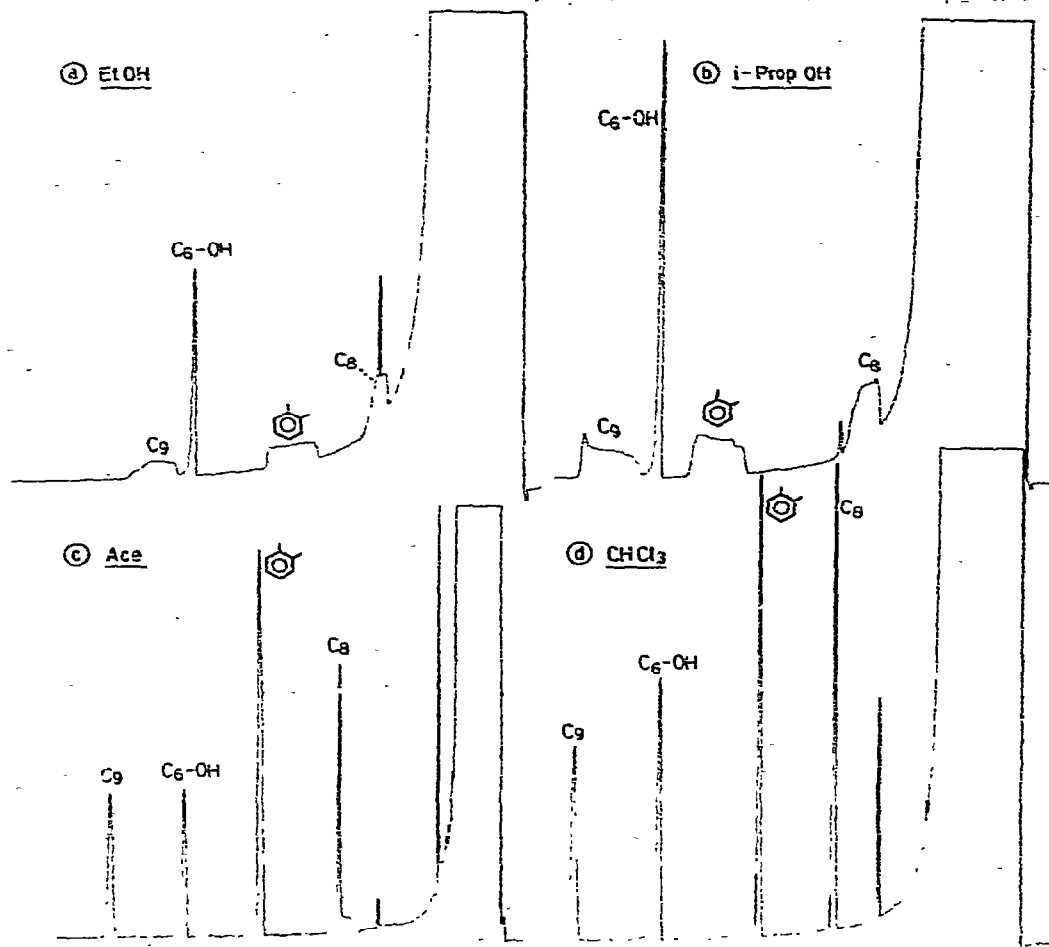Fig. 4 shows the behaviour of some components in four medium to polar

Fig. 4. Partially trapped components (*n*-octane, *n*-nonane, *o*-xylene) and 1-hexanol in medium to polar solvents: Column: 16 m × 0.30 mm, glass capillary, coated with 1.1 μm OV-73; 0.25 atm H₂ as carrier gas; temperature, 27°C; splitless injections of 1.5-μl samples. Polar solvents create strong peak broadening effects if partial solvent trapping is involved, because the evaporation of these solvents requires more time than that of apolar solvents. With ethanol as solvent *n*-octane is hardly solvent trapped. The less volatile *n*-nonane and even the *o*-xylene were still fully evaporated when the solvent was evaporated. The trapping efficiency for apolar or slightly polar components increases with decreasing polarity of the solvent. Nevertheless, solvents like acetone (or ethyl acetate) still do not fully trap *n*-octane. Chloroform trapped all the components tested.

solvents. The n-octane peak in ethanol (Fig. 4a) is broadened, although to only about half the width of the o-xylene peak. Its shape confirms a very weak trapping (comparable to chloroform in n-hexane shown in Fig. 2a). The sharp peak on top of the n-octane peak corresponds to a polar impurity present in 1-hexanol (its polar nature was deduced from the fact that the peak is sharp). The last peak of the chromatogram, n-nonane, is broader than the n-octane peak. Due to its lower volatility, n-nonane is more extensively trapped than n-octane, although the peak shape indicates that most of the material still left the ethanol rather early. The o-xylene peak indicates that it is more extensively trapped than n-nonane —the result of the increased polarity of the aromatic (b.p. of n-nonane, 150°C; of o-xylene, 144°C). 1-Hexanol was added to the mixture to indicate the shape of a non-broadened peak.

The reduced polarity of 2-propanol increased the trapping efficiency for non-polar components when compared with ethanol. The n-octane peak in Fig. 4b is broader than in Fig. 4a. According to the shape of the n-nonane peak, a considerable quantity of n-nonane was retained in the 2-propanol layer until the solvent was evaporated. Acetone (Fig. 4c) allowed the elution of all components as perfect peaks with the exception of n-octane. Ethyl acetate as solvent produced an almost identical result. Chloroform (Fig. 4d) gave perfect peaks for all components tested. In fact, its medium polarity produces a solvent trapping effect for a very broad range of compounds. Unfortunately this is of limited use because of the high GC retention on medium to polar stationary phases. The series of solvents used in Fig. 4 can be extended to include n-hexane, which resulted in perfect peaks for all components with the exception of 1-hexanol.

Recondensation of the solvent may also occur during split injections. If this is associated with a solvent trapping effect, it can be neglected, although retention times may be slightly increased. However, there are problems if partial solvent trapping effects occur as shown in Fig. 5. It may be argued that the amount of sample entering the column during a split injection is too small to produce a solvent effect. However, this ignores the fact that the recondensation of the sample may drastically alter the splitting ratio[15]. The chromatogram in Fig. 5 was obtained by an injection of 2 μl of the 2-propanol solution (as in Fig. 4b) at a pre-set splitting ratio of 30:1. Due to recondensation, the true splitting ratio was about 5:1.
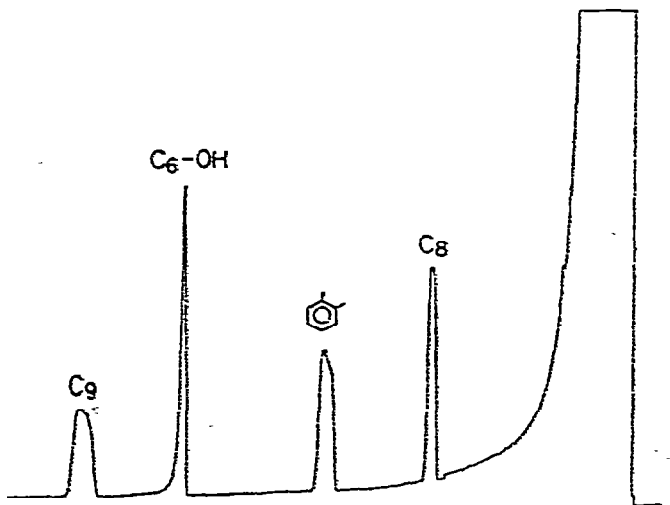

Fig. 5. Partial solvent trapping in split sampling. Column and conditions as in Fig. 4. Sample components, as in Fig. 4, dissolved in 2-propanol. Although the pre-set splitting ratio was 30:1, the recondensation of the solvent increased the flow into the column and altered the splitting ratio to about 5:1.

7. BAND BROADENING IN TIME

The peak broadening due to the partial solvent trapping effect has the chracteristics of band broadening in time, as described for peaks broadened because of a slow sample transfer from the injector to the column[9,10]. The typical characteristics of band broadening in time are:

(a) All peaks are broadened equally in terms of time or millimetres on the chart paper (isothermal runs). The first molecules within a solute band are ahead of the last ones by the same time, but not by the same distance in the column.

(b) The broadening of the peaks is reduced during temperature programming due to an increasing cold trapping effect.

The first characteristic is confirmed by the chromatograms in Figs. 2 and 3. The second is accentuated if it is caused by the partial solvent trapping effect. The reconcentration by the cold trapping effect is overlapped by an increased trapping efficiency of the solvent layer for components with an increasing boiling point. Fig. 6 illustrates this for a series of n-alkanes (C_8–C_{13}), diluted 1:300,000 in ethanol, injected in splitless mode onto a column at 27°C. After the elution of n-octane the column temperature was programmed. The interpretation of this chromatogram requires a comparison with Fig. 4a. In Fig. 4a the n-octane peak was about half as wide as the n-nonane peak. In Fig. 6 these two peaks have similar widths due to the sharpening of the n-nonane peak by the cold trapping effect. The n-decane peak comprises a relatively small, broadened base of partially and a dominating sharp peak of fully trapped material. The width of the base in this case is drastically reduced since the elution temperature of n-decane was about 30°C above that of n-nonane. For such a temperature difference the cold trapping effect reduces the initial band width by a factor of four. The n-undecane peak is perfect: the cold trapping effect would have reduced the initial band width by another factor of three, and it may be assumed that the n-undecane has been fully trapped by the ethanol.

Fig. 6 shows that the peak distortion due to partial solvent trapping is a phenomenon of the early part of a chromatogram.

8. INDEPENDENCE OF THE STATIONARY PHASE

It is often said that solvent effects depend on the stationary phase of a column. However, at least for solvent trapping effects, there is no plausible explanation or supporting data in the literature.

Fig. 7 attempts to show that the partial solvent trapping effect is not dependent on the stationary phase. Solvent trapping occurs in the first 40–80 cm of the column length. Using a column coated with Carbowax 400, the chromatographic characteristics of the inlet section of length 1 m were varied as follows:

(a) the inlet was coated with Carbowax 400;

(b) the inlet was washed free from stationary phase;

(c) 1 m of a column coated with 0.3 μm of OV-73 was coupled to the front of the Carbowax 400 column.

These configurations were tested with the mixture used in Fig. 2. Similar experiments were carried out with non-polar columns and test mixtures in polar solvents. No differences were detected. Stationary phase-dependent mechanisms such as extraction of components from the condensed solvent into the stationary phase underneath the solvent layer did not appear to be important. All three chromatograms in Fig. 7 are identical.
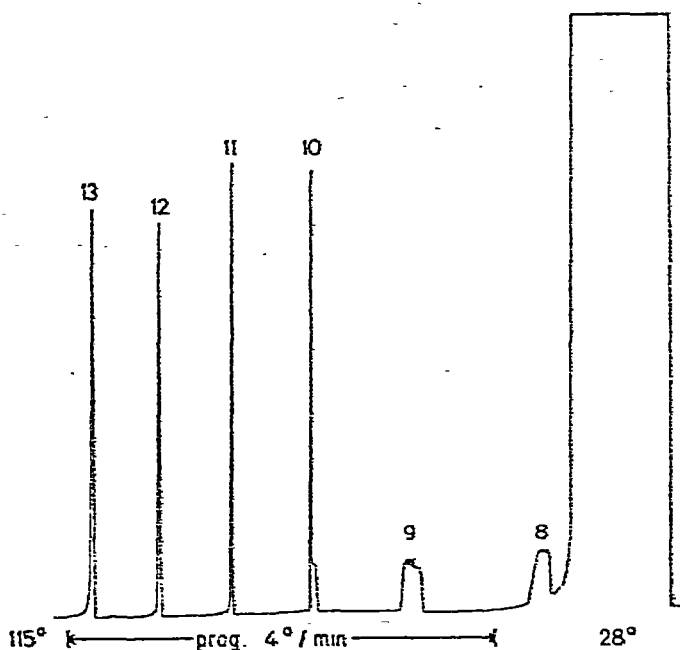
Fig. 6. Partial solvent trapping creates a band broadening in time. n-Alkanes C_8 to C_{13} in ethanol, splitless injection of a 2-μl volume. The increasing trapping efficiency of ethanol for n-C_8 to n-C_{10} is overlapped by an increasing reconcentration of the broadened bands due to the cold trapping effect by temperature programming.
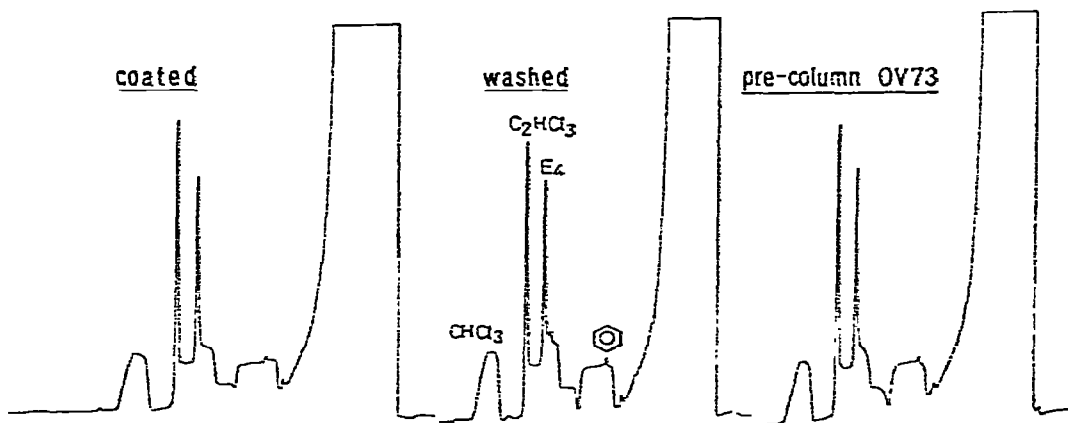

Fig. 7. Partial solvent trapping effects do not depend on the stationary phase of the column (with the exception of columns coated with extremely thick films of the stationary phase when containing a retention gap[12]). Column, conditions and test mixture, see Fig. 2; splitless injection of a 2-μl volume. The first 1 m of the column, where the partial solvent trapping effect occurs, was varied: coated with Carbowax 400 (as the remainder of the column), empty (washed) or replaced by a pre-column coated with 0.3 μm of OV-73.

9. ACKNOWLEDGMENT

10. SUMMARY

The "solvent trapping" effect is used to reconcentrate bands in the column inlet which have become broad due to the injection (splitless, direct or cold on-column sampling). Condensed solvent forms a thick layer in the column inlet which may be considered as a temporary stationary phase. To serve as a trap, the retention of the sample components in this solvent layer must be high.

Chromatograms run under solvent trapping conditions may contain broad, distorted peaks, usually in the early part. These peaks represent components which were not or only partially trapped in the condensed solvent. Non-trapped components injected by the splitless method exhibit peak shapes determined by the (slow) sample transfer from the injector to the column. Their widths are similar to the splitless period (40–60 sec). Non-trapped components introduced by cold on-column injection form negligibly broadened peaks.

Partially trapped components may exhibit very broad peaks. Such components evaporate from the condensed solvent in the column inlet, usually from the moment of injection until the solvent is evaporated. Their peak widths are usually determined by the evaporation time of the solvent, which may last 5 seconds to several minutes. The partial solvent trapping effect does not depend on the injection technique (vaporising or cold on-column), nor on the stationary phase of the column. Partial solvent trapping is frequently observed for the most volatile sample components, if non-polar components are injected with polar solvents or if medium to polar solutes are analysed in non-polar solvents.

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