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DETERMINATION OF THE DEPTH OF RETENTION GAPS IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The retention power of uncoated but deactivated capillary tubes was determined by two independent techniques: (1) by the increase of the retention times of some test compounds on a separating column provided with a retention gap and (2) indirectly by the reconcentration effect on a band with a known band broadening in space. The retention power of such pre-columns was expressed in terms of the apparent film thickness, treating the retention power of the support surface as if there went a layer of non-polar stationary phase. The lowest retention power was determined for a silylated fused-silica pre-column (apparent film thickness 0.002 μm, providing a reconcentration of bands broadened in space by a factor of 100–200 if separation columns having standard film thicknesses are used). A persilylated glass pre-column showed nearly double the retention power of the fused-silica one. Roughening the inner surface of the pre-columns approximately doubled the retention power as compared to the smooth tubes. Packed retention gaps had an excessively high retention power. Of the pre-columns tested, the silylated ones were the only retention gaps with sufficient inertness to avoid adsorption of sample components.

INTRODUCTION

The use of a retention gap was proposed two years ago as a means to reconcentrate bands broadened in space[1,2].

Band broadening in space is the result of flooding by solvent. In on-column sampling, the sample is introduced as a liquid into the head of the column. Splitless injections at low column temperatures cause the solvent to recondense in the first few centimetres of the column inside the oven. In both cases the liquid flows further into the column, driven by the carrier gas flow[3]. It floods approximately 15–30 cm per microlitre of sample volume injected until the thickness of the liquid layer is reduced to a mechanically stable film. All sample material in this liquid is spread over the same length of the column inlet, *i.e.*, the whole of the sample material in on-column

injection, but only the part of the sample material which was transferred from the warm bottom of the injector into the oven-thermostatted column in splitless injection. The components spread in the column inlet by the flooding solvent tend to produce broadened and usually also distorted or split peaks, with the exception of the components eluting at a column temperature close to that of the injection.

Since all bands spread by the flow of liquid have the same widths in terms of column length (or area of the column wall), we called the broadening effect "band broadening in space"[1,4] —in contrast to the "band broadening in time" where bands have the same widths if determined in units of time, e.g., transfer time from the injector to the column in splitless injection or evaporation time of the solvent in the column inlet in the case of partial solvent trapping[5,6]. The characteristics of these two types of band broadening are very different, as are the reconcentration techniques.

A special problem for the band broadening in space is posed by solvents which do not wet the walls of the column inlet, because such liquids migrate very far into the column, e.g., methanol in non-polar columns or silylated retention gaps[7]. Furthermore, the question remains as to, why band broadening in space does not always occur to the extent expected from the length of the flooded zone, e.g., for alkanes as solvents, and why there is a dependence on the type of stationary phase present in the column inlet, as pointed out by Sandra et al.[8]. The expansion of the liquid by evaporation and recondensation should be considered as part of the answer.

Bands broadened in space are reconcentrated at the beginning of the stationary phase if the column inlet, at least in as far as it is flooded by the sample, has a substantially reduced retention power compared to the coated column. In practice this means that an uncoated inlet section is used. Such a "retention gap" accelerates the migration of the spread material. If the material migrates, e.g., ten times more rapidly in the retention gap than in the coated column, it is reconcentrated by a factor of ten also. Thus the extent of reconcentration is equal to the reduction in the retention power of the retention gap as compared to the main column.

Retention gaps have become widely used also for keeping non-volatile by-products of the sample away from the stationary phase, to avoid phase stripping by the liquid sample and to minimize the retention power of a layer of "dirt" in the inlet.

For on-column injection, some workers investigated the possibilities to avoid band broadening in space at its source by using column temperatures during sampling of about 10°C above the boiling point of the solvent[3,7,9-12]. This approach appears to be surprisingly effective. However, it requires the use of a secondary cooling[13] or an equivalent system to avoid losses of sample by backflow. It may broaden peaks eluted near to the column temperature during the injection[10] and finally it severely limits the column temperature and/or the volatility of the solvent. Although a number of important applications for this technique have been described we do not believe that it could replace the use of retention gaps.

Retention gaps with an internal diameter similar to that of the separating column assure a complete reconcentration for sample sizes up to several microlitres. However, for three very different applications we were interested in using far larger retention gaps —larger in terms of length as well as internal diameter.

(a) The injection of large sample sizes by the on-column technique would be

desirable for many applications where sensitivity is a problem. However, large sample volumes flood the column for long distances and create correspondingly severe band broadening in space. Analyses involving temperature programming require retention gaps which are sufficiently large to retain the spread liquid from the coated column. What is the maximum length of the flooded zone (or of the retention gap) which still allows a sufficient reconcentration? The answer to this question would serve as a background to determine the maximum allowable sample volume.

(b) It has been pointed out repeatedly that narrow bore capillary columns would be useful to reduce analysis times and to increase separation efficiencies[14]. Probably there would have been a move towards such columns some time ago if the sampling problems had been overcome. For many applications it is not acceptable to be restricted to split injection (with a high splitting ratio) because of the required sensitivity. Splitless injection is excluded because the very low carrier gas flow-rates are not sufficient to transfer the sample vapours from the injector to the column[15]. Even on-column sampling appears to require a certain minimal carrier gas flow-rate[16]. However, this flow-rate might be around 0.5 ml/min, rather than 3 ml/min as in splitless injection. We have mentioned previously that on-column injection into narrow bore columns is technically feasible if wider bore retention gaps are used[17]. Such pre-columns with an internal diameter of 0.32 mm or similar have a relatively large internal volume compared to that of the narrow bore main column. What is the maximum tolerable size of the pre-column to exclude peak broadening?

(c) If relatively large bore retention gaps are acceptable, pre-columns of 0.5–0.6 mm I.D. to allow on-column injections using standard syringes with normal rather than thin-walled needles should be considered. This would facilitate manual sampling, but primarily it would allow ordinary autosamplers to do automatic on-column injections. Even if this technically simple version of an automatic on-column sampler would have considerable limitations, it would be very desirable for an important range of samples. Its weakness is again the very large internal volume of the retention gap.

Large pre-columns may cause peak broadening by two mechanisms. At the column temperature during the injection and slightly above, peak broadening is caused by the enlargement of the vapour cloud of parts of the evaporated sample by diffusion in the dead volume of the pre-column. This broadening may be reduced by solvent effects. At column temperatures more than about 40°C above the temperature during the injection, possible peak broadening is due to band broadening in space. Even this kind of band broadening increases with increasing diameter of the pre-column. It may be assumed that a certain sample volume floods a certain surface area of the column wall. Since the surface area per length of a tube is proportional to the diameter, the length of the flooded zone is inversely proportional to the radius of the column. The band broadening effect, however, is proportional to the internal volume of the flooded column section, thus to the square of the capillary radius. As a result, the band broadening in space is doubled if the radius of the pre-column is doubled compared to the main column, e.g., from 0.16 to 0.32 mm in the case of narrow bore columns and from 0.3 to 0.6 mm for the automated on-column injector.

Both types of band broadening, visible at isothermal as well as at higher column temperatures, depend on the "efficiency" of the retention gap, although in the first case only because of a possible solvent effect.

An uncoated, deactivated capillary tube still has some retention power due to the interaction of the sample components with the inner surface of the tube ("adsorption"). Even if this retention power is negligible for many aspects, it becomes important for large retention gaps. It is the key to find an answer to the question of the maximum tolerable size of a retention gap.

There is the purely pragmatic way of trying various retention gaps to find a particular answer for a particular separation system. But since the maximum size of a retention gap depends on the length and the width of the separating column as well as on the film thickness of the stationary phase, such information would be of little general value. A more systematic approach requires the determination of the retention power of a realistic retention gap.

We could not find any information on the retention power of a deactivated but uncoated glass or fused-silica capillary. We had some rough ideas about this retention power because of earlier experiments on columns with extremely thin films. On Carbowax-deactivated barium carbonate columns coated with non-polar silicones, the retention power was no longer reduced as expected when the film thickness of the stationary phase was lowered below about 0.03 μm[18]. The samples in this case were polycyclic aromatic hydrocarbons. We concluded that the retention power of the support surface contributed to the retention power of the coated column about as much as a film of the non-polar stationary phase of 0.01-μm thickness. We also found that non-polar columns with persilylated support surfaces have poor separation efficiencies if the film thickness is below about 0.03 μm —probably because the retention power of the support surface began to interfere.

This paper concentrates on the description of two methods to determine the retention power of a non-coated pre-column. The retention power of such capillaries could not be measured by retention times on just these columns because no reasonable peaks could be obtained. Thus more sophisticated methods had to be applied. The two independent methods gave similar results. Since they have both their merits we describe them both. We also present some results which give some idea of the depth of a retention gap for different types of pre-columns.

The retention power of a chromatographic column is expressed by the phase ratio, β, i.e., the ratio between the volume of gas in the column and the volume of stationary phase. However, the phase ratio varies if two columns with identical characteristics of the internal surface but different diameters are compared. As our attention was focused on the surface characteristics, we preferred a parameter which is independent of the volume of the gas phase. We have chosen the equivalent or apparent film thickness, treating the retention power of the support surface as if there were a thin layer of a stationary phase. The calculations were made on the basis of a non-polar stationary phase, both because of experimental reasons (we compared the retention power of the retention gap with that of a non-polar column coated with a known film thickness) and because the result could be applied directly to the most commonly used non-polar columns.

EXPERIMENTAL

Pretreatment of the retention gaps

Two pieces of glass capillary (Durobax) were etched with aqueous potassium

hydroxide for 1 h at 90°C, which gave them an opaque appearance. One of them was leached and persilylated according to ref. 19. The other one and a further piece of the same glass type but not etched were deactivated with Carbowax 20M. A plug of a 0.1% solution of Carbowax 20M in dichloromethane was pushed through these columns at a rate of about 5 cm/sec. The columns were dried and heated to 280°C under a moderate flow-rate of hydrogen during 30 min. They were washed with 1 ml of dichloromethane before use.

The packed pre-column was prepared using the tip of a Pasteur capillary pipette (WU, Mainz, F.R.G.), of length 10 cm and an I.D. adjusted to the O.D. of the separation column (0.9 mm). Five millimetres above the bottom of this tube a short plug of silanized glass wool was introduced, followed by acid-washed and DMCS-treated Chromosorb G (80–100 mesh). This packing had a height of 6.5 cm and an internal volume for hexane of 27 μl. The separation column was inserted 3 mm into the pre-column and sealed by shrinkable PTFE tubing.

Direct determination of the retention power

For the direct determination of the retention power of a retention gap we compared the retention times of some compounds on a regular column with and without the retention gap. The separating column was chosen to be small (6 m × 0.17 mm I.D.), and coated with the minimum film thickness for which the retention power of the support surface was still negligible (0.05 μm SE-54). This column produced a pressure drop of 0.5 atm for a carrier gas flow-rate of 1 ml/min (hydrogen). Its dead time was 8.2 sec at 42°C. The retention times for 2,6-dimethylphenol, n-pentylbenzene, 1-nonanol and n-dodecane were determined isothermally at 42°C. These compounds were injected by stream splitting (200:1) as a solution diluted 1:3000 in pentane to exclude solvent effects which might influence the retention times.

Then a retention gap (8 m × 0.52 mm I.D.) was connected to the separating column by means of shrinkable PTFE tubing. At the above column temperature and inlet pressure the dead time of the arrangement was 104 sec; the value calculated from the volume was 102 sec. The retention times of the compounds mentioned above were determined using a solution diluted 1:1000.

The use of extremely large retention gaps in front of a very small separation column has two advantages. First, the wide-bore pre-column allows one to assume that there is no pressure drop through the retention gap. Thus the flow-rate through the main column is independent of whether there is a retention gap or not. This is important because of problems in determining flow-rates with sufficiently high accuracy. Secondly, the very low linear gas flow-rate through the retention gap (8.3 cm/sec) as compared to the separation column (73 cm/sec) amplifies the retention power of the retention gap. Without such amplification the differences in retention times with and without the retention gap are small and hardly significant.

The apparent film thickness, d_f, of the retention gaps were calculated using the relations

$$\beta = \frac{K}{k} = \frac{r}{2d_f}$$

where K is the distribution constant in the liquid and the gas phase, k the capacity

ratio, *i.e.*, the retention time divided by the dead time, and r is the radius of the column. Using the indices rg for retention gap and s for separation column:

$$\frac{\beta_{rg}}{\beta_s} = \frac{r_{rg}}{2d_{f_s}} \cdot \frac{2d_{f_s}}{r_s} = \frac{K_{rg}}{K_s} \cdot \frac{k_s}{k_{rg}}$$

If the distribution constants K are identical because the apparent film thickness is calculated on the basis of the stationary phase in the separating column, it follows:

$$d_{f_{rg}} = \frac{r_{rg}}{r_s} \cdot \frac{k_{rg}}{k_s} \cdot d_{f_s}$$

Some experimental data for a retention gap with a roughened internal surface (etched with potassium hydroxide), leached and persilylated are shown in Table I.

Determination by the reconcentration effect

The depth of the retention gap was determined indirectly by the reconcentration effect on a band with a known broadening in space. The experimental peak width of a test compound was compared with the calculated width assuming the pre-column had the same retention power as the separating column.

In order to obtain a well defined band broadening in space, the retention gap of interest was dynamically coated with a 2-ppm solution of *n*-octacosane (n-C_{28}) in hexane or acetone. A plug of this solution was pushed through the column at a rate of about 5 cm/sec. After a brief evaporation of the solvent by a stream of air, the retention gap was installed into the gas chromatograph and attached to the separating column (that used for the direct determinations described above). The joint was made of shrinkable PTFE tubing to allow ease of connection and disconnection. If the retention gap consisted of fused silica, we used butt connectors obtained from Carlo Erba Strumentazione (Milan, Italy). The carrier gas, supplied by the vaporizing injector, was set to 0.5 atm and the oven temperature immediately programmed at 25°C/min from 40 to 190°C. The n-C_{28} began to elute after an isothermal run time

TABLE I

DIRECT DETERMINATION OF THE RETENTION POWER OF A RETENTION GAP OF GLASS (DUROBAX), ETCHED WITH POTASSIUM HYDROXIDE, LEACHED AND PERSILYLATED

Retention times, (t_R min), on the separation column and on the combination of retention gap and separation column, calculated retention times on the retention gap alone, capacity ratios, k, for the separation column and the retention gap and finally the apparent film thickness of the retention gap, $d_{f_{rg}}$ μm, are given for some test compounds. Dead times: separation column, 8.2 sec; separation column and retention gap, 104 sec.

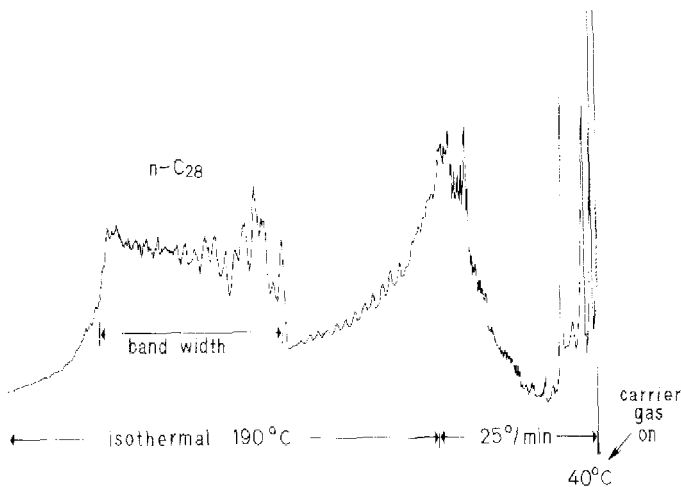| Compound	t_{R_s}	$t_{R_{rg} \cdot s}$	$t_{R_{rg}}$	k_s	k_{rg}	$d_{f_{rg}}$
2,6-Dimethylphenol	2.15	4.17	2.02	15.7	1.16	0.011
n-Pentylbenzene	2.68	5.27	2.59	19.6	1.49	0.012
1-Nonanol	3.95	8.30	4.35	28.9	2.51	0.013
n-Dodecane	4.92	9.60	4.68	36.0	2.70	0.011

Fig. 1. Experimental result obtained during the determination of the retention power in a pre-column according to the second, indirect method. The pre-column (Carbowax-deactivated, roughened glass) was coated with n-C_{28} on the lab bench. It was attached to the separating column in the GC oven by PTFE tubing; the carrier gas was turned on and the n-C_{28} eluted at 190°C. The measured band width was compared with that calculated assuming the same retention power in the retention gap as in the separating column (over 2 h) to determine the reconcentration effect on the n-C_{28} band broadened in space.

of about 9 min. Fig. 1 shows an example of the n-C_{28} peak obtained. The peak width of n-C_{28} determined at approximately half height ranged between 1.5 and 8 min.

Calculations on the band broadening in space are based on isothermal retention times. Therefore the retention time of n-C_{28} was determined by a split injection (200:1) at 190°C of a solution of the compound diluted 1:3000 in pentane, using the separating column without the retention gap but with a short piece of a straightened capillary tube attached to the column by shrinkable PTFE tubing a serve as a removable inlet.

The apparent film thickness in the retention gap was calculated on the basis of the following considerations. We have shown previously that the band broadening in space is proportional to the (isothermal) retention time of a component[1]. The broadening should be expressed, e.g., in per cent of the retention time of a peak. We have also shown that such broadening is equal to the percentage of the flooded zone of the total length of the column. This is true for fully coated columns with a constant diameter. For pre-columns of a wider bore than the separation column (hypothetically coated with a film thickness to provide the same retention power as the separating column) the change of the linear velocity of the carrier gas must be considered. The carrier gas velocities in the different column parts are inversely proportional to the cross-sections; retention volumes are directly proportional to the cross-section. Thus instead of being equal to the proportion of the length of the flooded column section, the peak broadening is equal to the proportion of the product of length and cross-section, i.e., of the volume of the flooded part as compared to the total column volume.

The retention gap (8 m × 0.52 mm I.D.) described above as an example for the direct determination of retention power constituted 92% of the total column

volume. The most advanced material of the n-C_{28} (2 in Fig. 2a) started to chromatograph at the joint between the pre-column and the separation column. Its retention time was, as expected, equal to that of n-C_{28} directly injected into the main column, 15.5 min in the temperature-programmed run, corresponding to an isothermal retention time of 10.3 min determined as described above. These retention times indicate the start of the elution of a very broad band (see Fig. 2). In the hypothetical case where the pre-column has the same retention power as the separating column, the band width would correspond to 92% of its retention time (equal to the percentage of the column volume coated with n-C_{28}). The isothermal retention time of 10.3 min corresponded to 8% of the retention time during which no n-C_{28} eluted. From there the band would have extended to a retention time of 139 min, producing a peak width of 129 min (over 2 h!). However, the retention gap in question only produced a n-C_{28} peak of 5.3 min in width. The reduced retention power of the retention gap reconcentrated the band by a factor of 24 —or, to return to Fig. 2b, the molecule starting its migration in the inlet of the retention gap, 1 in Fig. 2, passed through the retention gap 24 times more rapidly than calculated for the hypothetically coated pre-column. Thus the retention gap had a retention power (β) 24 times less than that
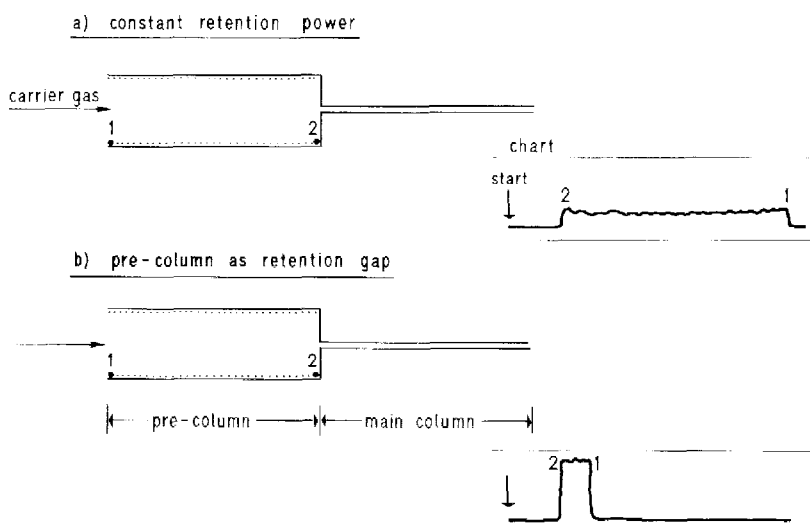

Fig. 2. Determination of the retention power of a (very wide bore) pre-column by the reconcentration of a band with a known broadening in space. The pre-column was coated with a very thin layer of n-C_{28}, shown as a dotted line, extending from molecule 1 in the entrance to molecule 2 in the exit of the pre-column which was attached to the narrow bore separation column. In (a) the pre-column is assumed to be coated with stationary phase having the same retention power as the separation column. In this hypothetical case n-C_{28} would be eluted as an extremely broad peak. If molecule 1, passing through the whole column, is considered to have the reference retention time, molecule 2 is eluted with a retention time reduced according to the proportion of the column volume it has to pass through before being eluted. In (b) the pre-column is not coated with stationary phase and behaves as a retention gap. The retention time of molecule 2 remains as in (a), but molecule 1 migrates much more rapidly through the pre-column and its delay to molecule 2 is reduced. The reconcentration of the band is equivalent to the acceleration of molecule 1 in the retention gap, *i.e.*, to the reduction of the retention power in the pre-column as compared to the separation column (the depth of the retention gap).

of the separation column. The apparent film thickness of the retention gap tested was 0.0063 μm.

RESULTS

The apparent film thicknesses of three differently pretreated glass retention gaps determined by the method based on the retention times are listed in Table II. The values are different for compounds of different polarities, which shows that the support surface was not of the same polarity as the SE-54 serving as a base for the calculations. The differences are especially important for the Carbowax-deactivated retention gaps where the retention power for *n*-pentylbenzene was nearly double that for *n*-dodecane. In the silylated retention gap, even the more polar *n*-nonanol showed only 20% more retention than *n*-dodecane.

A comparison of the results in Table II allowed the following conclusions:

(a) Roughening of the support surface doubled the retention power of the retention gap (if both surfaces were deactivated with Carbowax 20M). This may be explained by the increase of the surface area by roughening. If the quantity of non-extractable Carbowax 20M is assumed to be constant per unit of surface area, a column with a roughened internal surface contains more organic material for a given length than a smooth column. This is a point of high interest, because roughening of the inner surface of the retention gap shortens the flooded zone for a given volume of a sample. However, it appears that this reduction of the band broadening in space is accompanied by an increase of the retention power, and thus a reduced reconcentration effect by the retention gap.

(b) The silylated (rough) retention gap showed a significantly lower retention power than the gap deactivated with Carbowax 20M. Surprisingly, this was even true for *n*-dodecane which should not be assumed to be strongly retained by a polyglycol.

(c) Silylation was the only method to achieve an adequate deactivation of the retention gap. 2,6-Dimethylphenol and 1-nonanol were not eluted at all from the Carbowax 20M-deactivated retention gaps. Although the extreme size of the retention gaps tested accentuated adsorption effects the importance of this point for practical work should not be underestimated.

TABLE II

APPARENT FILM THICKNESSES (μm) OF THREE DIFFERENTLY PRETREATED RETENTION GAPS DIRECTLY DETERMINED BY MEANS OF RETENTION TIMES

Gaps: 1 = glass (Durobax), deactivated with Carbowax 20M; 2 = as 1 but etched with potassium hydroxide, Carbowax 20M-deactivated; 3 = etched, deactivated by leaching and persilylation. ne = Not eluted.

Compound	Retention gap		
	1	2	3
2,6-Dimethylphenol	ne	ne	0.011
n-Pentylbenzene	0.014	0.031	0.012
1-Nonanol	ne	ne	0.013
n-Dodecane	0.009	0.017	0.011

An unexpected result was obtained concerning the deactivation procedure with Carbowax 20M. The retention power of the retention gap was determined before and after washing out the extractable parts of the Carbowax 20M after the thermal treatment. It was reduced only by a factor of two for n-pentylbenzene and was hardly affected for n-dodecane. This indicates that a large proportion of the Carbowax 20M introduced by the dynamic coating with the 0.1% solution in dichloromethane was bonded to the support surface or otherwise chemically modified so as to become non-extractable, and might explain the high retention power of the Carbowax 20M-deactivated retention gaps.

Table III shows apparent film thicknesses obtained for the n-alkane n-C_{28} by the method based on the reconcentration effect of the retention gap, including results from the three retention gaps characterized by the first method (Table II). If the values determined for n-dodecane by the first method and for n-C_{28} by the second method are compared for the last three retention gaps, the two methods provided similar, although not identical results. The differences are between 10% and a factor of nearly two, the first method consistently producing higher values. This may be partly due to the neglect of the increased volume of the carrier gas at the exit of the separation column as compared to the gas volume under 0.5 atm in the retention gap. Nevertheless, our conclusions are not affected by these differences. Since the results of the second method (Table III) are more directly related to the subject of our interest, we consider them to be more important.

In addition to the three conclusions drawn from the results in Table II, the following points are of interest:

(d) A persilylated retention gap of glass (14 m × 0.32 mm I.D.) had nearly double the retention power of a retention gap of fused silica with identical geometry, deactivated by an analogous procedure (available from MEGA through Carlo Erba Strumentazione, Milan, Italy). This difference was expected because of the more intensive attack on the glass during leaching with 20% hydrochloric acid than during the hydrothermal treatment of the fused silica. The roughened retention gap had a noticeably higher retention power than the smooth piece of glass despite the fact that the former was leached less intensively before silylation than the latter. This confirms point (a), that roughened retention gaps have a higher retention power than smooth ones.

(e) It was surprising to find that the retention gap of raw fused silica had a higher retention power than the silylated one (with the same geometry), although tested with an alkane, which is expected to be most strongly retained by a silylated

TABLE III

APPARENT FILM THICKNESSES (μm) DETERMINED BY THE RECONCENTRATION EFFECT OF THE RETENTION GAP

Glass (Durobax), Carbowax 20M deactivated	0.0081
Glass (Durobax), etched with potassium hydroxide, Carbowax 20M deactivated	0.010
Glass (Durobax), etched with potassium hydroxide, leached, persilylated	0.0063
Glass (Duran), leached, persilylated	0.0040
Fused silica, leached, persilylated	0.0023
Fused silica, untreated	0.0030
Glass, packed with Chromosorb G	0.093

surface. Burning out the raw fused-silica capillary at 320°C with air passing through it (1 h) only slightly reduced the apparent film thickness to the 3 nm indicated in Table III. We conclude that persilylation at least does not increase the retention power of a fused-silica retetention gap.

(f) The apparent film thickness of a packed retention gap cannot be directly compared with the values of open tubes. However, there remains the fact that commercially available deactivated Chromosorbs have a very high retention power. This is not surprising when considering the enormous surface areas of these materials. Previous, unpublished experiments have shown that pre-columns packed with various types of Chromosorb, quartz or glass materials require intensive further deactivation. Such treatments (Carbowax-deactivation or persilylation) increased the retention power of these packed pre-columns to a level above that of separation columns with even moderately thick films, thus being equivalent to a retention "hill" instead of a retention gap with a corresponding peak broadening effect.

To summarize, persilylation of open tubes appears to give the best retention gaps, because it is the only method to provide a satisfactory inertness and because it only produces a very weak retention. The question of whether it is useful to roughen the inner surface of the retention gap cannot be answered yet. This and the application of our new information to the fields listed in the introduction will provide interesting subjects for further studies.

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