CHROMSYMP. 1608

INTRODUCTION OF WATER AND WATER-CONTAINING SOLVENT MIXTURES IN CAPILLARY GAS CHROMATOGRAPHY

I. FAILURE TO PRODUCE WATER-WETTABLE PRECOLUMNS (RETENTION GAPS)

KONRAD GROB, Jr.*

Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland)

and

ZHANGWAN LI

West China University of Medical Sciences, Chengdu, Sichuan (China)

SUMMARY

The introduction of large volumes of water or water-containing solvent mixtures in capillary gas chromatography (GC) is of wide interest for the direct analysis of aqueous samples, and also for coupling reversed-phase liquid chromatography to GC. Water is a very difficult solvent for GC owing to its high surface tension (poor wetting properties), the very large volume of vapour produced per unit volume of liquid, the high boiling point and the poor properties concerning solvent effects. This paper deals with failures to transfer aqueous samples by retention gap techniques. Precolumns that could serve as retention gaps were either water-wettable or sufficiently inert for running GC, but never both at the same time.

INTRODUCTION

Water —an important sample matrix and solvent

A large proportion of the samples to be analysed by gas chromatography (GC) have an aqueous matrix, including most biological samples and many environmental samples. In some instances (*e.g.*, drinking water), more or less direct injection of the sample would be attractive for accelerating the analysis or to allow fully automatic on-line analyses. However, to achieve the sensitivity required, the volumes of water to be introduced must substantially exceed those introduced today.

For most samples (waste waters, biological fluids), an enrichment and a clean-up step are a prerequisite. Convenient on-line systems involve solid-phase extractions or (which is very similar) a preconcentration and preseparation by liquid chromatography (LC) on reversed-phase packing materials. Straight desorption or elution from these systems almost necessarily occurs with reversed-phase eluents, often containing substantial proportions of water. Switching to normal-phase LC systems with solvents of low polarity is possible, but presupposes complete removal of the water by

evaporation as an intermediate step[1,2]. On-line extraction into solvents of low polarity is an alternative that can profit from work carried out for LC coupled with mass spectrometry[3] or flow-injection analysis (FIA)[4], and was used by Roeraade[5] and Fogelqvist *et al.*[6] for on-line water analysis. However, switching to normal-phase systems is attractive only if a more direct transfer within the reversed-phase system is impossible.

A further application, involving the transfer of large amounts of water to the capillary gas chromatograph, concerns reversed-phase LC coupled to GC for samples where preseparation by reversed-phase LC is superior to that by normal-phase LC.

Previous work

Direct injection of water is not new to GC. However, in capillary GC, injection of aqueous samples has been successful in only three instances. First, if very small volumes were introduced, *e.g.*, by the split method, where the presence of condensed water in the column inlet is unlikely or the amount is too small to form a droplet that can move further into the column (see Schomburg and co-workers[7,8], who also found that capillaries coated with Carbowax produced better results than apolar columns, tracing this back to wettability problems). Second, if the column temperature was high enough to rule out the flow of condensed water in the column; this was achieved by the splitless method or by on-column injection under special conditions[9].

Third, introduction of water by normal on-column injection (1–2 μl) was successful in a special case[10,11], the determination of volatile C_1–C_2 halocarbons in waters. A 1–2 μl volume of water is injected on-column into a capillary column coated with an extremely thick film of an apolar stationary phase. A substantial proportion of the water passes as a liquid through the whole column, as noted by the deposition of the dissolved salts in the column outlet, heated in the detector block. Solutes retained by the water are spread throughout the column (extreme band broadening space) and cannot be analysed. However, volatile, apolar components are not trapped and instantly evaporate from the water matrix in the column inlet. The use of uncoated precolumns is not only unnecessary, but also pointless as long as flooding into the separation column cannot be prevented.

An indirect injection method through multi-dimensional GC was proposed by Schomburg and co-workers[12,13]. It involves removal of water by GC on a column packed with Tenax. A different approach was used by Zlatkis *et al.*[14], who extracted the organics from the aqueous solution into the stationary phase of a GC capillary column before reconcentrating the sample and running the analysis. Experimenting with a similar approach, we were not very successful[15].

Water — a difficult solvent

Water certainly is one of the most difficult solvents for sample introduction in GC. It does not wet commonly used capillary surfaces (see below), has a high boiling point, requiring high solvent evaporation temperatures, and produces a very large volume of vapour per unit volume of liquid (about six times that of hexane). Further, it retains solutes poorly, giving rise to partial solvent trapping up to components eluted at high temperatures, and is chemically aggressive, destroying the deactivation of precolumns and possibly certain solutes.

Nevertheless, some transfer techniques seem to be promising, allowing the

introduction of water in fairly large amounts when some special precautions are taken. Results will be presented in a series of papers, describing different aspects and techniques. This paper reports experiments and observations made when we were trying to find water-wettable precolumns suitable for GC. Further papers will deal with the wettability of silylated surfaces by mixtures of organic solvents with water (*e.g.*, reversed-phase eluents) and their application to retention gap techniques, and the stability of precolumn deactivations when used for the introduction of water or mixtures containing water. Finally, promising results were obtained by concurrent evaporation of solvents (LC eluents) containing water when co-solvent effects were applied.

Retention gap technique

Retention gap techniques[16] are used for injecting large volumes of liquid, *e.g.*, by the on-column injection technique[17], or for coupling LC to GC (by the use of the conventional retention gap technique or partially concurrent eluent evaporation). In coupled LC–GC, retention gap techniques are preferred to the alternative transfer techniques, involving concurrent eluent evaporation, when it is important to obtain solvent trapping. Solvent trapping is the main solvent effect allowing elution of sharp peaks of accurate size, starting at the column temperature during eluent evaporation. Uncoated precolumns are also used as a column guard, retaining involatile sample by-products[18,19], but this is not of interest in this paper.

The sample liquid, driven by the carrier gas, is allowed to spread into a precolumn of low retention power (retention gap). As the carrier gas continues to flow during the sample transfer process, the solvent evaporates from the rear to the front of the sample film. This direction of the solvent evaporation, the prerequisite for creating solvent trapping effects[20], presupposes a column temperature below the solvent boiling point corrected for the current carrier gas inlet pressure.

To obtain solvent trapping, a price must be paid. The flow of the sample liquid into the column, caused by the flow of the carrier gas, spreads the sample material over a relatively long capillary section, the so-called flooded zone. The resulting "band broadening in space" must be reconcentrated at the entrance of the separation column by using the retention gap effect[21]. The latter is based on a large difference in retention powers between the "flooded" column inlet and the separation column. This is usually achieved by using a precolumn without a stationary phase film. This inlet must be of sufficient length to retain the liquid sample; no liquid must run into the separation column.

Wettability of the precolumn

Retention gap techniques rely on the formation of a sample film on the wall of the precolumn, which in turn presupposes wettability. For instance, a 1 m × 0.32 mm I.D. precolumn retains 3–6 μl of liquid if the surface is wetted (flooded zones of 17–30 cm/μl, depending primarily on temperature)[22,23]. However, a single microlitre of liquid runs through several metres of a capillary column, when not wetting the surface, leaving droplets here and there (Fig. 1). Under such conditions, unreasonably long precolumns would be required. Further, the volume of liquid retained per unit length of the precolumn becomes unreliable, as there is no control over how often a droplet of liquid remains on the capillary wall. Hence, retention gap techniques become awkward as soon as the sample does not wet the precolumn surface.
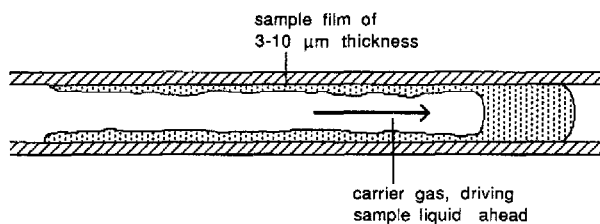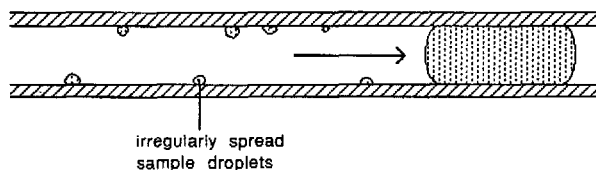
Wetted capillary surface

sample film of
3-10 μm thickness

carrier gas, driving
sample liquid ahead

Non-wetted capillary surface

irregularly spread
sample droplets

Fig. 1. Influence of wettability of the capillary precolumn wall on retention of liquid. Film formation causes 3–6 μl of liquid to be retained per metre of a 0.32 mm I.D. capillary, whereas this volume is far smaller and poorly reliable for a non-wetting liquid.

Wettability of the precolumn surface must be achieved by a compromise with other properties: the surface must be well deactivated to rule out adsorptivity towards the solutes to be analysed, *i.e.*, the precolumn must not deteriorate the performance of the GC system. Further, the deactivation must be thermostable up to high temperatures (350°C) and chemically stable when in contact with the solvents during solvent evaporation. As will be shown in a subsequent paper, the latter is a serious problem, particularly when dealing with water.

Surface tensions of solvents
Wettabilities of differently treated precolumns by the most important organic solvents have been tested previously[22]. It was pointed out that the critical parameter was the surface tension and not the polarity of the solvent. For instance, wettability with ethers, 1-propanol and 2-propanol was found to be more easily achieved than with benzene or dichloromethane.

As a first approximation, wettability is expected to be achieved if the surface tension of a liquid is below the critical energy of the surface to be wetted or, more pragmatically, if adhesion forces exceed the cohesion forces. Surface tensions for some important solvents are given in Table I (from refs. 24 and 25). Some of the values given are extrapolated from others at temperatures near that listed. Surface tensions decrease linearly with increasing temperature (Eötvös rule).

Acetonitrile, benzene, dichloromethane, dioxane and toluene are recognized as difficult solvents, but the surface tensions at 25°C only go up to 34 dyne/cm. Water, however, has a surface tension far exceeding that of all other solvents, namely 72 dyne/cm. This explains the experimental finding that it is very difficult to achieve a surface that is water-wettable.

TABLE I

SURFACE TENSIONS OF VARIOUS SOLVENTS

Solvent	Surface tension (dyne/cm)			
	25°C	50°C	70°C	100°C
Acetone	22.5	19.5		
Acetonitrile	28	24	22	
Benzene	27.7	23.8	22	18
Chloroform	26.2	22.5	20	
Cyclohexane	25.7	22.8	20.4	
Dichloromethane	27.5			
Diethyl ether	16.7	12.9	10.7	
Dioxane	34	30.9	28.4	
Ethanol	21.5	19	17	14.7
+20% water	24	22.5		
+50% water	29.5	28		
+75% water		34		
Ethyl acetate	22.2	19	18	14
n-Hexane	17		13.5	
Methanol	22.5		17.5	14.8
+10% water	25	22.5		
+20% water	27	25		
+50% water	35	33		
+75% water	46	43		
+90% water	58	55		
n-Octane	20	18	16	
2-Propanol	20.5	19	17	
1-Propanol	23	21	19	17
Toluene	27	23.5	22	19
Water	72	68	64	59

Critical surface energies

To achieve wettability by samples with a high surface tension, the capillary surfaces should have properties that create strong interactions with the sample liquid. These properties are usually described in terms of critical surface energies, the measurement of which was recently reviewed by Ogden and McNair[26]. Table II lists critical energies (tensions) of some glass or fused-silica surfaces, taken from refs. 27–31. Analogously deactivated glass and fused silica result in almost identical critical surface energies.

Many surface energies appear to be variable, as is known, e.g., from problems concerning the coating of fused silica with Carbowax. Critical surface energies given for raw glasses appear to be very low, while the value for cyanopropylhydrosilioxane-treated fused silica is higher than expected from our experience concerning the wettabilities of similar surfaces.

From the critical surface energies given in Table II, the choice of a deactivation providing wettability for solvents with high surface tensions seems obvious: silylation with cyanopropylhydrosiloxane or deposition of a thin layer of immobilized Carbowax. However, both critical surface energies are still too low to allow water to spread on these surfaces.

TABLE II

CRITICAL SURFACE ENERGIES OF GLASS AND FUSED-SILICA SURFACES TREATED WITH DIFFERENT REAGENTS

Treatment	Critical surface energy (dyne/cm)
Untreated Pyrex glass	31.5
Untreated soft glass	30
Soft glass, HCl etched	> 52
Raw fused silica	28–50
Treated fused silica:	
20% nitric acid, 200°C, 10 h	46
Hexamethyldisilazane (HMDS) or D_4	20.2
Diphenyltetramethyldisilazane (DPTMDS)	33.1
Tetraphenyldimethyldisilazane (TPDMDS)	35.3
Triphenylsilylamine	36.6
Cyanopropylhydrosiloxane	≥ 49
Carbowax	≈ 44

Data on critical surface energies and tensions must be considered with care. For instance, raw fused silica was poorly wetted by benzene or dichloromethane, and wettability of DPTMDS-treated glass or fused silica with methanol is critical, despite the fact that the surface tension of methanol is far below the critical energy of the phenylsilylated surface. Such discrepancies are probably due to the dependence of wettability on the nature of the interactions, which in turn depend on the chemical functionalities of the solvent and the surface.

EXPERIMENTAL

Etching of soft glass
    Soft glass of 0.52 mm I.D. was etched by filling the capillary with 2–3% potassium hydroxide solution and heating at 110°C for 4 h. The capillary was thoroughly rinsed with water and heated at 350°C for dehydration. The resulting capillary is whitish owing to a strongly roughened internal surface.

Carbowax deactivation
    Carbowax "baked" to the capillary surface. Carbowax deactivation was achieved in two ways. First, the classical method, introduced by Aue et al.[32] and Cronin[33] was applied, designed for deactivating capillary surfaces before coating them with a stationary phase. The capillary was rinsed with a 0.1% solution of Carbowax 20M in dichloromethane, followed by baking at 280°C for 2 h. The excess of Carbowax was rinsed out with dichloromethane, leaving behind a layer of non-extractable (bonded?) Carbowax.
    Carbowax "bonded" to the surface. The capillary was statically coated with a very thin layer of immobilized Carbowax, using a method analogous to that originally introduced by Traitler et al.[34]. Glass capillaries were leached and dried in a stream of carrier gas at 350°C for 4 h. They were then coated with a 50 ppm solution

of Carbowax 20M in dichloromethane, containing glycidoxypropyltrimethoxysilane or vinyltriethoxysilane and dicumyl peroxide (10% of each, relative to the Carbowax). After pumping off the solvent, the capillary was flushed with nitrogen and sealed. The reagents were allowed to react at an oven temperature increasing at 3°C/min from 160 to 200°C; the final temperature was maintained for 8 h.

In situ polymerization of polyethylene glycol

A series of experiments were directed towards polymerizing ethylene oxide to short polyethylene glycol chains, bonded to the silanol groups of the leached glass surface. The leached and dried glass capillary was flushed with hydrogen chloride gas, then with ethylene oxide. The capillary ends were sealed in the flame and the capillary was heated at 200°C for 2 h. From determinations of the resulting retention power (comparing the retention times with those of columns of known film thickness), we deduced that nearly complete polymerization had occurred. However, about 60–80% of the polyglycol polymer was extractable with dichloromethane, alcohols or water, indicating poor attachment to the surface silanols.

Leaching and silylation

Soft glass was leached according to Grob[35] by filling 93% of the capillary with 18% hydrochloric acid and heating at 150°C overnight. The capillary was rinsed with 1% hydrochloric acid and dried statically at 280°C for 2 h, applying a vacuum at both ends. Silylation occurred with 1,3-bis(3-cyanopropyl)tetramethyldisiloxane (Petrarch, Bristol, PA, U.S.A.). A plug of the reagent was pushed through the column, the air was displaced with nitrogen and the capillary was sealed and heated at 360°C overnight. The capillary was then rinsed with toluene, methanol and diethyl ether. Duran glass was leached at 160°C, the other conditions being the same as above.

Barium carbonate treatment

The barium carbonate treatment corresponded to that applied for the preparation of polar columns (B1)[36] and resulted in a roughened surface.

Test of wettability

Wettability was tested on 5 m × 0.52 mm I.D. sections of the capillary of interest, with the exit connected to a 10 m × 0.32 mm I.D. whitish glass capillary that allowed us to observe water leaving the capillary. The volume of water injected was increased until some water passed from the capillary to be tested into the whitish capillary. The carrier gas flow-rate was adjusted to 10 ml/min (1 bar inlet pressure) and the oven temperature was 70°C. In some instances, the front of the flooded zone could be directly observed. Lengths of flooded zones below 30 cm/μl were interpreted as indications of wettability; longer flooded zones (and usually they rapidly exceed 1 2 m) indicate that no stable film of liquid was formed.

Adsorptivity of precolumns

Precolumns were connected to an apolar separation column and tested by injection of the standard test mixture[37] or a mixture of alkanes.

RESULTS AND DISCUSSION

Our intention was to find a glass or fused-silica surface that is well deactivated and wettable by water. We did not succeed, as we obtained either deactivation or wettability, but not both at the same time. Apparently, interaction forces (essentially the same as adsorption) get out of control as soon as the surface is of sufficient activity to be water-wettable. The forces between the liquid and the capillary surface, required to achieve wettability, must be so strong that the adsorptivity of solutes becomes unacceptable.

The results are summarized in Table III. Where wettability was achieved, the length of the zone flooded by water is indicated. Capillaries had an I.D. of 0.52 mm (causing flooded zones to become shorter than for 0.32 mm I.D. capillaries).

Raw fused silica was not wetted by water, in contrast to the raw glasses tested. However, raw glasses are too adsorptive to allow their use as GC precolu..ins. The same is true of leached glass (very high concentration of silanols on the surface).

Silylated surfaces (introducing cyanopropyldimethylsilyl or phenyldimethyl groups) were well deactivated but not wetted.

Carbowax deactivation

The most commonly applied technique for reducing the critical surface tension of water involves the use of detergents. Addition of detergents to aqueous samples is impossible as the detergents would accumulate at the front end of the flooded zone after evaporation of the water. Therefore, we wanted to bond them to the capillary surface. Carbowax was the non-ionogenic detergent chosen.

It was repeatedly found that Carbowax-deactivated precolumns were not wettable during the first test but that good wettability was observed later, independent

TABLE III

FUSED-SILICA AND GLASS SURFACES, TESTED FOR WATER WETTABILITY AT 70°C

Capillary surface	Wettability	Length of flooded zone (cm/μl)
Raw fused silica	No	
Raw soft glass	Yes	20
Deactivated with Carbowax	Yes	15[a]
Soft glass, etched (roughened) with KOH	Yes	17
+ Deactivated with Carbowax	Yes	14[a]
+ Leached + deactivated with dicyanopropylmethyldisiloxane (DCPTMDS)	No	
+ leached + deactivated with diphenyltetramethyldisilazane	No	
Raw Duran glass	Yes	13
Leached	Yes	13
Leached + deactivated with Carbowax	No	
Leached + ethylene oxide	No	
Leached + silylated with DCPMTDS	No	
Leached + BaCO$_3$ treatment	Yes	15
Leached + BaCO$_3$ treatment + Carbowax	Yes	16[a]

[a] Probably only after removal of the Carbowax by water.

of whether Carbowax was "baked" to the capillary surface or "bonded" to it, using silane reagents and cross-linking with a peroxide. We interpret these findings by assuming that the Carbowax layer was removed by the water. With a long glass capillary precolumn, some droplets of accumulated material (Carbowax), located near the front end of the flooded zone, could even be observed visually.

While freshly Carbowax-deactivated surfaces were inert, they became highly adsorptive after a few transfers of water. Finally, even alkanes were eluted as strongly tailing peaks. This confirms our assumption that the deactivation of water-wettable surfaces was completely destroyed. From these experiments, we conclude that smooth, Carbowax-coated surfaces are not wetted by water and that Carbowax, bonded to the surface either by "baking" or by bonding through silanes, is readily stripped away by water.

Roughened surfaces

As is known from earlier procedures used for capillary columns with polar stationary phases, roughening the surface of the internal capillary wall improves wettability. We hoped that this would compensate for the reduced surface energy resulting of better deactivation. However, these hopes were dashed; roughened, leached, and silylated surfaces were not wetted by water.

High resistance of water plugs

Using 0.32 mm I.D. precolumns and injecting 20–100 μl of water, we experienced very high resistance of the water plugs in water-wetted column inlets. At normal inlet pressures, the water plugs rapidly came to a stop and blocked the carrier gas flow. Inlet pressures exceeding 1 bar had to be applied to keep the water plugs moving at all. This prompted us to use wide-bore (0.52 mm I.D.) capillaries as precolumns for the introduction of water or solvent mixtures containing a high proportion of water.

REFERENCES

1 A. T. Boo and J. Krohn, *J. Chromatogr.*, 301 (1984) 335.
2 E. Noroozian, F. A. Maris, M. W. F. Nielen, R. W. Frei, G. J. de Jong and U. A. Th. Brinkman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 17.
3 B. L. Karger, D. P. Kirby, P. Vouros, R. L. Folz and B. Hidy, *Anal. Chem.*, 51 (1979) 2324.
4 B. Karlberg, *Fresenius Z. Anal. Chem.*, 329 (1988) 660.
5 J. Roeraade, *J. Chromatogr.*, 330 (1985) 263.
6 E. Fogelqvist, M. Krysell and L.-G. Danielsson, *Anal. Chem.*, 58 (1986) 1516.
7 E. Bastian, H. Behlau, H. Husmann, F. Weeke and G. Schomburg, in R. E. Kaiser (Editor), *Proceedings of the 4th International Symposium on Capillary Chromatography, Hindelang, 1981*, Hüthig, Heidelberg, 1981, p. 465.
8 G. Schomburg, in *Proceedings of the 7th International Symposium on Capillary Chromatography, Gifu, 1986*, Hüthig, Heidelberg, 1986, p. 27.
9 B. S. Middleditch, N.-J. Sung, A. Zlatkis and G. Settembre, *Chromatographia*, 23 (1987) 273.
10 K. Grob and A. Habich, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 11.
11 K. Grob, Jr., *J. Chromatogr.*, 299 (1984) 1.
12 G. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 112 (1975) 205.
13 G. Schomburg, E. Bastian, H. Behlau, H. Husmann, F. Weeke, M. Oreans and F. Müller, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 4.
14 A. Zlatkis, F.-S. Wang and H. Shanfield, *Anal. Chem.*, 55 (1983) 1848.
15 K. Grob, Jr. and B. Schilling, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 726.
16 K. Grob, Jr., *On-Column Injection in Capillary GC*, Hüthig, Heidelberg, 1987.

17 K. Grob, Jr., G. Karrer and M.-L. Riekkola, *J. Chromatogr.*, 334 (1985) 129.
18 K. Grob, Jr., *J. Chromatogr.*, 287 (1984) 1.
19 K. Grob, Jr. and B. Schilling, *J. Chromatogr.*, 391 (1987) 3.
20 K. Grob, Jr., *J. Chromatogr.*, 279 (1983) 225.
21 K. Grob, Jr., *J. Chromatogr.*, 237 (1982) 15.
22 K. Grob, Jr., H. P. Neukom and M.-L. Riekkola, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 319.
23 K. Grob, Jr. and B. Schilling, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 531.
24 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 66th ed., 1985, pp. F-32–F-35.
25 *Landolt-Börnstein, Physikalisch-Chemische Tabellen I*, Springer, Berlin, 1923, p. 20.8.
26 M. W. Ogden and H. M. McNair, *J. Chromatogr.*, 354 (1986) 7.
27 G. Alexander and G. A. F. M. Rutten, *J. Chromatogr.*, 99 (1974) 81.
28 T. Welsch, R. Müller, W. Engewald and G. Werner, *J. Chromatogr.*, 241 (1982) 41.
29 K. D. Bartle, B. W. Wright and M. L. Lee, *Chromatographia*, 14 (1981) 387.
30 K. E. Markides, B. J. Tarbet, C. L. Woolley, C. M. Schregenberger, J. S. Bradshaw, M. L. Lee and K. D. Bartle, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 378.
31 K. E. Markides, B. J. Tarbet, C. M. Schregenberger, J. S. Bradshaw, M. L. Lee and K. D. Bartle, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 741.
32 W. A. Aue, C. R. Hastings and S. Kapila, *J. Chromatogr.*, 77 (1973) 299.
33 D. A. Cronin, *J. Chromatogr.*, 97 (1974) 263.
34 H. Traitler, L. Kolarovic and A. Sorio, *J. Chromatogr.*, 279 (1983) 69.
35 K. Grob, *Making and Manipulating Capillary Columns for Gas Chromatography*, Hüthig, Heidelberg, 1986.
36 K. Grob and G. Grob. *J. Chromatogr.*, 125 (1976) 471.
37 K. Grob, Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 149.