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SOLVENT EFFECTS IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

A survey of the effects of large amounts of solvent on peak shapes and retention times is given. Components with an elevated boiling point are spread in the column inlet by a flow of condensed solvent; their bands are broadened and distorted by "band broadening in space". More volatile components are subject to "solvent trapping" effects, determined by their retention in the condensed solvent in the column inlet. "Phase soaking" is a solvent effect that occurs beyond the flooded inlet in the coated column and affects components eluted in the neighbourhood of the solvent or of a sample component that behaves similarly. In general, it tends to reconcentrate bands eluted after the solvent and to broaden those before the solvent.

INTRODUCTION

The "solvent effect" has been used for about 15 years to create sharp peaks in splitless sampling if cold trapping is excluded. It has been used to reconcentrate the initial bands, which are broadened owing to the slow sample transfer from the injector to the column (splitless injection period of 40–80 sec). In order to achieve a solvent effect, it has been recommended that the column should be kept at least 20°C below the boiling point of the solvent[1–6] in order to allow the solvent to recondense in the column inlet.

In on-column sampling, the "solvent effect" is required to release the sample components within a short time from the column inlet. Simultaneous evaporation of solvent and sample components would create broad inlet bands.

Despite its widespread use, the "solvent effect" remained an ill-defined concept. The expression includes all types of effects created by the solvent during chromatography of a sample —a very broad area, which calls for more detailed specification. We have shown that, *e.g.*. the "solvent effect" in splitless injection is the result of two fundamentally different effects.

Solvent effects are important for injection techniques that introduce large amounts of solvent into the head of the column (splitless and on-column, but occasionally also split sampling). However, identical effects are observed in the neighbourhood of large, overloading peaks of components that are able to modify the regular stationary phase for components which migrate with them in the column for a certain distance. Therefore, it appears to be justified to extend the concept of the solvent effects to include the influences of any sample components on the chromatography of other components.

This paper describes the two most important mechanisms leading to solvent effects. The description concentrates on on-column sampling because the vapourizing injection techniques are complicated by the sample transfer from the injector to the column, although the same principles apply.

BAND BROADENING IN SPACE

The liquid introduced by on-column injection usually forms a short plug, which is driven into the column by the carrier gas. The plug loses some liquid from its rear, as in dynamic coating (although at a substantially increased migration speed). The plug disappears after having rushed through 10–60 cm of the column (0.5–3-μl sample volumes), leaving a thick layer of sample on the capillary wall. This layer is mechanically unstable and forms waves and short-lived lenses, which flow further into the column. The flooded zone in the column inlet ultimately grows to about 20 cm per microlitre of sample (capillaries of 0.25–0.32 mm I.D.).

The flooded column inlet is chromatographically relevant because of two independent effects, the "solvent trapping" for the volatiles at the column temperature during the injection and the "band broadening in space" for the non-volatiles.

The flooding solvent spreads the sample components over several tens of centimetres of the column inlet. The components that are eluted at least 50°C above the column temperature during the injection remain deposited where the evaporating solvent has left them. Thus, they start their chromatographic development with a band width corresponding to the length of the flooded zone. Broadened and distorted or even split peaks may result, as described by several workers[7–9]. We have called this phenomenon "band broadening in space", because the parameter that determines the broadening effect is the local spreading of the material. The characteristics of this phenomenon are fundamentally different from "band broadening in time", where the important parameter is chromatographic time[10,11]. As a generally applicable method of reconcentrating bands broadened in space we have proposed the introduction of a "retention gap", i.e. the elimination of the stationary phase from the flooded column inlet[12,13] in order to accelerate the migration of the spread material within this zone. For on-column injection reduction of the broadening effect was proposed by selecting a column temperature during the injection that is 10°C above the boiling point of the solvent, in combination with the use of a secondary cooling system to avoid the partial backflow of sample[8,14]. However, the method severely restricts the choice of the chromatographic conditions; the reconcentration effect is limited, and the method requires some care to avoid broadening of the early peaks as well as losses in the accuracy and precision of results due to backflow of sample vapour.

SOLVENT TRAPPING

The volatile sample components do not remain broadened in space. Their band shape is determined by their volatility in the solvent layer of the column inlet. The solvent layer originally has an average thickness of more than 10 μm and later of about 5 μm, i.e., ten times the thickness of an average film of stationary phase. Accordingly, its retention power is high.

The most common case is the "full trapping" of a sample component, i.e., complete retention of the sample component in the solvent until the solvent itself has evaporated. A fully trapped component is released within a short time (about 0.5–2 sec), thus as a relatively narrow band with a delay corresponding to the evaporation time of the solvent in the column inlet (which may range from a few seconds to several minutes[15,16]).

"Partially trapped" components are less strongly retained by the solvent and evaporate together with the solvent over an extended period of time. Their bands are broadened and distorted, as shown in refs. 8 and 17. The distortion of the bands usually ranges between the two extremes shown in Fig. 1. Weakly retained components finish their evaporation before the solvent itself has evaporated. Their advanced fraction starts chromatographic development more or less immediately on injection, whereas the last material is delayed by less than the evaporation time of the solvent. The typical band shape is a hump or a stool. Of more strongly retained solutes, a proportion of the material remains in the solvent and is only released on the evaporation of the last portion of the solvent. This fully trapped material is released as a narrow band and forms the back of the chair-like band. The base width of such bands is usually close to the evaporation time of the solvent in the column inlet.

Very volatile or weakly solvated components are not appreciably retained by the solvent. For such "non-trapped" components the condensed solvent is nearly irrelevant, and their band shape reflects the sample transfer into the column, i.e., the band is narrow by on-column sampling and broadened according to the sample transfer time in splitless injection.

PHASE SOAKING

Band broadening in space and solvent trapping affect the shape and retention time of the solute bands in the flooded column inlet. Bands broadened in space start their chromatographic development only some time after the last portion of solvent has left the column and are not further modified by solvent effects. However, sol-
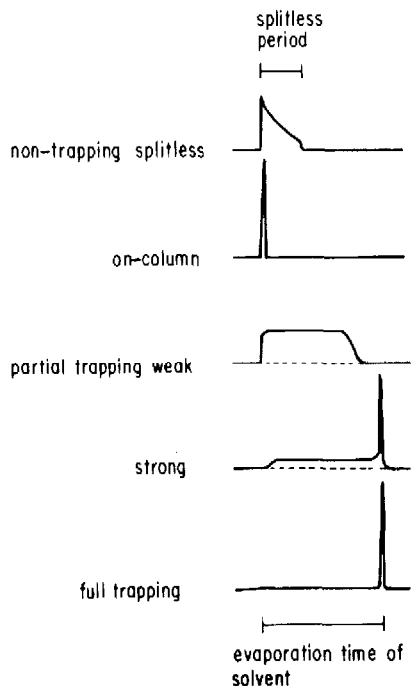

Fig. 1. Typical band shapes resulting from solvent trapping of components with different retentions in the layer of condensed solvent of the column inlet (flooded zone). The shape of these bands may be further modified by phase soaking in the coated column beyond the inlet section.

vent-trapped bands of the more volatile sample components start to migrate in a column filled with solvent vapour and are subject to an additional solvent effect, taking place in the coated column beyond the flooded inlet section. The carrier gas, saturated with solvent from the wet column inlet, loads the stationary phase with solvent. Well retained solvent may "soake" the regular stationary phase to such an extent that its film thickness is locally doubled or tripled. If polarity shifts are excluded, the retention power of the soaked column increases accordingly. Soaking of methylsilicone stationary phases with alkanes (pentane, hexane or heptane) was found to retard the migration of alkanes as solutes by factors between 2.5 and 4 (ref. 18). If the solvent improves the solvation of a component in a stationary phase of different polarity (e.g., dichloromethane as a soaking solvent for alkanes in Carbowax 400 or for alcohols in OV-1) the retardation may easily exceed factors of ten.

Phase-soaking shifts both absolute and relative retention times of solutes, which will co-emigrate with the solvent for a certain distance[19,20]. However, the more spectacular effects concern band shapes. In general, bands migrating behind the solvent are reconcentrated, whereas peaks eluted before the solvent are broadened.

The reconcentration effect by phase soaking may be considerable. We have studied a case where the band width of a partially trapped component was reduced from 2 min to less than 1 sec[21]. This reconcentration took place between the second and fifth metres of the capillary column and depended on the migration speed of the solute band relative to the solvent band.

The rear of the solvent band (soaked zone) accelerated its migration during the passage through the column. Only after it had passed 2 m of the column length did it move more rapidly than the solute band in the soaked zone. The rear of the very broad solute band was overtaken, i.e., it escaped from the soaked zone. However, the solute migrated 3.5 times more rapidly in the solvent-free than in the soaked zone. Hence, the rear solute material was basically again more rapid than the rear of the solvent band and, therefore, it kept close behind the solvent. Because the front solute material was still retarded by the soaked phase, the rear material could catch up and reduce the total band width. In our case, the rear of the solute band was able to follow the (still accelerating) rear of the solvent band until it met the front of the solute band, and this resulted in complete reconcentration. Only shortly afterwards did the solvent "run away" from the solute and left it for normal chromatographic development, at about 5 m from the entrance of the column.

The processes involved in the broadening of the band by partial solvent trapping and in the reconcentration by phase soaking are illustrated schematically in Fig. 2.

If the rear of the solute band is unable to follow the accelerating rear of the solvent band, the reconcentration of the band remains incomplete, because the solvent passes the front of the solute band before the rear of the solute band can join it. The front and the rear of the solute band then migrate under the same conditions, i.e., at the same speed.

The decisive parameter for full or only partial reconcentration of a band by phase soaking is the retardation factor of the solute in the soaked system, i.e., the ratio of the migration speeds in the original and in the soaked stationary phase[18]. A high retardation means that the solute material is greatly accelerated when released by the soaking solvent and that it will be able to follow the further accelerating solvent for a longer distance. A retardation factor of about 3 appeared to be the minimum for complete reconcentration.

column inlet ———■|■——— coated column
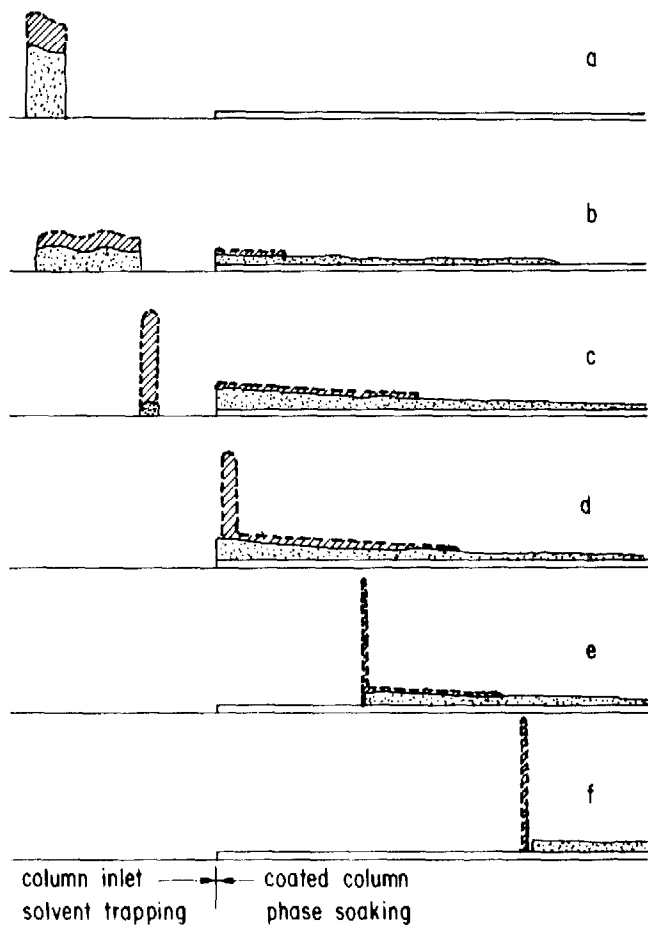solvent trapping   phase soaking

Fig. 2. Partial solvent trapping and complete reconcentration by phase soaking of a sample component eluted after the solvent. The column contains an uncoated inlet (retention gap) for the clear separation of the two solvent effects. (a) The injected solution forms a thick film on the wall of the capillary inlet. The solute (hatched surface) spreads in the condensed solvent (dotted surface). (b) The liquid expands and evaporates (withdraws) at the same time at its rear. Most of the evaporated solvent is retained by the stationary phase. The soaked phase has an increased retention power for the first solute material that evaporates from the solvent and enteres the coated column (forming the broad and low "basement" of the partially solvent-trapped band). (c) The moment before the last portion of solvent evaporates. The fully trapped part of the solute (the "tower" of the band) is concentrated in this solvent and will be released together with the solvent. (d) The column inlet is dry. The solute band is located in the soaked zone and migrates rather more rapidly than the rear of the solvent band (soaked zone). (e) The solvent accelerates its migration and leaves the "tower" behind in the solvent-free stationary phase, where the "tower" can migrate several times more rapidly than in the soaked zone. But the "tower" only gets as far as the rear of the solvent band and then migrates together with the latter towards the front of the "basement", swallowing the "basement". (f) The solvent accelerates to a migration rate exceeding that of the reconcentrated solute band. The solute starts its normal chromatographic development (and separation from other components) and may already have reached the second half of the column.

A strong phase soaking effect is desirable for all solutes eluted after the solvent (or a dominant sample component behaving similarly), especially if the sample contains partially solvent-trapped components.

On the other hand, phase soaking tends to broaden peaks eluted before the solvent. The basic mechanism is shown in Fig. 3. The advanced solute material is less
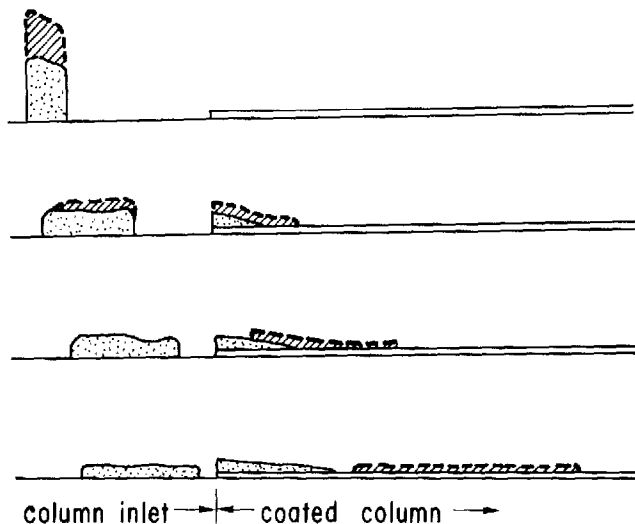
column inlet —▶|◀— coated column —▶

Fig. 3. Effect of solvent trapping and phase soaking on a peak eluted before the solvent. The component is weakly retained by the solvent, released long before the solvent completes its evaporation. The broadened solute band enters the column coated with now solvent-soaked stationary phase. It rapidly migrates to the flat descent of the solvent hill. There the band is further broadened by the phase-soaking effect. The rear of the solute band is held back by the soaked stationary phases, whereas the amount of solvent in the stationary phase (and the retention power) decreases toward the front of the band, which lets the advanced material migrate at a higher speed.

retained than the rear part of the band, because it leaves the soaked part of the stationary phase first. However, this broadening effect is far less powerful than the reconcentration effect on peaks eluted after the solvent. It hardly affects non-trapped components, because the latter start their chromatographic development before a relevant amount of solvent has soaked the stationary phase. Thus, band broadening due to phase soaking only affects bands which were already broadened by partial solvent trapping. A number of additional reasons, including the fact that the front of the solvent band migrates at a constant speed (not accelerated as its rear), causes the broadening effect to be weak and to be significant only for a narrow range of components, eluted shortly before the solvent[22,23].

The term "reverse solvent effect" has been proposed[24] for the broadening of peaks eluted before the solvent by solvent effects. "Defocusing phase soaking effect" would correspond to the phenomenon and mechanism described by these authors, who neglected the dominant partial solvent trapping effect.

CONCLUSIONS

A detailed investigation of the phenomena related to the solvent effects runs the risk of creating a picture so complex that it will frighten many chromatographers or even stop them from using this technique. However, it must be kept in mind that the "solvent effect" has been used successfully for 15 years. This goes to show that even a simplified concept was in this case an adequate basis for achieving good results in a broad range of applications.

We have investigated the solvent effects, first, out of curiosity, and second, because in every-day work we have repeatedly encountered peaks that were broad-

ened or distorted by solvent effects, sometimes to such an extent that they could be mistaken for disturbances of the baseline. Further, a sound understanding of solvent effects is desirable as a basis for new developments[25] and to permit a systematic and comprehensive search for predictable weaknesses in the technique.

It would be difficult to produce a real chromatogram with as many types of distorted peaks as shown in Fig. 4, which summarizes peak distortion by solvent effects. The chromatogram is assumed to be obtained by on-column injection with temperature programming, starting with the elution of the solvent peak. The sample is thought to consist of components with very different polarities.

Band broadening in space is easily recognized by the same distortion of all peaks eluted at least 50°C above the injection temperature (more precisely, the temperature at which the solvent was fully evaporated). It may be avoided by a retention gap in the column inlet.

Deformation of peaks eluted after the solvent, less than *ca.* 50°C above the elution temperature of the solvent, is due to partial solvent trapping that was not balanced by phase soaking. Peak shapes may be improved by selecting a solvent with increased trapping efficiency (aiming for full trapping) and/or a stronger phasesoaking effect (to reconcentrate partially trapped solutes). A solvent of medium polarity is usually preferable to alkanes or very polar solvents. Many such problems are easily solved in this way, but there are components such as chloroform for which only a few combinations of solvent/stationary phase and injection technique give well shaped peaks[26].

Peaks eluted before the solvent are often strongly distorted. Full trapping of such components is exceptional. Most solutes are partially trapped; the most volatile and weakly solvated ones are non-trapped. Phase soaking may accentuate the broadening of partially trapped solutes eluted shortly before the solvent.

The conditions required for obtaining well shaped peaks eluted before the solvent are in many respects the opposite of what is recommended for obtaining
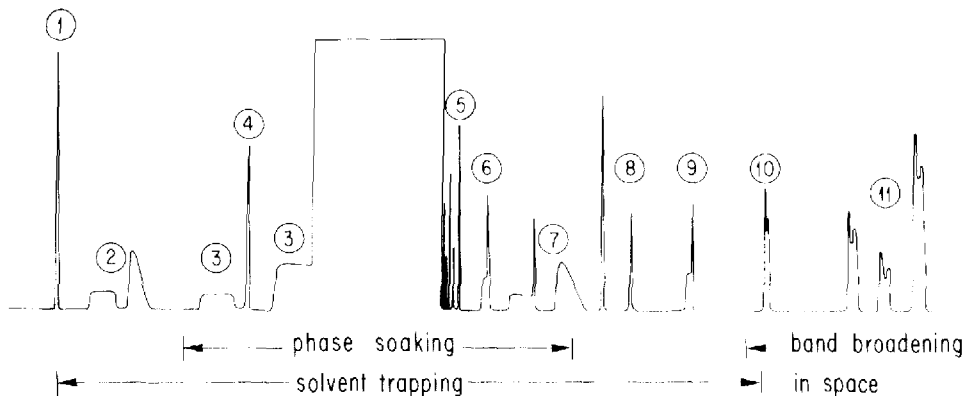

Fig. 4. Hypothetical chromatogram with an accumulation of distorted peaks of different types. On-column injection and temperature programming, started at the elution of the solvent peak. Peaks are characterized as follows: (1) non-trapped without (defocusing) phase soaking; (2) partially trapped with different trapping efficiencies; (3) partially trapped and broadened by phase soaking; (4) non-trapped and negligibly broadened by phase soaking due to weak retardation by the soaked column; (5) very sharp peaks with greatly increased retention time; partial or full solvent trapping and intensive phase soaking; (6) partially solvent-trapped component with partial reconcentration by phase soaking; (7) partially trapped with different efficiencies, no reconcentration by phase soaking; (8) fully trapped; (9) partially trapped, not reconcentrated by phase soaking but focused by cold trapping (increased column temperature due to temperature programming); (10) beginning of band broadening in space; (11) band broadening in space.

sharp peaks after the solvent. They are aimed at non-trapping, which calls for solvents of extreme polarity, as far as possible opposed to the polarity of the solute in order to minimize retention (solvation) of the sample component of interest. Further, non-trapping requires on-column sampling, because splitless sampling would create broadened bands, owing to the slow sample transfer into the column.

Keeping the causes of peak broadening due to solvent effects in mind, strategies for suppressing undesirable effects are obvious. However, in practice, such problems may make great demands on the chromatographer, because of the interdependence of the parameters he wishes to optimize. The solute may no longer be separated from the solvent peak, the best solvent may not be available in sufficient purity or one component may require conditions that are contraindicated for another solute. For certain samples the solvent effects even preclude the use of splitless or on-column sampling, and split injection must be applied with corresponding loss in sensitivity.

However, for most samples, the solvent effects help to create sharp peaks. They allow splitless injection at lower column temperatures, where cold trapping is excluded as a technique for reconcentrating slowly transferred bands. On-column sampling generally relies on solvent effects. On the other hand, it should be kept in mind that solvent effects increase retention times. The cases where solvent effects cause band broadening rather than reconcentration may be important as such, but they also allow a better understanding of the mechanisms involved.

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