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HIGH OVEN TEMPERATURE ON-COLUMN INJECTION IN CAPILLARY GAS CHROMATOGRAPHY

II*. AVOIDANCE OF PEAK DISTORTION

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SUMMARY

High oven temperature on-column injection often produces distorted peaks, particularly when running isothermal chromatograms at the injection temperature. Peak distortion may be due to solute material pulled backwards into the cold column neck, but more often it is due to premature release of solute material from the temporarily cooled column inlet and thermal defocusing of the initial bands during this transition. The sources of peak distortion are described together with the possibilities of avoiding such problems. Summarized guidelines on how to use high oven temperature on-column injection are given.

INTRODUCTION

High oven temperature on-column injection in capillary gas chromatography (GC), *i.e.*, on-column injection at column temperatures well above the boiling point of the solvent, is particularly attractive for rapid isothermal analyses at elevated temperatures. Conventional on-column injection requires cooling of the column below the boiling point of the solvent before injections can be carried out. Cooling and heating of the GC oven for injection considerably prolongs analysis times (frequently to a multiple of the time required for isothermal analyses). Further, such changes in the oven temperature often disturb the baseline (baseline drifts and "ghost" peaks due to impurities cold trapped during the cooling period) and render absolute retention times less reproducible. If analyses involve temperature programming, it is usually no longer very important how far the GC oven must be cooled. Therefore, it is the rapid isothermal analysis at high column temperatures that would profit the most from the possibility of injecting into columns above the boiling point of the solvent.

In Part I[1] we discussed high-temperature on-column injection based on the use of a temporarily cooled column inlet section. Injectors equipped with an extended secondary cooling (Carlo Erba), movable on-column injectors (J & W) and injectors

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allowing oven-independent thermostating of the column inlet (Varian) are suitable for this purpose. However, the technique is not simple as there may be losses of sample material backwards leaving the column.

This paper deals with the shape of the initial solute bands created by the two high oven temperature on-column techniques described. The initial band shapes influence the shape of the eluted peaks. However, distorted initial bands may also affect quantitative analysis: under certain conditions solute material is eluted before the main peak in such a way that it remains undetected and, as a consequence, the integrated peak is too small.

High oven temperature on-column injection is again not as simple in these respects as conventional on-column injection because of additional band broadening effects and severe disturbances of solvent effects.

TWO TYPES OF BAND BROADENING

There are two fundamentally different types of band broadening: band broadening in time and in space[2,3].

Band broadening in space

Band broadening in space is due to spreading of the solute material within the column inlet section which is flooded by the sample liquid. The initial bands are characterized in terms of band length, this length corresponding to the length of the flooded zone. Band broadening in space only affects peaks eluted at least 50°C above the injection temperature.

Band broadening in space is virtually non-existent in high oven temperature on-column injection because the sample liquid cannot flow more than about 10 cm into the oven-thermostated column (the sample liquid is rejected by its own vapour pressure). The length of the initial bands, assuming a temporarily cooled inlet 10 cm long, is at most *ca.* 20 cm, which causes peak broadening only in special instances. In fact, on-column injection at column temperatures slightly exceeding the boiling point of the solvent was first proposed for avoiding band broadening in space[4–7].

Band broadening in time

Band broadening in time originates from slow introduction of solute material into the column (*e.g.*, splitless injection) or from slow release of the material from the column inlet. Band widths are expressed in terms of time, whereby initial band widths correspond to the introduction time or the time of release. It is this type of band broadening that frequently causes problems in high oven temperature on-column injection.

TWO CONCEPTS OF HIGH OVEN TEMPERATURE ON-COLUMN INJECTION

In Part I[1] two concepts of high oven temperature on-column injection were distinguished. These concepts are again kept apart because the mechanisms determining the width and shape of the initial solute bands are different.

Sample coating cooled inlet

According to the first concept, the sample liquid is coated on to the wall of

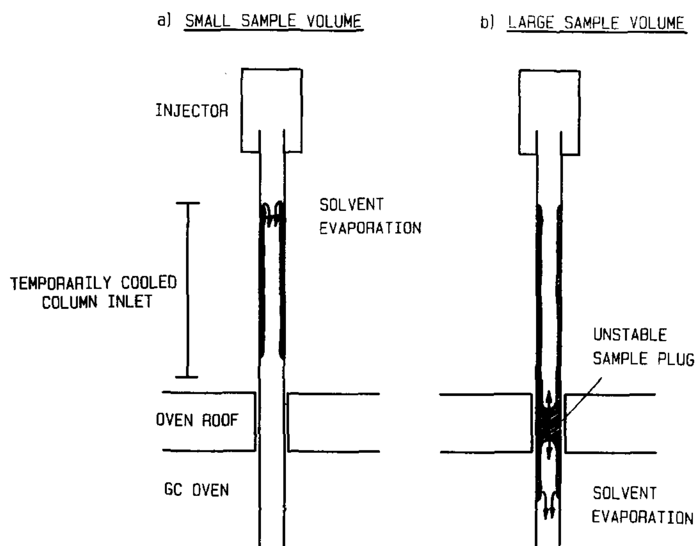

Fig. 1. The two concepts of high oven temperature on-column injection and their implications on solvent effects. (a) A relatively small sample volume (up to about 0.4 μl) is injected, ensuring that the whole sample liquid remains within the temporarily cooled inlet. Solvent evaporation proceeds from the rear to the front of the flooded zone, producing a solvent trapping effect. (b) A larger sample volume is injected, causing some sample liquid to flow into the entrance of the oven-thermostated column. First, the solvent evaporates at the front where the column temperature exceeds the boiling point of the solvent. Subsequently, evaporation continues at the rear of the sample layer within the cooled inlet as in (a).

the column inlet section, which is temporarily cooled below the boiling point of the solvent. The length of the flooded zone must not exceed the length of the cooled inlet as no sample liquid is allowed to flow into the oven-thermostated column (see Fig. 1).

Desorption on heating. According to the concept, the solute material is released from the temporarily cooled inlet on heating of the latter. This, however, presupposes that the solute material remains within the cooled inlet until the latter is heated. Although this is realistic for solutes eluted at high column temperatures, the situation is more complex for volatile solutes; the latter tend slowly to leak out of the cooled inlet and to start chromatography before the inlet is heated. Slow release from the inlet produces broad bands.

Solvent trapping. As solvent evaporation within the cooled inlet proceeds from the rear to the front of the sample layer, there is solvent trapping, a solvent effect[8]. Solvent trapping retains the solute material in the highly retaining solvent envelope up to completion of solvent evaporation. This is particularly important for volatile solutes that escape from the solvent-free, cooled column inlet. It means that solute material starts to leave the cooled inlet at the moment when heating of the inlet is permitted. It follows that heating of the column inlet should occur precisely at the end of solvent evaporation, as earlier heating may cause a backflow and later heating causes distorted initial solute bands.

The kind of distortion of the solute bands obtained by retarded heating of the column inlet is shown schematically in Fig. 2. Solute material prematurely released

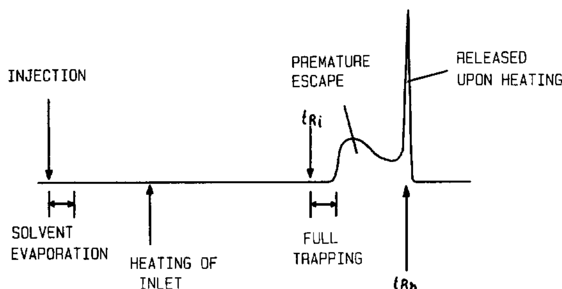

Fig. 2. Typical peak distortion caused by delayed heating of the temporarily cooled column inlet when working according to the concept of coating the whole sample liquid on the cooled inlet. The first solute material elutes with a retention time corresponding to the GC retention time (duration of separation process) plus the solvent evaporation time (t_{R_i}, chromatographic retention time measured from injection). The sharp peak represents material introduced into the oven-thermostated column by heating the inlet. Its retention time corresponds to the chromatographic retention time determined from the moment of heating (t_{R_h}). The ratio of the areas in the pre-peak and the sharp peak depends strongly on the volatility of the solutes in the temporarily cooled inlet (the pre-peak becomes invisible if the retention power of the cooled inlet is sufficient to render premature escape small). Perfectly shaped initial bands (and peaks) are obtained in any case if the inlet is heated exactly at the end of solvent evaporation.

from the cooled column inlet starts to elute with a retention time that exceeds the GC retention time by the solvent evaporation time. Heating of the column inlet causes rapid desorption of solute material that was still located in the cooled inlet. The width of the shoulder representing the prematurely released material corresponds to the delay of heating the inlet. Of course, the shape of a solute band distorted by this pattern depends on the volatility of the solute in the cooled inlet. Also, whether the shape of the initial band is still visible on the finally eluted peak depends on the extent of band broadening during chromatography and on whether cold trapping, the result of increasing column temperature between injection and elution, reconcentrated the band.

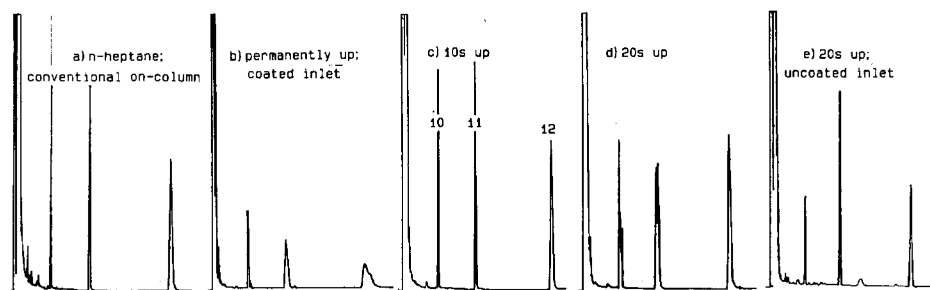

Fig. 3. Peak distortion due to delayed heating of the column inlet. Isothermal runs at 90°C, using a movable on-column injector and an 8 m × 0.32 mm I.D. glass capillary column coated with PS-255 of film thickness 0.4 μm, equipped either with a coated [(a)–(d)] or with an uncoated (e) fused-silica inlet 1 m long. Injection volumes, 0.4 μl; C_{10}–C_{12} n-alkanes (10–12) in n-heptane (a) or n-hexane [(b)–(e)]. (a) Basis of comparison for peak shapes; (b) solute bands broadened owing to slow release from permanently cooled inlet; (c) nearly perfect chromatogram achieved by heating the inlet 10 s after injection; (d) distorted peaks due to delayed heating (20 s after injection); (e) as (d) but using a retention gap, due to the low retention power rapidly releasing solute bands at the end of solvent evaporation (solvent trapping).

Example. Fig. 3 shows chromatograms of isothermal runs at 90°C obtained using the movable on-column injector from J & W as described in Part I[1]. Chromatogram (a) serves as a basis for comparison. It was produced by conventional on-column injection of a 0.4-μl volume of an *n*-heptane (b.p. 100°C) solution containing C_{10}–C_{12} *n*-alkanes. As no temporary cooling of the column inlet was needed, the injector was permanently in the down position. Under these conditions the initial bands are known to be perfectly sharp. Chromatograms (b)–(e) were produced by high oven temperature on-column injection of solutions in *n*-hexane (b.p. 69°C, 0.4-μl volumes). For chromatogram (b) the injector was permanently in the up position, resulting in peaks reflecting the slow release of the solute material from the cooled inlet. The least volatile solute, *n*-C_{12}, is most strongly broadened as its lower volatility caused it to leave the cooled inlet more slowly than the other solutes. Chromatogram (c) was obtained under almost optimal conditions: the injector was lowered 10 s after injection, and no obvious peak distortion is observed. A closer look, however, reveals that the *n*-C_{10} peak is slightly broader than in chromatogram (a) (typically, band broadening in time is first observed for the very sharp peaks). Apparently solvent evaporation took about 9 s, and some *n*-C_{10} left the column inlet about 1 s before heating of the column inlet.

Heating of the column inlet only 20 s after injection caused obvious distortion of the first two solute peaks. The beginning of the peaks corresponds to that in chromatogram (b). However, instead of waiting until the last solute material had left the inlet at low temperature, the remainder was rapidly desorbed by heating, forming sharp initial bands for the latter material.

From the fact that the *n*-C_{12} peak is almost as sharp as in reference chromatogram (a), it may be concluded that for certain applications heating delayed by as much as 11 s does not cause obvious peak broadening. It very much depends on the sharpness of a peak how critical the correct selection of the moment of heating is, because contributions to peak widths are added as squares[9], with the effect that peak broadening becomes small if the initial band widths are reduced to less than 50% of the chromatographic contribution to the peak width.

Chromatogram (e) will be discussed below.

Barrier against back-flow

The second concept of high oven temperature on-column injection is based on the assumption that a volume of sample liquid is injected, causing some liquid to leave the temporarily cooled inlet and to flow into the entrance of the oven-thermostated column. The sample liquid is rejected in the hot zone, flung backwards into the cooled zone (acting as a barrier against back-flow into the injector) and pushed into the entrance of the heated column again by the carrier gas, resulting in a rapid movement backwards and forwards (see Fig. 1).

Solvent evaporation in two steps. In a first step the sample solvent evaporates at the front of the flooded zone. The solvent vapour pressure stops the carrier gas flow into the column, and only solvent vapour passes through the column. There is no solvent trapping during this period of solvent evaporation because there is no condensed solvent ahead of the position where solute material is released from the evaporating solvent. As solvent evaporation is completed in the zone where the column temperature exceeds the boiling point of the solvent, solvent evaporation con-

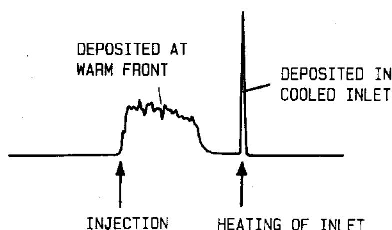

Fig. 4. Initial band shape of a solute injected with a volume of solvent causing some liquid to run into the entrance of the oven-thermostated column, represented as would be recorded by a detector positioned at the beginning of the oven-thermostated column. Some solute material is released from the solvent at the front (Fig. 1), producing an initial band width corresponding to the evaporation time of the solvent that flowed into the hot zone. After completion of evaporation at the front no solute material is released as there is solvent trapping during solvent evaporation in the cooled inlet. Solute material elutes as a sharp band from the cooled inlet provided that the inlet is heated exactly at the end of solvent evaporation. The initial band shape shown may be modified by a kind of cold trapping occurring within the temperature gradient from the cooled inlet to the oven-thermostated column (see Fig. 5).

tinues at the rear of the flooded zone; the carrier gas starts to flow again, carrying a proportion of solvent vapour through the column determined by the solvent vapour pressure within the cooled inlet. As solvent evaporation now proceeds from the rear to the front, there is solvent trapping of the volatile solutes, corresponding to the process taking place when working according to the first concept.

Fig. 4 shows schematically the typical initial band shape of a solute introduced by the second concept of high oven temperature on-column injection. First, there is an irregular release of solute material into the column during solvent evaporation at the entrance of the heated column. Irregularity stems from the fact that on one occasion solute material is carried far into the hot column whereas another time it is deposited more in the rear, cooler zone. The following solvent evaporation within the temporarily cooled inlet occurs below the boiling point of the solvent and therefore solute material is retained by solvent trapping. No solute material enters the oven-thermostated column during this period. Release of the solvent-trapped material corresponds to that described above; in Fig. 4 it is assumed that the inlet is heated at the end of solvent evaporation (otherwise further peak distortion according to that in Fig. 2 would be obtained).

Sharp initial bands? For the first concept there is a generally viable concept for obtaining sharp initial solute bands: heating of the column inlet at the moment solvent evaporation is completed. For the second concept there is no way that is as general and simple because there is no solvent trapping effect hindering solute material from leaking into the oven-thermostated column immediately after injection, *i.e.*, at a moment when heating of the column inlet is not permitted. So far, no sharp peaks can be expected in isothermal runs at the injection temperature when using the second concept.

Focusing within a temperature gradient. Using the movable on-column injector, perfectly shaped peaks of sufficient area were often obtained at high analysis temperatures despite injecting sample volumes that caused some liquid to run into the entrance of the oven-thermostated column. This suggests activity of an additional reconcentration mechanism.

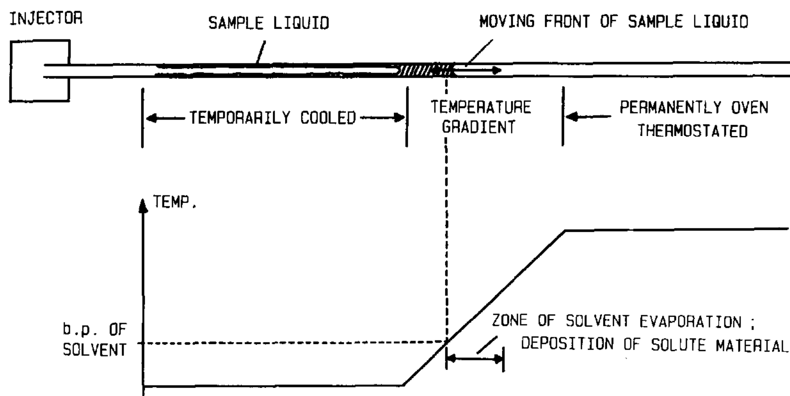

Fig. 5. Solute reconcentration due to cold trapping within the temperature gradient between the temporarily cooled column inlet and the permanently oven-thermostated column (for movable on-column injectors the column section passing through the roof of the GC oven). If solvent evaporation were a smooth process, it would occur at the position where the column temperature corresponds to the boiling point of the solvent. In reality, however, the sample liquid moves beyond this point (cooling of the position and delayed evaporation). Solute material is deposited within the range where solvent evaporation occurs. If the temperature within this range is sufficiently below the analysis temperature, the solute material is cold trapped and is released only on heating the inlet.

The temperature gradient from the cooled to the oven-thermostated column section of the injector used was relatively flat and corresponded to a column length of about 4 cm. If solvent evaporation were a smooth process, the solvent would evaporate at the beginning of the gradient at the point where the column is at a temperature corresponding to the boiling point of the solvent (see Fig. 5). The solute material is released from the solvent envelope and deposited on the column wall at the point of solvent evaporation, at a point that is far too cool to allow the solute material to migrate at a significant speed. It accumulates there and starts chromatography when the inlet is heated. In reality, the often violent solvent evaporation carries solute material considerably beyond the point where the column temperature corresponds to the boiling point of the solvent, *i.e.*, into a zone of higher temperature.

In order to achieve sufficiently efficient cold trapping of solute material, the temperature gradient must fulfil two requirements. First, there must be a sufficient difference between the boiling point of the solvent and the analysis temperature. Cold trapping requires the solute material to be placed at a position that is at least *ca.* 70°C below the analysis temperature. Second, the temperature gradient must be flat and long, accounting for the fact that the liquid moves too far into the hot column: the longer the gradient, the lower is the temperature of the position where the most advanced solute material is deposited. The distance the liquid covers beyond the position at the boiling point of the solvent certainly depends on the slope of the temperature gradient. However, other factors are less temperature dependent: the density of locations initiating solvent evaporation (acting as boiling stones), the stopping distance of a moving plug of liquid and the length of the capillary section necessary for transferring the heat required for solvent evaporation from the oven atmosphere to the liquid (solvent evaporation cools the column considerably).

Reconcentration within a temperature gradient improves with increasing analysis temperature and decreasing boiling point of the sample solvent. It is shown in Fig. 6 that our temperature gradient did not allow reconcentration of solutes eluted at 190°C when using *n*-hexane as solvent. On the other hand, reconcentration was just about complete during analyses of sterols involving an oven temperature of 250°C (*n*-hexane).

There is little chance of finding generally valid guidelines on the conditions that would provide complete reconcentration within a temperature gradient because the latter depends on too many factors (temperature gradient profile, volatility and nature of the solvent, carrier gas flow-rate, surface properties of the column inlet). It appears to be necessary to experiment with each particular instance, special care being required for detecting low pre-peaks, the area of which is usually not integrated. If, for a moment, some sample liquid enters very far into the hot column, some solute material is released into the oven-thermostated column and elutes before the bulk of the solute material. Up to about 20% of the solute material may be eluted prior to the major peak, marginally lifting the baseline, without being noticed. It is therefore recommended to compare peak areas with areas obtained by injecting the same sample volume under conventional conditions (column temperature below the boiling point of the solvent).

Example. Fig. 6 shows two chromatograms illustrating the difference between the initial bands produced by injection of a small sample volume, coating only the cooled inlet, and a larger volume introducing some liquid into the entrance of the oven-thermostated column. The injector was left in the up position for the duration of a run (10 min) in order to show leakage of solute material from the cold trap in the cooled column inlet. The sample contained solutes of intermediate volatility, C_{17}–C_{19} *n*-alkanes in *n*-hexane (of course, the volatility of the solutes strongly influ-

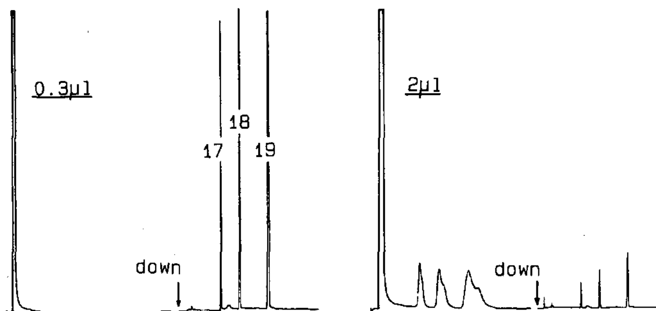

Fig. 6. In practice it is often observed that the injection of small sample volumes creates sharp peaks whereas the injection of larger volumes produces distorted peaks. If small sample volumes are injected, the whole sample liquid remains within the cooled inlet (first concept described in the text). Virtually no solute material leaves the column inlet even if the inlet is cooled longer than required by solvent evaporation, provided that the analysis temperature is above about 180°C (see the first part of the left-hand chromatogram, where the injector was left in the up position and the oven temperature was 190°C). Heating of the inlet ("down") releases sharp bands of solutes (second part of the chromatogram). Injecting larger sample volumes, the sample liquid carries solute material into the warm entrance of the oven-thermostated column from where the latter is immediately released (first part of right-hand chromatogram). Only the small proportion of solute material deposited in the cooled inlet is released on heating the inlet.

ences the outcome of such experiments!). The column was coated up to its entrance; the analysis temperature was 190°C.

Injecting a 0.3-μl volume, no solute peaks were observed as long as the injector was in the up position. Heating of the column inlet produced three perfectly shaped peaks corresponding to the solute material that remained in the cooled inlet after the first 10 min period. From the fact that no peaks or shoulders are eluted during the first part of the run with the inlet still being cooled it is tempting to conclude that no solute material was released during this period. However, integration of the peak areas revealed that about 50% of n-C_{17} is missing, indicating that half of the material had slowly left the cooled inlet before the latter was heated, raising the baseline to a hardly noticeable extent. Losses of n-C_{19} amounted to only 20%, owing to the lower chromatographic migration speed of n-C_{19} compared with n-C_{17}. Of course, one would not leave the column inlet cooled during 10 min after injection. However, the experiment serves as a warning that one cannot rely on the appearance of pre-peaks or shoulders for detecting whether solute material prematurely started chromatography. Disappearance of a peak area in the baseline may cause severe errors in quantitative analysis.

Injection of a 2-μl volume produced broad peaks of large area eluted during the period the column inlet was cooled. The corresponding material had been carried into the temperature gradient zone by the flowing liquid. It did not directly reach the oven-thermostated zone, as shown by the fact that the initial bands became strongly broadened by thermal defocusing. Heating of the inlet produced sharp peaks representing the solute material from the truly cooled inlet. They correspond to the peaks in the left chromatogram, but are smaller because the sample liquid was diluted, accounting for the larger injection volume.

In a realistic case the column inlet would have been heated about at the end of solvent evaporation. Evaporation of a 2-μl volume of n-hexane took about 25 s. The resulting peaks were distorted by broad (25 s) pre-peaks (similar to Fig. 4, although without a valley between the pre-peak and the main peak). Under the conditions used, isothermal analysis yielded sharp peaks only if the sample volume was restricted to about 0.8 μl.

COATED COLUMN INLET OR RETENTION GAP?

In conventional on-column injection (and also in splitless injection[10]), the use of an uncoated column inlet (retention gap) is advantageous for the reconcentration of bands broadened in space[11] (necessary only if sample volumes exceeding 1–2 μl or liquids not wetting the column surface are injected) and for reducing negative effects of sample by-products[12]. In high oven temperature on-column injection a new factor becomes important: the gas chromatographic retention power within the cooled inlet and the temperature gradient zone.

Retention gap at low analysis temperatures

Whether a coated or an uncoated column inlet is preferable depends on the analysis temperature used. In Fig. 3, where the analysis temperature was 90°C, the retention gap provided the best result [chromatogram (e)].

As a rule of thumb, the retention power within a retention gap corresponds to

that of a standard thin film column kept at a temperature about 100°C higher. This means that the retention power within the retention gap section cooled to ambient temperature was below that of the separation column kept at 90°C, and that the solutes left the cooled inlet at a speed exceeding that of their migration through the column. As a result, the initial bands were focused rather than thermally defocused as if using a coated column inlet [comparable chromatograms are (d) and (e)].

At low analysis temperatures the use of a retention gap simplifies high-temperature on-column injection as the moment of heating the column inlet becomes non-critical (in fact, the inlet does not need to be heated at any time!).

Continuing with the rule of thumb mentioned above, the retention power within the cooled retention gap corresponds to that of the oven-thermostated coated column at oven temperatures around 120–140°C. At lower analysis temperatures a retention gap provides some (unnecessary) focusing, whereas at higher analysis temperatures there is thermal defocusing of the solute bands. However, up to about 150°C such defocusing is negligible, and the use of a retention gap is clearly advantageous.

Coated inlets at elevated analysis temperatures

Solute material eluted at high analysis temperatures can be kept within the cooled column inlet, provided that the latter is coated. If there is sufficient retention power in the column inlet to prevent significant escape of solute material from the cooled inlet, the moment of heating is again not critical. As solute materials are

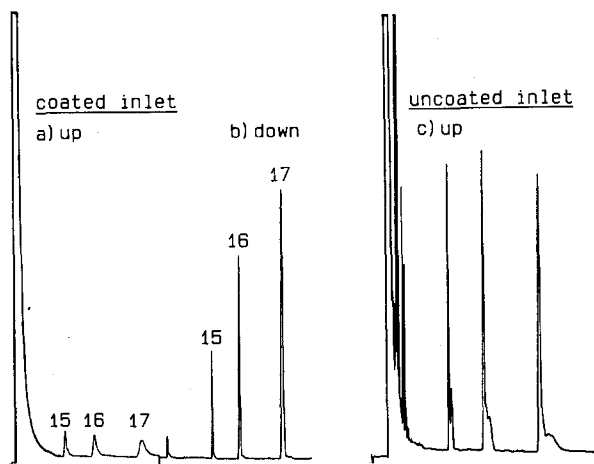

Fig. 7. Basically, high oven temperature on-column injection requires the column inlet to be heated exactly at the end of solvent evaporation. However, if sample volumes are injected that can be coated on the temporarily cooled inlet, it can mostly be arranged that delayed heating does not harm the peaks (which is convenient, as the accurate solvent evaporation time is unknown). Intermediate analysis temperatures (150–190°C) are an exception to this. On the one hand, a coated column inlet does not fully retain the solute material: in (a), where the injector was permanently in the up position, considerable amounts of solute material (C_{15}–C_{17} *n*-alkanes) escaped from the cooled inlet. On the other hand, solutes do not leave a retention gap sufficiently rapidly to form sharp initial bands (c). The injector was again in the up position; in this instance no peaks were detected after heating the inlet (chromatogram not shown). The analysis temperature was 170°C.

released only on heating the inlet, retention times must be measured from the moment of heating the inlet (if a retention gap is used with relatively low analysis temperatures, retention times must be measured from the moment of injection).

In Fig. 6 (left) an example is shown where the escape of solute material from the cool inlet was low enough to cause no significant losses in peak areas if heating of the inlet would have been delayed by, *e.g.*, 10 s. Conditions (analysis temperature 190°C), however, were near the border-line below which solute escape begins to be important.

Fig. 7 shows chromatograms obtained from isothermal runs at 170°C, where leakage from the cooled inlet was no longer negligible. The sample volume was 0.4 μl according to the concept of coating the cooled inlet. A first analysis was again run with the injector remaining in the up position to show elution of solute material from the cooled inlet. The coated column inlet first released a considerable amount of solute material, but retained other material up to the moment the inlet was heated. This is due to the fact that the front of the column inlet kept above the oven roof is considerably warmer than the rear, owing to heat from the oven. It should be noted that again most of the n-C_{15} material is not present in either the first or in the second peak; most of it lies on the baseline between the two peaks. Using a retention gap all solute material left the column inlet before heating (the second part of the analysis, a straight baseline, is not shown). Most of the material was released at the end of solvent evaporation (solvent trapping process) as a sharp band. Some material, presumably deposited in the cooler rear of the sample-coated inlet, entered the oven-thermostated column with a delay and is repesented by the peaks or shoulders eluted after the main peaks.

At analysis temperatures between 150 and 190°C there is no obvious answer as to whether a coated or an uncoated column inlet is preferable. On the one hand, the retention power of the retention gap cooled to ambient temperature is too high for rapid release of the solute material, and on the other, the retention power of the coated column inlet is insufficient to retain the material.

DETERMINATION OF SOLVENT EVAPORATION TIME

The solvent evaporation time is a key parameter in high oven temperature on-column injection, as in many instances the column inlet must be heated at the end of solvent evaporation. Unfortunately, it is impossible to give simple guidelines for the duration of solvent evaporation as the latter depends strongly on many parameters (carrier gas flow-rate, injection volume, volatility of the solvent, vapour volume created per unit volume of liquid). Therefore, the solvent evaporation time must be determined for each particular application.

The current method of heating the column inlet as the solvent starts to elute is certainly not suitable as there is no relationship between the appearance of the solvent peak (approximately corresponding to the dead time of the column) and the solvent evaporation time.

The solvent evaporation time can be roughly calculated from the width of the solvent peak; at high column temperatures the width of the solvent peak is primarily determined by the solvent evaporation time. Contributions from retention in the separation column (phase soaking phenomenon) are small. It is recommended that

pure solvent (of the type and volume of interest for the samples) be injected, leaving the injector permanently in the up position. If highly solvent-sensitive detectors (*e.g.*, flame ionization detectors) are used, the attenuation should be high in order to preclude tailing from contributing to the width of the solvent peak. The peak width is measured at the top.

Estimates of solvent evaporation times obtained by the above method tend to be slightly high. On the one hand, this introduces some safety margin, ruling out premature heating of the inlet. On the other hand, there may still be some distortion of rapidly eluted peaks (as, *e.g.*, in Fig. 3c), which would call for a small adjustment towards earlier heating.

SUMMARIZED GUIDELINES

From the above considerations, the following guidelines for the use of high oven temperature on-column injection can be derived.

Sample coating cooled inlet

(1) Determine the maximum sample volume from the length of the column inlet that is temporarily cooled below the boiling point of the solvent, measured from the injection point. As a rule of thumb, a 0.5-μl volume can be injected on to a 10-cm section of a coated inlet and a 0.4-μl volume on to a retention gap.

(2) Use a retention gap for isothermal and short-range temperature-programmed runs at column temperatures up to about 150°C and coated column inlets at higher temperatures.

(3) Inject by rapidly depressing the plunger (to separate the sample liquid well from the needle tip). The speed of other manipulations is not important.

(4) Heat the column inlet after completion of solvent evaporation. The solvent evaporation time is determined from the width of the solvent peak (see above).

(5) Check the quantitative results by comparison with results obtained using conventional on-column injection, *i.e.*, injecting at column temperatures below the boiling point of the solvent.

Injection of larger sample volumes

Here we refer to the technique of introducing more sample liquid than can be retained on the wall of the temporarily cooled inlet and which uses the cooled inlet as a barrier against a back-flow.

(1) There is no clear upper limit to the sample volume. If the temporarily cooled inlet is at least 10 cm long, up to *ca.* 3 μl of liquid can be safely kept within the inlet. A cooled inlet 13 cm long permits the injection of up to about 10 μl of liquids that wet the inlet surface.

(2) Injection of up to 3-μl volumes should occur rapidly; larger volumes must be injected more slowly (about 1 μl/s).

(3) The column inlet should be coated with immobilized stationary phase.

(4) Initial bands must be reconcentrated by cold trapping, which means that injection must be carried out at least about 70°C below the analysis temperature. At analysis temperatures above *ca.* 240°C this may be unnecessary if there is sufficient reconcentration within the temperature gradient between the cooled and the oven-thermostated parts of the column.

(5) Use high carrier gas (hydrogen) flow-rates and avoid solvents of high volatility such as *n*-pentane or diethyl ether (returning sample plug!).

(6) Check the quantitative results by injections at column temperatures well below the boiling point of the solvent, and check for memory effects due to solute material deposited behind the injection point.

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