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SPEED OF TEMPERATURE INCREASE WHEN USING LARGE RETENTION GAPS IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The retention gap provides an optimal re-concentration effect only if the solutes are allowed to pass through the retention gap at about 80–120°C below the elution temperature. The corresponding chromatogrpahic time must be provided either by a suitable temperature programme started at the injection temperature or at least 120°C below the elution temperature, or by an intermediate isothermal step at a temperature at which the solute passes the retention gap with a retention time corresponding to a capacity ratio between 2 and 5.

INTRODUCTION

The retention gap is a deactivated but uncoated pre-column kept in the gas chromatographic (GC) oven, which is used in splitless and on-column injection to re-concentrate broad solute bands at the beginning of the separation column[1]. The retention gap re-concentrates solute bands broadened in space[2], but is also effective if other band broadening occurs, *e.g.*, due to diffusion, overloading or adsorption inside the pre-column.

Retention gaps of large internal volume have been proposed for several purposes:

(a) Long retention gaps allow injections of large sample volumes. A 50 m × 0.3 mm I.D. retention gap accepts sample volumes between 250 and 600 μl[3].

(b) With long retention gaps it is possible to transfer directly sections (peaks) of a high-performance liquid chromatographic (HPLC) run into a capillary gas chromatograph, hence effecting on-line coupling of HPLC and GC[4].

(c) Large-bore retention gaps (0.5 mm I.D.) allow automatic on-column injection into standard capillary columns (0.2–0.3 mm I.D.)[5].

(d) Narrow-bore capillary columns cannot be used with splitless injection because of an insufficient carrier gas flow-rate[6]. However, on-column injection is possible if a retention gap is used that is wide enough to take the needle of the on-column syringe.

These four application fields have many technical aspects in common, some of which still require further investigation to establish their limitations and to work out practically oriented guidelines for the user.

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This paper deals with the re-concentration power obtained by the retention gap, and in particular the dependence of the latter on the temperature at which the solutes pass the retention gap. This subject is of interest if rapid heating of the column between the injection and the elution of the solutes of interest is applied. Such changes in the column temperatures are often necessary because the injection must be carried out at a column temperature that cannot far exceed the boiling point of the solvent. The subject discussed in this paper is not relevant if an analysis is carried out at the injection temperature or if the temperature programme is started at the injection temperature.

MAXIMUM RETENTION POWER OF A RETENTION GAP

To a first approximation, the re-concentration power of a retention gap may be calculated as the ratio of the retention powers in the retention gap and the separation column[1,7]. The length of the band broadened in space in the retention gap is divided by the factor by which the two retention powers differ and results in the length of the solute band in the inlet of the separation column. The retention power of silylated retention gaps expressed in terms of "apparent film thickness" of an apolar stationary phase is of the order of a few nanometres[7,8]. Hence re-concentration factors of 100–1000 may be achieved. As will be discussed below, such calculations yield a maximum re-concentration power, which may be reduced by non-ideal operating parameters.

RE-CONCENTRATION MECHANISMS

If large sample volumes are introduced, resulting in long flooded zones, two independent mechanisms are active in re-concentrating the solute bands. If a solute is eluted at the column temperature during the injection or slightly above, it starts the chromatographic process as a sharp band at the moment when the last portion of the solvent is evaporated in the retention gap (solvent trapping[9]) or when released by the soaked stationary phase (phase soaking[9]). The solute material in the rear of the band is recombined with the advanced material during the time the advanced material is hindered in its migration by the solvent. These solvent effects work whether the column inlet is coated with stationary phase or not. The retention gap provides no re-concentration for these solutes. Problems arise if solutes are only partially solvent trapped and not re-concentrated by phase soaking[9].

If a temperature programme is started at the injection temperature, the solutes eluted within the first few tens of degrees above the injection temperature are still re-concentrated by the solvent effects. However, the solutes eluted at least 80–120°C above the injection temperature (depending on the retention powers of the retention gap and the separation column) migrate too slowly at the injection temperature to be able to follow the withdrawing rear of the flooded zone when the solvent evaporates. They are not re-concentrated by the solvent effects and remain spread over a part or the full length of the flooded zone in the retention gap. Their re-concentration relies on the retention gap, in particular on the much lower temperature at which they pass the retention gap. Leaving the retention gap, they are stopped by the much higher retention power at the beginning of the separation column. They are blocked

there until the oven temperature is further programmed to reach a level that allows them to migrate in the separation column. However, the chromatographer must allow the time necessary for this process. The required time increases with increase in the internal volume of the retention gap, but decreases with increase in the carrier gas flow-rate.

Problems in the re-concentration of solute bands arise if excessively rapid temperature programming or ballistic heating is applied. Such rapid heating may have the effect that the last solute material arrives at the entrance of the separation column only when the oven temperature has already reached a temperature that allows the solute to migrate rapidly in the separation column. Under such conditions the front end of the solute band may have migrated far into the separation column until the rear end of the band entered the separation column, instead of "waiting" at the entrance of the separation column for the arrival of the last solute material.

DEAD TIME OF THE FLOODED RETENTION GAP SECTION

The problem described above cannot be explained by consideration of the retention powers in the retention gap and the separation column alone. The dependence of the re-concentration power on operating parameters, in particular on factors that influence the temperature at which the solutes pass the retention gap, is due to the neglected dead time of the flooded retention gap section. The considered retention powers are related to adjusted retention times (t'_R), in this instance primarily to the adjusted retention of solute material to migrate from the rear to the front end of the flooded section, neglecting the dead time or gas hold-up time, *i.e.*, the retention time of non-retained solute material to cover the length of the flooded zone. This neglect of the dead time is also the reason why the ratio of the retention powers in the retention gap and the separation column provides an estimate of the maximum re-concentration power —a maximum that may be noticeably reduced by the choice of the operating parameters.

The problem may be illustrated by a simplified model that overestimates the importance of the dead time of the flood retention gap section. A solute is injected at an oven temperature that is too low to allow a noticeable migration in the retention gap. When the solvent is evaporated, this solute is spread over the full length of the flooded zone in the retention gap. Now the oven temperature is increased with a "vertical" profile (within an extremely short time) to the level at which the solute is eluted isothermally. At this elution temperature the solute has no appreciable retention in the retention gap; it is almost completely evaporated. The material at the front end of the flooded zone is ahead of that at the rear end by the dead time of the flooded retention gap section. If this section has a length of 50 m, this dead time easily exceeds 1 min. This lead of the advanced material is maintained to the elution of the solute, resulting in a correspondingly strong peak broadening.

Fig. 1 compares schematically the peak shapes and the effect of the retention gap if the solute passes the retention gap far below or at the elution temperature.

RESULTS AND DISCUSSION

Example of peak broadening involving band broadening in space

The effect of the heating rate on the peak widths is demonstrated in Fig. 2. A

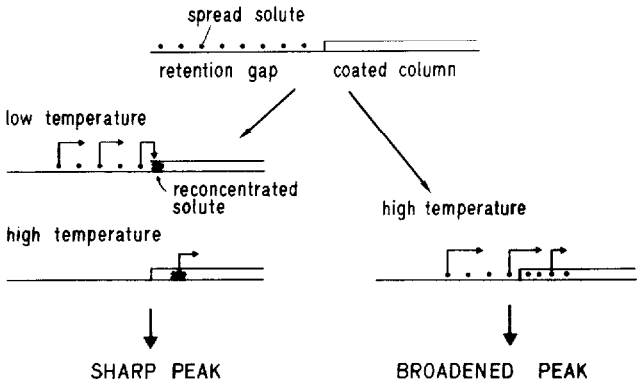

Fig. 1. Spread solute material in the retention gap optimally re-concentrated on the beginning of the separation column only if the solutes are allowed to pass the retention gap at a temperature 80–120°C below the elution temperature. The solute material is stopped at the beginning of the coated column and re-concentrated there. However, if the oven temperature is ballistically heated, the advanced solute material migrates into the separation column before the rear material has arrived at the entrance of the separation column.

10 m × 0.50 mm I.D. fused-silica retention gap (silylated with diphenyltetramethyldisilazane, obtained from MEGA through Carlo Erba) was joined by a butt connector (Carlo Erba) with a 15 m × 0.30 mm I.D. glass capillary coated with SE-54 of 0.15-μm film thickness. The carrier gas (hydrogen) flow-rate was 3 ml/min. A 100-μl volume of a solution containing C_{18}–C_{20} *n*-alkanes (0.1 ppm) in pentane was injected at 37°C, keeping the column temperature constant until the solvent peak was fully eluted. In a first run the column temperature was subsequently ballistically increased to 140°C and the solutes were eluted with a temperature programme of 5°C/min (upper chromatogram in Fig. 2). The peaks were broadened considerably, although the ballistic heating (increasing the oven temperature by about 50°C/min) is still far from a "vertical" temperature increase considered in the model discussed above; the broadening corresponds to about 10% of the dead time of the flooded retention gap. In a second run the column temperature was increased ballistically to 80°C and maintained there for 7 min to allow the passage of the solutes through the retention gap. Then the column was heated ballistically to 140°C, followed by temperature-programmed elution of the solutes as before. In this second instance no significant peak broadening was detected compared with a run by split injection using the separation column alone; hence the retention gap achieved virtually complete re-concentration of the bands. The time required for solutes to pass through the retention gap at 80°C was determined by trial and error. Periods shorter than 7 min resulted in broadened peaks (particularly of *n*-C_{20}), whereas longer periods neither improved nor deteriorated the peak shapes.

Example of peak broadening involving split injection

The band broadening in the retention gap is not due exclusively to band broadening in space, as shown in Fig. 2. The solute may start to pass through the retention gap as a narrow band and become broadened only later, *e.g.*, owing to overloading effects in the retention gap. Narrow initial bands of the C_{13}–C_{15} *n*-alkanes were introduced by split injection into the same retention gap–separation column combi-

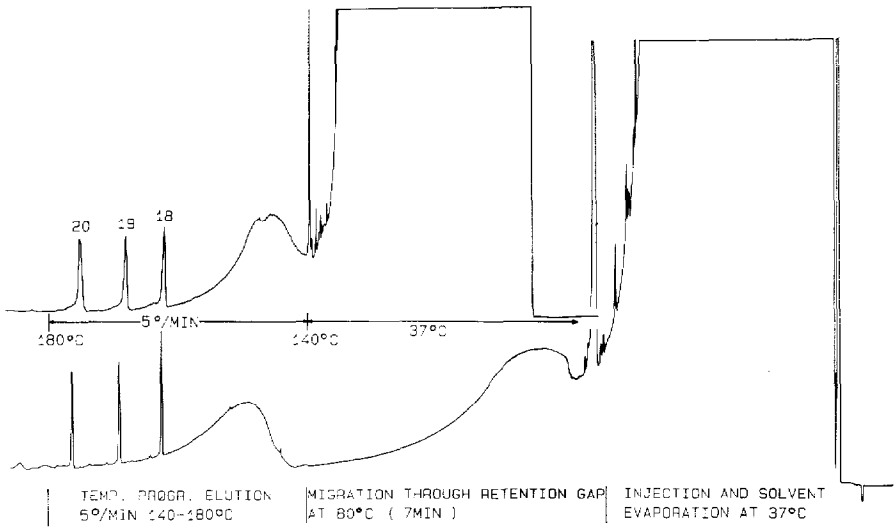

Fig. 2. Peak broadening due to excessively rapid temperature increase involving a retention gap with a large internal volume. Injection of 100 μl of C_{18}–C_{20} of *n*-alkanes (18–20) in pentane with a ballistic temperature increase from 37 to 140°C in the upper chromatogram. Lower chromatogram, as described above, but with an intermediate isothermal step at 80°C to pass the solutes through the retention gap.

nation as used for the experiment described above. The injection temperature (50°C) was chosen such that the solutes were able to migrate noticeably but with considerable retention in the retention gap. After various waiting periods the oven was heated ballistically to 120°C and programmed to 160°C. The rapid heating of the separation system prevents the complete re-concentration of the solutes at the entrance of the separation column, and hence partly conserves the shapes of the solute bands as created by the chromatography in the retention gap.

Ballistic heating immediately after the injection prevented chromatography of the solutes in the retention gap and therefore resulted in virtually perfect peaks. With a 30-sec, and even more with a 60-sec period before the heating, all peaks were broadened. If the isothermal period at 50°C was extended to 2 min, the first two peaks were perfect again, because this solute material had arrived at the entrance of the separation column and was re-concentrated there. It took nearly 5 min until all the *c*-C_{15} material had left the retention gap. Hence the solute bands were broadened progressively during the passage through the retention gap and re-concentrated at the beginning of the coated column.

The sequence of chromatograms in Fig. 3, showing the state of the migration through the retention gap at various times, gives some insight into another type of band broadening that occurs in the retention gap. The retention gap may be considered as a separation column with very poor characteristics. First of all its capacity is extremely low. At the low migration temperature used primarily the gas phase is overloaded because the concentration of the solutes in the gas phase, dictated by the partition ratio (K) on the uncoated surface, is so high that it exceeds the vapour pressure of the solutes[10]. Gas-phase overloading is characterized by a rapidly rising but slowly returning pen, *i.e.*, the peak distortion observed in Fig. 3. Overloading of

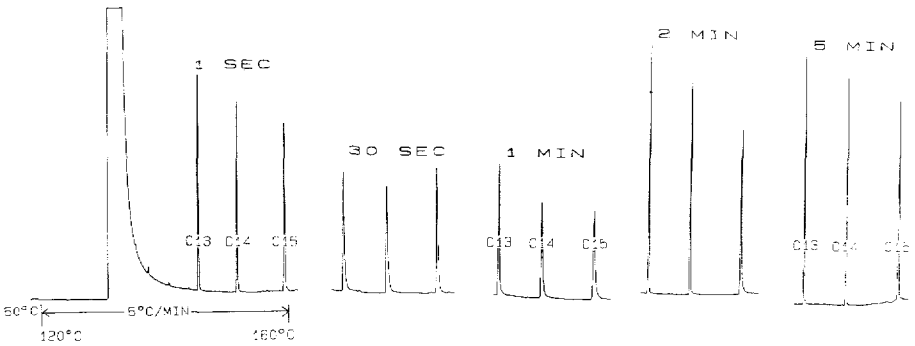

Fig. 3. Broadening of initially sharp bands (introduced by split injection) in a large retention gap, which may become visible if re-concentration is hindered by rapid heating. Injection at 50°C, at which the solutes (C_{13}–C_{15} *n*-alkanes) migrate with considerable speed through the retention gap. However, the retention gap is a poor separation column, and the solutes are strongly broadened, primarily by overloading. Rapid heating to 120°C, started immediately (1 sec) after the injection, conserved the original band shapes as it prevented chromatography in the retention gap. If the heating was started with a delay as indicted above the chromatograms the bands became the broader the longer they migrated through the retention gap, but were re-concentrated again on reaching the entrance of the separation column (which took nearly 5 min for C_{15}).

the liquid phase results in peaks of reversed asymmetry. The overloading is particularly severe for narrow initial bands because of the high load of solute material over a short section of the retention gap. Experiments have confirmed that the peak distortion depends strongly on the amount of solute material chromatographed (about 30 ng per solute in Fig. 3).

The above experiment was designed to show the band broadening effect. Under most conditions (*e.g.*, if the mixture had been injected at higher or lower temperature) no peak broadening would be observed.

Band broadening versus re-concentration

The higher the oven temperature, the more rapidly the solutes elute from the retention gap and the narrower are their bands when they enter the separation column. On the other hand, the band is more efficiently re-concentrated at the entrance of the separtion column the lower is the temperature when the solutes arrive at the beginning of the separation column, because the migration speed of the advanced material in the coated column is lower. These are not two factors that cancel each other. The re-concentration power increases more rapidly than the band broadening if the temperature during the passage of the solutes through the retention gap is lowered. The resulting improvement of the peak widths is shown in Fig. 4.

The band widths of dioctyl phthalate (DOP) eluted at various temperatures from the retention gap alone (lower chromatograms in Fig. 4) are compared with those eluted from the separation column after the re-concentration (upper chromatograms).

A 50 m × 0.30 mm I.D. glass capillary, leached and persilylated with diphenyltetramethyldisilazane[11], was used as a retention gap and coupled by a butt connector to a 28 m × 0.32 mm I.D. glass capillary column coated with SE-54 of 0.4-μm film thickness. The carrier gas (hydrogen) inlet pressure was 1.8 atm. A 300-μl

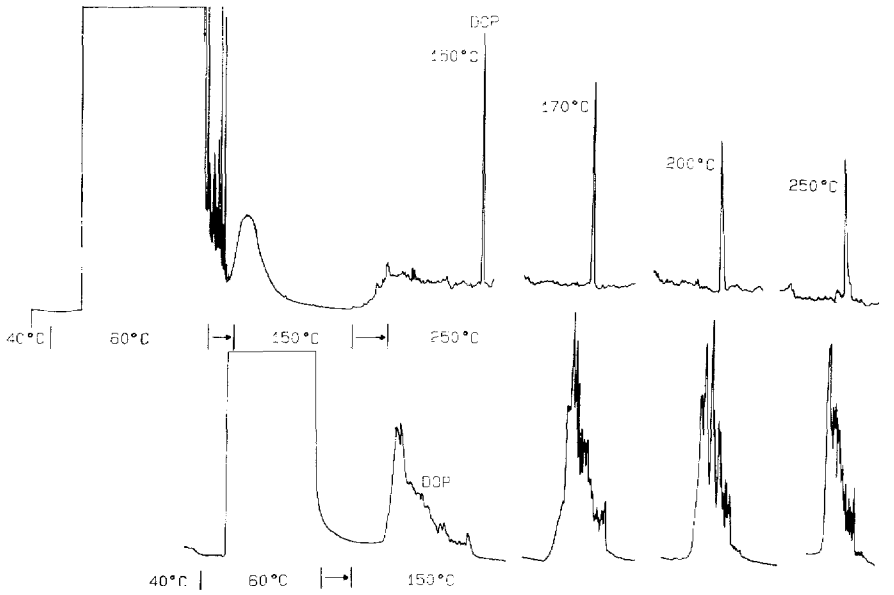

Fig. 4. Band widths of dioctyl phthalate (DOP) eluted from the retention gap alone (lower chromatograms) and from the combination with the separation column (upper chromatograms). Injections of 300 μl of DOP in pentane at 40°C, solvent evaporation at 60°C (1.8 atm inlet pressure), then ballistic heating to an intermediate temperature (indicated in the upper chromatograms) to pass the DOP through the retention gap. DOP eluted from the separation column after ballistic heating to 250°C. If the intermediate temperature was 150°C (the two chromatograms on the left) the DOP eluted as a very broad band from the retention gap, but was efficiently re-concentrated at the beginning of the separation column, resulting in a perfect peak eluted from the separation column. Higher temperatures for the passage of the DOP through the retention gap reduced the band width eluted from the retention gap, but reduced even more the re-concentration at the entrance of the separation column, overall resulting in broadened peaks. The two chromatogram sections on the right show the results without intermediate isothermal step, applying ballistic heating directly to 250°C.

volume of DOP in pentane (0.05 ppm) was injected on-column at 40°C and 30 sec after the injection the column temperature was increased to 60°C to accelerate the solvent evaporation. After the complete elution of the solvent the column temperature was increased ballistically (40–50°C/min using a Model 4160 gas chromatograph from Carlo Erba).

In a first run the oven temperature was increased directly to the elution temperature of DOP (250°C), resulting in considerable broadening of the DOP peak. The following runs were carried out with intermediate isothermal steps of 4, 6 and 12 min duration at 200, 170 and 150°C before heating to 250°C. The duration of the isothermal step was adjusted to the time required for the elution of the DOP from the retention gap. An improvement in the peak shape was observed when the intermediate isothermal temperature was lowered. No significant further sharpening of the DOP peak was observed at 130 and 120°C.

The observed peak widths are explained by the band widths eluted from the retention gap and the re-concentration at the entrance of the separation column. To obtain the lower chromatograms in Fig. 4 the exit of the retention gap was connected to the flame-ionization detector and the carrier gas inlet pressure was lowered to 1.3

atm to provide approximately the same gas velocity in the retention gap as in the experiment with the attached separation column. When the retention gap was heated ballistically to 250°C, the last DOP material eluted at about 240°C, *i.e.*, before reaching the final temperature. Comparing the width of the band eluted from the retention gap (Fig. 4) with that of the peak eluted under the same conditions from the combined retention gap and separation column, it is concluded that the band was re-concentrated at the entrance of the separation column by a factor of about 8.

Ballistic heating of the retention gap to only 200°C resulted in an approximately 25% broader band. This is due to the (still small) retention power of the retention gap for the DOP and the prolonged retention time of the rear material of the DOP band. On the other hand, the DOP material entered the separation column at a lower temperature and was therefore more efficiently re-concentrated. The improved re-concentration dominates the increased band broadening, shown by the fact that the peak width measured at the base is reduced by about 25%.

At even lower oven temperatures during the passage of the DOP through the retention gap the retention power of the pre-column increases exponentially, causing a corresponding increase in the band width at its exit. The efficiency of the re-concentration increases still more rapidly, but at about 150°C the two opposing factors become similar in effectiveness and the net re-concentration resulting from a lower transfer temperature through the retention gap is no longer important. On the other hand, the time required for the DOP to pass through the retention gap starts to increase very rapidly, from 12 min at 150°C to 30 min at 130°C and more than 45 min at 120°C. From a practical point of view, 150°C is the optimum temperature in this particular instance.

CONCLUSIONS

An optimal re-concentration effect by the retention gap may require adjusted analytical conditions. The re-concentration of solutes at the entrance of the separation column resembles a cold trapping effect, the re-concentration power of which is determined by a temperature difference, in this instance by the temperature difference between the migration through the retention gap and the separation column. The solutes must pass the retention gap at the lowest temperature at which the solutes still pass the retention gap within a reasonable time (with a retention time corresponding to a capacity ratio, k, between 2 and 5). This may preclude rapid (ballistic) heating from the injection to the elution temperature. More time must be allowed at the intermediate temperature for the passage through the retention gap the longer is the dead time of the retention gap (and hence the larger its volume and the lower the carrier gas flow-rate).

The problem may be solved by using a temperature programme started at the injection tempereature or at least 120°C below the elution temperature of the solutes of interest. If the retention gap and the separation column have similar inner diameters, the temperature programming rate should be adjusted to the longer of the two, *e.g.*, to about 2–3°C/min for a 50-m column, independent of whether the retention gap, the separation gap or both are of this length, and regardless of the length of the shorter column part. If a retention gap with a much wider bore than the separation column is used (*e.g.*, for automatic injection), the length of the retention gap should

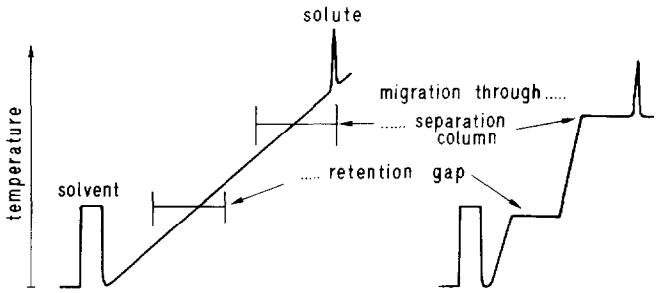

Fig. 5. Two options for increasing the column temperature for the elution of a solute far above the injection temperature. The easier way is the application of a temperature programme started at the injection temperature or at least 120°C below the elution temperature. The solutes select the temperature ranges for migration through the two column parts. Schematic representation of a chromatogram whereby the height of the baseline indicates the oven temperature. A faster analysis is achieved by rapid heating to an intermediate isothermal temperature, adjusted to pass the solute through the retention gap at a minimal temperature, followed by rapid heating (isothermal or temperature programmed) for elution of the solute.

be corrected by the square of the ratio of the two inner diameters to obtain a reasonable estimate of the time (programming rate) requirements of such a retention gap. During such a temperature programme the solutes find the appropriate temperatures for migration through the two column parts, as shown in Fig. 5.

A possibly more rapid analysis might be achieved by the application of two isothermal steps with a temperature difference of 80–100°C, the first adjusted to pass the solute(s) through the retention gap and the second adjusted to the separation process in the coated column (Fig. 5). The duration of the first isothermal step must be determined either by running the retention gap alone (as shown for the DOP in Fig. 4) or by trial and error. Usually a time corresponding to 3–4 times the dead time of the retention gap is appropriate.

REFERENCES

1 K. **Grob, Jr.**, *J. Chromatogr.*, 237 (1982) 15.
2 K. **Grob**, Jr., *J. Chromatogr.*, 213 (1981) 3.
3 K. Grob, Jr. and B. Schilling, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, in press.
4 K. Grob, Jr., D. Fröhlich, B. Schilling, H. P. Neukom and P. Nägeli, *J. Chromatogr.*, 295 (1984) 55.
5 Carlo Erba, Milan, in preparation.
6 K. Grob, Jr. and A. Romann, *J. Chromatogr.*, 214 (1981) 118.
7 K. Grob, Jr. and K. Grob, *J. Chromatogr.*, 270 (1983) 17.
8 K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, in press.
9 K. Grob, Jr., *J. Chromatogr.*, 279 (1983) 225.
10 K. Yabumoto, D. F. Ingraham and W. G. Jennings, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 248.
11 K. Grob, G. Grob, W. Blum and W. Walther, *J. Chromatogr.*, 244 (1982) 197.