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OBSERVATION OF A PEAK UNDER THE ACTION OF "PHASE SOAKING", A GAS CHROMATOGRAPHIC SOLVENT EFFECT, DURING PASSAGE THROUGH A CAPILLARY COLUMN

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SUMMARY

"Phase soaking", a solvent effect in gas chromatography that occurs in capillary columns beyond the flooded inlet section (where solvent trapping takes place), is described for an experimental sample, a solution of *n*-octane in *n*-heptane. *n*-Octane was only partially trapped by the condensed *n*-heptane in the column inlet and started its chromatography in the analytical part of the column with a band width of 2 min. However, it was subsequently re-concentrated by phase soaking to a band of less than 1 sec in width. This re-concentration was studied by the determination of the band width and migration speed of the *n*-octane and its position relative to the solvent band at different points in the column. It was found that the *n*-octane band was re-concentrated between 2 and 5 m in the analytical part of the column. The mechanisms involved in the re-concentration were (a) a reduced migration speed of the advanced material as long as the column was soaked with solvent vapour and (b) a different migration speed within the solute band when crossed by the rear edge of the solvent band.

INTRODUCTION

In two previous papers[1,2] we described solvent trapping as a solvent effect that occurs when the injection creates condensed solvent in the column inlet. The sample components are pre-chromatographed on the layer of condensed solvent. We discussed three different types of solvent trapping, as follows. *Fully trapped* components are retained by the condensed solvent until the solvent is evaporated itself. Thus the chromatography of fully trapped solutes is delayed by the time required to evaporate the solvent. They start chromatography as sharp bands. *Partially trapped* components are volatile and evaporate prematurely from the solvent layer. Commonly their evaporation lasts as long as the evaporation of the solvent, which may range from a few seconds to several minutes. This slow release causes their band at the beginning of the gas chromatographic (GC) process to be distorted and often strongly broadened. *Non-trapped* solutes are only negligibly retained by the condensed solvent and start chromatography more or less immediately after introduction into the column.

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The shape of their band reflects the transfer into the column by the injection technique used. Thus splitless sampling causes broad bands and on-column injections sharp bands.

We have also shown[2] that in addition to the solvent trapping in the column inlet there were other solvent effects modifying the chromatography of some solutes in the main, analytical part of the column. Such a solvent effect is the subject of this paper.

The "solvent effect" was subject of a number of previous papers, although only a few authors attempted to explore the mechanisms involved[3,4]. They referred to our own deficient explanation of the solvent effect of 6 years ago[5], which neglected the solvent trapping. Recently we studied the solvent effects in the analytical part of the column more systematically and obtained interesting but complex results. This paper tries to offer an introduction to the subject by a detailed description of a single experiment with a simple two-component mixture. We plan a more comprehensive treatment of the subject in the near future.

PHASE SOAKING

We propose to use the term "phase soaking" to specify the solvent effect to be discussed because we assume that saturation of the stationary phase with solvent causes the effects we observed. Phase soaking may occur anywhere in the coated column except at the flooded inlet section (the solvent trapping zone).

Before describing the experiment, a short outline of phase soaking will be given as a background. The evaporating solvent in the column inlet[6] saturates the carrier gas with solvent vapour. From the injection (split, splitless or on-column) to the complete evaporation of the solvent a constant amount of solvent vapour enters the analytical part of the column. These solvent vapours are partly retained by the stationary phase and saturate (soak) the latter to an equilibrium with the saturated gas phase, strongly "overloading" it. The amount of retained solvent may apparently even exceed the amount of stationary phase in some parts of the column. This strongly modifies the characteristics of the stationary phase, usually increasing its retention power. As the evaporation of the solvent in the column inlet is completed, the soaked stationary phase begins to dry. As for the condensed solvent in the inlet, the evaporation of the retained solvent is restricted to the rear edge of the soaked zone where the carrier gas becomes saturated with solvent vapours —the situation of an extremely overloaded peak[7].

Two aspects of phase soaking modify the chromatography of sample components. First, most solutes migrate more slowly within the soaked zone than on the "dry" stationary phase. They are typically retarded by a factor between 1.5 and 8. Second, the shape of the solute bands is modified when the solute band is crossed by the edge of the soaked zone. For a peak eluted after the solvent, this crossing has usually a re-concentrating effect because the advanced solute material is still in the soaked zone when the rear edge of the solute band migrates with a higher velocity in the "dry" part of the column behind the solvent band. If the solute band moves more rapidly than the solvent band, it crosses the front edge of the solvent and becomes broadened ("reverse solvent effect"[4]).

EXPERIMENTAL AND RESULTS

n-Octane in n-heptane as an experimental sample

Splitless or on-column injections of *n*-octane dissolved in *n*-heptane at column temperatures near 30°C gave a sharp *n*-octane peak, whether run on a non-polar OV-1 or a very polar Carbowax 400 column. This is as would be expected from common experience. A more detailed study, however, reveals a far more complex picture as a band broadening effect (partial solvent trapping) and a re-concentration effect (phase soaking) are involved, which fortunately compensate each other. We have chosen this sample for our experiments because both effects are strong and relatively easy to quantitate.

In a previous paper[2] we have shown that an on-column (or splitless) injection of *n*-octane in *n*-hexane produces a perfectly sharp *n*-octane peak because of full solvent trapping. However, *n*-octane is no more fully trapped if *n*-heptane is the solvent. Splitless or on-column injection of 2 μl of *n*-octane in *n*-heptane (10 ppm) resulted in a premature release of 30% of the *n*-octane from the solvent layer; 70% of the *n*-octane was fully trapped up to the moment when the last of the *n*-heptane had evaporated. This is the result of an experiment described in ref. 2, where the flooded inlet section of the column was disconnected from the analytical part of the column to purge the sample material behind this joint and to determine the proportion of sample material that was already transferred to the analytical column by that time. The base width of the *n*-octane band at the beginning of the analytical part of the column was nearly 2 min. It was intriguing that such a broad band could reach the detector as a peak only 2 sec in width.

Experimental concept

The shape of the *n*-octane band was known at the beginning and the end of the analytical part of the column. To investigate the processes involved in the re-concentration of the band we wanted information about the shape and the retention time of the *n*-octane band at various points in the column.

Driessen and Lugtenberg[8] observed the migration of a fluorescent component through a glass capillary column. For a number of reasons we could not apply this technique to our problem. We therefore decided to observe the band at some selected points within the column. We did not do this by connecting column sections of various lengths to a selective detector (*e.g.*, mass spectrometer) because the experiment required rigorously constant chromatographic conditions. Instead, we extended the method already applied to investigate the solvent trapping[2] to the analytical part of the column.

The column was composed of an uncoated, milky inlet section of length 1 m, which allowed the observation of condensed solvent in the inlet[6], and an analytical part consisting of a 20 m × 0.30 mm I.D. glass capillary coated with a 0.15 μm film of OV-1. The analytical column was made up of 15 sections joined together with shrinkable PTFE tubing so as to allow easy and repeated disconnection and reconnection. The joints were located between the inlet section and the analytical column and after 1, 2, 3, 4, 5, 6, 8, 10, 12, 15, 25 and 49 of the total of 50 coils of the analytical part. These joints were used to interrupt the chromatographic process at selected times. When opened, all sample material from the inlet to that point was

flushed into the GC oven. After an appropriate purge time, the column parts were recombined to elute the part of the sample that had passed the joint before the latter was opened. The peak areas of eluted *n*-octane were integrated. To determine the shape of the band of *n*-octane and the time when it passed a certain joint, we repeated the experiment, altering the transfer time by increments of 2–15 sec. Integrated peak areas represented accumulated transferred material. Thus area differences between two neighbouring determinations were calculated and divided by the time between the measurements to yield areas per unit time.

Volumes of 2 μl of sample were introduced by cold on-column sampling; the column was at 27°C (open door to allow observation and manipulation); 0.3 atm of hydrogen was used as the carrier gas and the pressure regulator was not touched throughout the experiment.

Transformation of the band shape

Fig. 1 shows the shape of the *n*-octane band as it left the inlet section of the column. Ten seconds after the injection only a negligible amount of *n*-octane had been transferred into the analytical part of the column, whereas after 15 sec it was about 0.5% of the *n*-octane injected. Up to the moment of complete evaporation of the solvent, a surprisingly constant amount of *n*-octane per unit time was released from the inlet, giving the flat "base" of the band in Fig. 1. Two minutes after the injection most (70%) of the *n*-octane eluted within approximately 5 sec. This elution of the "tower" of the peak coincided with the evaporation of the last portion of

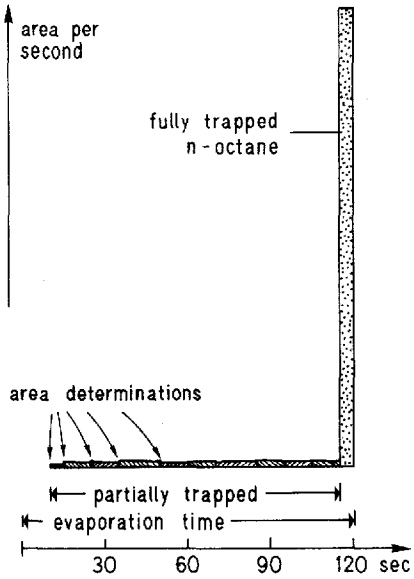

Fig. 1. Shape of the *n*-octane band as it started chromatography. Areas corresponding to solute material, which passed from the inlet section into the analytical part of the column, were determined at intervals of 5–15 sec. The *n*-octane band was composed of a flat "base" of width 110 sec consisting of partially trapped (prematurely released) material and a "tower" of solute material which was trapped until the condensed solvent in the column was evaporated itself.

solvent. Thus the "base" of the *n*-octane band represents partially and the "tower" fully trapped solute.

Two coils (0.8 m) from the inlet of the analytical part of the column, the band shape of *n*-octane was not altered (Fig. 2). Thus the "base" and the "tower" migrated with the same speed. At 5 coils, 2 m from the inlet, the "base" had a width slightly reduced from 110 to 95 sec. However, the dramatic changes just started there. At 8 coils (3.2 m) the width of the "base" was reduced to 55 and at 4 m to 25 sec. As can be seen in Fig. 2, the height of the "base", *i.e.*, the amount of *n*-octane passing the breakage per unit time, did not increase during these transformations. Thus re-concentration was not achieved by packing the area of the "base" into a shorter and higher band. The area of the "base" was reduced and the area of the "tower" increased correspondingly. The "tower" moved into the "base", incorporating the area of the latter. At 6 m from the inlet of the analytical column section no "base" could be detected. The width of the "tower" was too small to be determined by our method (less than 2 sec).

To summarize, the re-concentration of the *n*-octane band did not take place in the inlet of the analytical part of the column but between 2 and 5 m, over a surprisingly extended length of the column. The re-concentration occurred by a move of the "tower" into the "base".

Migration speeds

The re-concentration of the *n*-octane band by phase soaking was the result of a reduced migration speed of the solute in the soaked zone. By determination of the

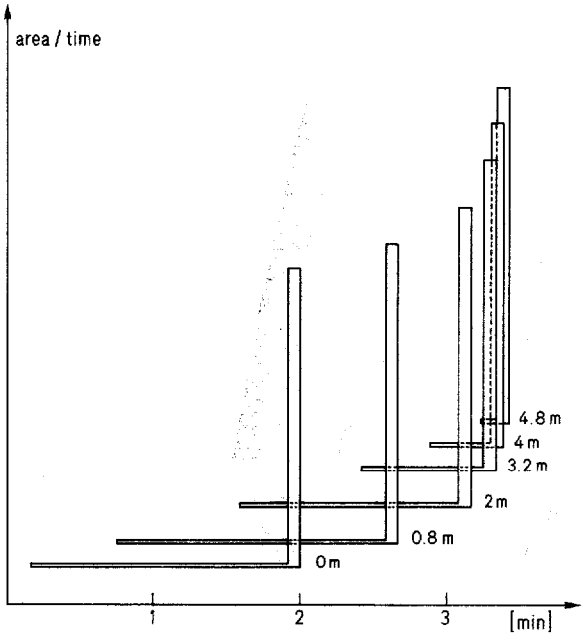

Fig. 2. Shape of the *n*-octane band at various points inside the analytical column (column without inlet of length 1 m). The band width was reduced between 2 and 5.5 m from 2 min to less than 1 sec.

times when the band passed certain points in the column, we were able to calculate average migration speeds between two breakages.

Two remarks should be made: (1) the average linear velocity of *n*-octane through the column was 9.5 cm/sec when solvent effects were virtually excluded (on-column injection of 0.1 µl of *n*-octane dissolved in *n*-pentane); (2) Figs. 1 and 2 show the band shape of *n*-octane with respect to retention time. The position of the band inside the column is just the reverse: as the "base" eluted first, it is ahead of the "tower" in Figs. 3 and 4, where the position in the column rather than retention times is shown on the abscissa.

Fig. 3 shows average linear migration velocities between two measuring points. The front of the "base" advanced about 2.4 cm/sec through the first 5 m of the analytical column, then the migration was accelerated to about 8.5 cm/sec, close to the linear velocity without solvent effects. Our experiment did not allow the changes in the migration speed to be determined in detail; we assume that it was more drastic than it appears in Fig. 3.

The reduction in the migration speed of the front of the "base" during the first 3.3 min by a factor of 3.5 is one of the two important aspects of re-concentration by phase soaking. At a non-reduced velocity the front of the "base" would have just started to leave the column when the re-concentration process was the most effective.

As the abscissa in Fig. 3 shows the position in the column (not time), it may be easily overlooked that the "tower" of the *n*-octane band started its migration only almost 2 min after the front of the "base". This is the reason why it had to rush behind the front of the "base" to achieve a re-concentration. It really did so, although

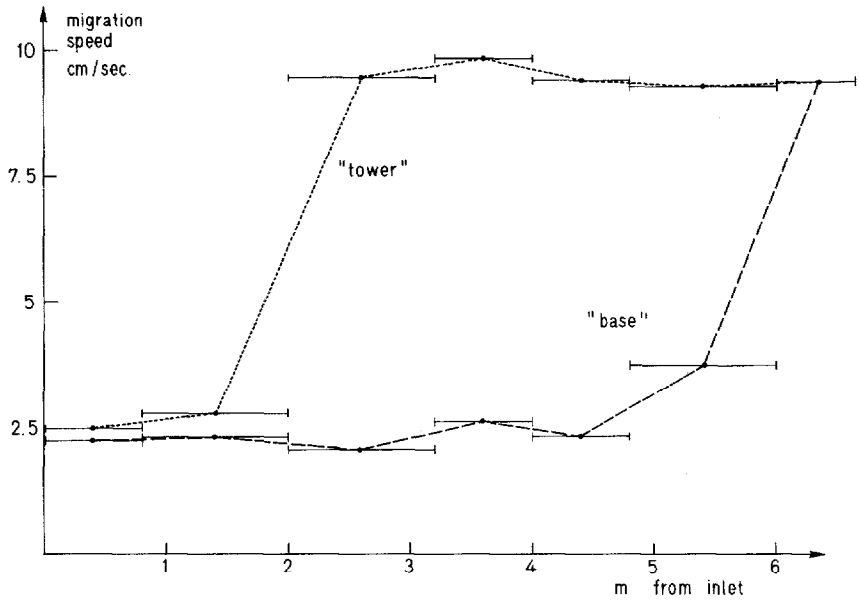

Fig. 3. Migration speeds of the "tower" and the front of the "base" at various points in the column. The front of the "base" migrated relatively slowly until it reached 5.5 m, where it accelerated to the velocity of *n*-octane when solvent effects are excluded. The "tower" started to move only 2 min later, but accelerated at 2 m to the "normal" velocity.

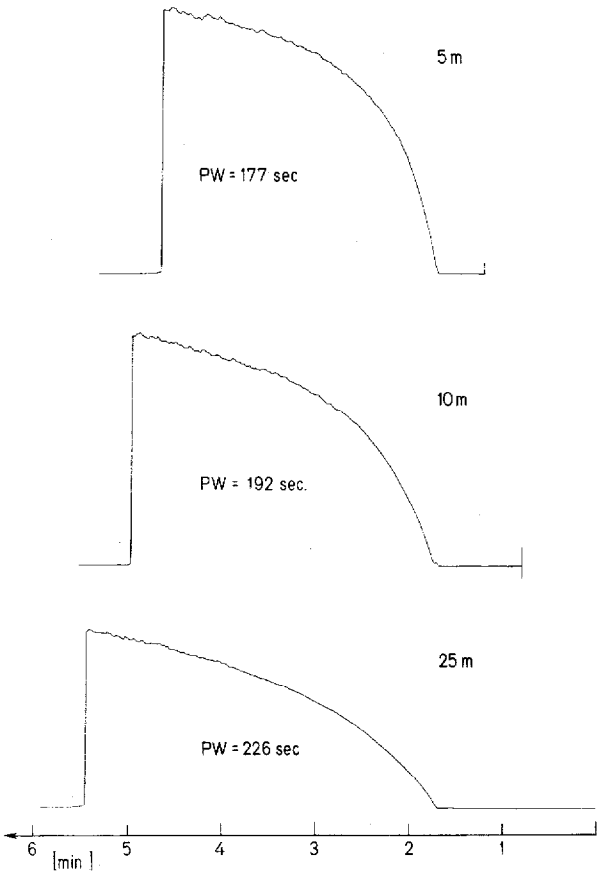

Fig. 4. FID chromatograms of the solvent peak at high attenuation, shown for a 5- and a 10-m section and the complete 20-m column. The width of the solvent peak (PW) is far from proportional to the length of the column, because the first 2 min of the peak width is due to the evaporation time of the solvent in the column inlet and because the migration speed of the solvent increased as it passed through the column (the reason why long columns improve the separation of volatile solutes from the solvent peak).

not immediately after its start. For the first 80 sec or nearly 2 m it migrated as slowly as the front of the "base", which explains why the band width remained the same during this period (see Fig. 2). Then, at about 2 m, *i.e.*, 4 m or 25 sec earlier than the front of the "base", the "tower" "took off" and migrated at nearly 9 cm/sec. This time difference allowed the "tower" to incorporate the "base" and to catch up with the front of the "base", which is the second important aspect of phase soaking that led to the re-concentration of the *n*-octane band.

The solvent peak

The changes in the migration speeds and the corresponding re-concentration effects remain unexplained as long as the solvent band is not brought into consideration. It is of particular interest to know at what time and where the *n*-octane was separated from the rear edge of the *n*-heptane band.

Fig. 4 compares solvent peaks, recorded at high attenuation with a flame-ionization detector (FID), when eluted from the complete column as well as from 10- and 5-m sections of the same column. The carrier gas flow-rate was kept constant by readjustment to give the same evaporation time of the solvent in the column inlet. The three solvent peaks are different in shape because of two overlapping factors. The solvent vapours entered the analytical part of the column at a constant rate during the evaporation time of the solvent (2 min). Thus the *n*-heptane band started chromatography with a rectangular shape. During passage through the coated column it underwent overloading processes and approached the shape of an overloaded peak, a triangle with a slow upwards slope and a rapid return to the baseline. This transformation from a rectangular to a triangular shape advanced in Fig. 4 with increased column length.

Fig. 4 shows also that the rear edge of the solvent peak is extremely steep (see also ref. 9). This is confirmed later in Fig. 7, which shows a greatly enlarged picture of the bottom of the solvent peak, and is plausibly explained by the fact that the band starts chromatography with a steep rear edge (the evaporation of the solvent ends abruptly), which is then accentuated by the overloading phenomenon. Thus the chromatographic properties of a spot in the column change dramatically when it leaves the soaked zone. This advocates a drastic change in the migration speed of part of the solute band when crossed by the rear edge of the solvent band.

The migration speed of the rear solvent edge was far from being constant throughout the column. A first approximation of its velocity may be deduced from Fig. 4, using the differences in the retention time of the rear edge of the solvent peaks. The data in Table I show that the average linear velocity increased from 10.4 cm/sec between 5 and 10 m of the analytical column section to 13 cm/sec in the second half of the column. In the first 5 m of the column this velocity was even lower than the migration speed of *n*-octane in the non-soaked column: the retention time of the rear edge of the solvent peak (3.5 min) is composed of the evaporation time of the solvent (2 min) and the retention time in the coated column (1.5 min). The rear edge of the solvent band consisted of material that entered the analytical column 2 min after injection. Thus the average linear velocity in the first 5 m of the column was 5.6 cm/sec. It may be concluded that the rear edge of the solvent migrated very slowly in the beginning and accelerated during passage through the column. This is important for extensive re-concentration by phase soaking because it explains why the *n*-octane "tower" migrated closely behind the rear edge of the *n*-heptane band for a relatively long period of time.

TABLE I

RETENTION TIMES AND AVERAGE MIGRATION VELOCITIES OF THE REAR EDGE OF THE SOLVENT BAND

Column length (m)	*Retention time (min)*	*Difference (min)*	*Migration speed (cm/sec)*
20	5.6		
		1.3	13
10	4.3		
		0.8	10.4
5	3.5		

We determined the relative position of the *n*-octane "tower" and the rear edge of the solvent band in more detail to confirm that this relative position decided when and where the "tower" accelerated its migration.

The position of the rear of the solvent band could not be determined by the technique used for the *n*-octane band because the solvent peak could not be quantitated with sufficient accuracy to decide whether all of the solvent had passed the point of interest (the solvent tended to leak out of the opened column). We used a reverse technique: at the time of interest we detached the inlet (section a in Fig. 5) from the analytical column (column parts b and c) and opened the joint of interest between parts b and c. The rear part of the solvent band was now in part b, if it had not already passed the joint. As a next step column part c had to be flushed, which was achieved by connecting it to the inlet a, omitting part b. Then part b with the possible rear of the solvent band was inserted between parts a and c (first attaching b to c, then to a) to analyse the contents of section b. This experiment was repeated until the rear edge of the solvent was detected within 2 sec. Immediately afterwards the position of the *n*-octane "tower" was confirmed.

Fig. 6 shows the times when the front of the *n*-octane "base", the "tower" and the rear edge of the solvent band passed various points in the column. The area between the front of the "base" and the "tower" is an indication of the width of the *n*-octane band. It was found that the rear edge of the solvent band was clearly behind the *n*-octane "tower" for the first 2 m of the analytical column section. Thus the "tower" migrated in the soaked zone. Around the joint at 2 m the solvent edge crossed the *n*-octane band. This coincides with the result shown in Fig. 3, *i.e.*, the "tower" accelerated its migration at that point. However, the "tower" and the solvent

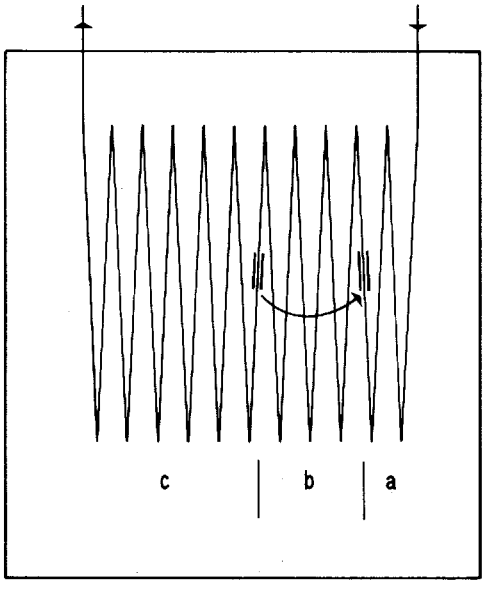

Fig. 5. Experimental procedure to determine the time when the rear edge of the solvent band passed a measuring point (a rejoined breakage) between sections b and c of the analytical column. Section a is the uncoated inlet where the solvent evaporated.

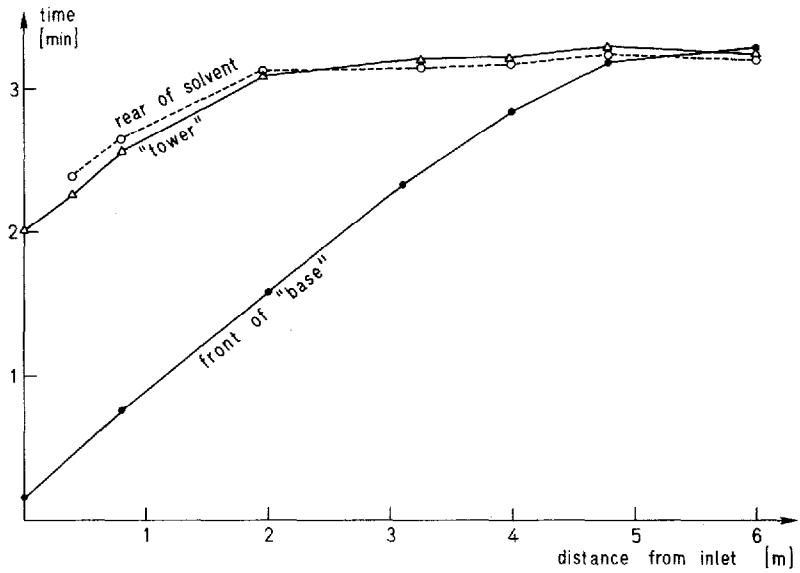

Fig. 6. Times when the front of the "base" and the "tower" of the *n*-octane band as well as the rear edge of the solvent passed the measuring points in the analytical column. The rear edge of the solvent overtook the "tower" of the solute band at about 2 m. As the "tower" left the soaked zone of the column, it accelerated its migration. The front of the "base" left the soaked zone only at around 5 m, which retarded it relatively to the "tower" and re-concentrated the band.

edge continued their migration with very similar speeds. At 3.2 m the solvent edge was ahead of the "tower" by about 2 sec and at 4.8 m by approximately 3 sec. The "base" remained in the soaked zone for a longer period of time. Its front was crossed by the rear solvent edge at about 5 m.

These results complete our picture of re-concentration by the phase soaking process as they confirm that the decisive changes in the migration speeds are due to changes in positions relative to the solvent band.

The re-concentration of the *n*-octane band was complete to the extent that it was not possible to determine a residual band width at 6 m. On the other hand, Fig. 6 suggests a remaining band width of about 3 sec, corresponding to the distance between the "tower" and the solvent band at the time when the front of the "base" was crossed by the rear edge of the solvent band. The distance between the "tower" and the solvent band would be expected to be the limitation of the re-concentration effect because at the moment the front of the "base" left the soaked zone, both edges of the solute band migrated with the same velocity. Unfortunately, our experiment did not yield results of sufficient accuracy to clarify this point.

Fig. 7 adds a few more facts about the residual band width. It shows three chromatograms of the mixture recorded with an FID. They were run on 5- and 10-m sections as well as with the full length of the column at a carrier gas flow-rate that was adjusted to give the same evaporation time for the solvent in the inlet section in all three instances. The 5-m column produced an *n*-octane peak that was separated from the solvent by only 1 sec. This should be compared with the 3 sec as given by Fig. 6. The difference may be partly due to experimental problems, partly owing to

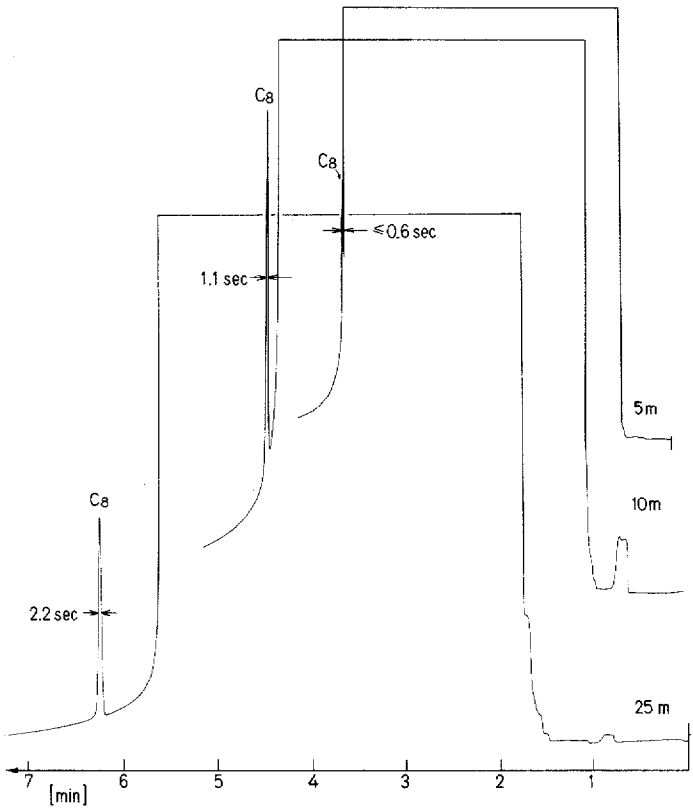

Fig. 7. FID chromatograms of the mixture as obtained from a 5- and a 10-m section and from the complete column. The chromatogram for the 10-m column allows the conclusion that the re-concentration process integrated the "base" into the "tower" of the band to an extent that left a band width of less than 1 sec.

the speed of the electrometer (Carlo Erba, Milan, Italy, Model 490) coming down from a 10,000 times higher solvent peak.

The chromatogram does not allow one to see whether the "base" was already fully integrated into the "tower" as it would have been on the solvent side of the *n*-octane peak. The peak width was about 0.6 sec, which may be influenced by the response time of the recorder (Perkin-Elmer, Norwalk, CT, U.S.A., Model 561). However, this width refers to the "tower" and not to the full band width including a possible "base". The 10-m column gave an *n*-octane peak of width 1.1 sec without any sign of a "base". It excludes a residual band width of more than 1 sec. The peak is far better separated from the solvent because of the increased difference in the migration speeds of the solvent and the solute in the second 5 m of the column.

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