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Journal of Chromatography A, 897 (2000) 247–258

JOURNAL OF CHROMATOGRAPHY A

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Video-taped sample evaporation in hot chambers simulating gas chromatography split and splitless injectors II. Injection with band formation

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Received 9 May 2000; received in revised form 31 July 2000; accepted 1 August 2000

Abstract

The processes in devices imitating a vaporising injector were video-taped using perylene as a fluorescent marker for non-evaporated sample. Processes are summarised which are observed after the sample liquid passed through a cool needle and left as a band of liquid moving at high velocity (as typical for injection by fast autosamplers). This liquid is shot past the column entrance unless stopped either by a packing, e.g., wool or by suitable obstacles. Packings of low thermal mass are locally cooled to the solvent boiling point and suck in the liquid. Stopping the liquid by obstacles is more difficult because solvent vapours prevent contact of the liquid with the hot surfaces, and was reliably achieved only by the laminar liner. For the same reason, transfer onto the liner wall only occurs for higher boiling liquids.

Keywords: Sample evaporation; Vaporising injection; Split/splitless injection; Band formation; Injection methods; Liner performance; Perylene

1. Introduction

1.1. Thermospray injection

Part I of this investigation [1] summarised observations made by video-taping the processes which follow injection under conditions causing partial solvent evaporation inside the needle and spraying of the liquid at the needle exit. Such nebulisation is usually followed by evaporation from droplets suspended in the gas phase and is preferably performed with an empty liner. Thermospray injection has been performed ever since solutions in volatile solvents were introduced into a hot injector, manually or by means of autosamplers other than a fast autosampler (see below).

Evaporation of solutes from droplets of their own liquid or matrix suspended in the gas phase is more gentle than evaporation from surfaces of the liner or packing materials since adsorption, retention, or degradation of solutes on active, possibly contaminated surfaces is avoided. Even high boiling material can be transferred to the column at rather low temperatures since it forms micro particles moved by the gas like fog.

Problems are related to sample evaporation inside the needle and aerosol formation. Particles of involatile material may enter the column and contami-

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0021-9673/00/$ – see front matter
PII: S0021-9673(00)00824-4

nate its inlet, but most of them are attracted to the liner wall. When injected in samples containing high loads of matrix material, solutes are likely to be dissolved in the particles transferred to the liner wall, leading to matrix effects.

1.2. Fast autosamplers

In 1979, the problems related to evaporation inside the syringe needle were described [2]: the volume of sample injected exceeds that measured on the barrel of the syringe almost by the internal volume of the needle, and selective loss of high boiling material inside the needle results in discrimination against the high boiling constituents. Such discrimination can be reduced by thoroughly heating the injector up to the septum cap [3], but it cannot be eliminated completely.

Around 1985, responding to these problems, Hewlett-Packard introduced the ''fast autosampler'' with a ''needle dwell time'' (time for inserting the needle, depressing the plunger, and withdrawal of the syringe) being so short that solvent evaporation inside the syringe needle could be suppressed [4]. An important part of this achievement was related to a low septum temperature: thermostatting of the injector was designed with a steep temperature gradient towards the injector head, minimising the heat transfer to the syringe needle [5].

The fast autosampler solved the problems related to sample/solvent evaporation inside the needle, but also introduced a new one: now all the solutions in volatile solvents commonly injected (not only those in a high boiling matrix) are ''shot'' as a band of liquid through the vaporising chamber (a stream of liquid either being continuous or consisting of droplets in a row moving too fast to be resolved by eye or the video camera used). The consequences of this were largely overlooked for more than a decade.

In 1992, visual experiments were described [6] which made use of the fluorescence of perylene in the liquid phase for monitoring the behaviour of liquid in devices imitating vaporising chambers. It was shocking to see a band of liquid leaving the exit of the syringe needle and rushing through long and bent glass tubes heated to 200°C with hardly any evaporation. However, at that time, it was not clear that band formation was, first of all, the problem introduced by fast autosampler injection.

At about the same time, Qian et al. [7] built an apparatus for the visual observation of the jet of sample liquid leaving the syringe needle upon injection by a fast autosampler. They concluded that the droplets did not lend themselves to rapid vaporisation within the gas phase of the injector: they formed a narrow band ''shot'' through the chamber.

1.3. Stopping the band of liquid

Up to the introduction of the fast autosampler, mostly empty injector liners were used. Packings with, for example, deactivated glass wool, were inserted for stopping liquids with a high boiling point (undiluted samples or solutions in high boiling solvents). Liners with built-in obstacles, such as the Jennings tube [8] or that with baffles, were designed for better mixing of the sample vapours with the carrier gas in order to distribute them more homogeneously across the liner when they reach the column entrance. They were not conceived for stopping a band of liquid.

The previous visual experiments revealed that stopping a band of liquid is rather difficult [9,10]: the liquid curved around obstacles like baffles or went through spirals or other deformed channels. The high mobility of the sample liquid is related to the law that a liquid cannot touch surfaces the temperature of which exceeds their boiling point: a cushion of vapours repels it from the surface and guides it through narrow channels and curves. Compared to the previous work, video taping helped observing many more details and draw additional conclusions.

2. Experimental

Most of the experimental details were given in Part I [1]. Liners with built-in obstacles were tested in a glass U-tube imitating an injector (especially manufactured by Restek, Bellefonte, PA, USA, Fig. 1): liners were inserted into the tube in the same way as into an injector body and tightened against by means of O-rings. The cup liner was from Hewlett-Packard, the baffled liner made in the laboratory from a Pasteur pipette, and the other liners from

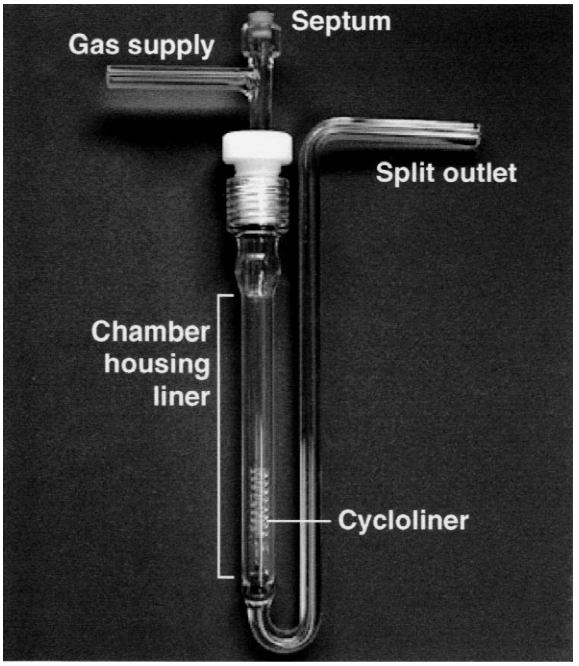

Fig. 1. Glass device imitating a vaporising injector for testing injector liners, here with a cycloliner being inserted. The device was immersed in a heated oil bath and irradiated by a strong UV lamp [1].

Restek. Unless stated otherwise, nitrogen was passed through the liner at a flow-rate of 40 ml/min (ca. 3 cm/s in the 5 mm I.D. tube), imitating a split injection with a modest split flow-rate.

Cool needle injections imitating fast autosamplers were performed inserting the needle into the heated zone by only about 1 cm. Introduction by 3 cm was usually sufficient to result in thermospray.

Results are primarily based on the visual observations in videos made available on a CD-ROM through Restek [11].

3. Summary of observations

3.1. Band formation

3.1.1. Suppressed evaporation inside the needle

Injection of a perylene solution in hexane, cyclohexane, dichloromethane, chloroform, ethanol, toluene, or dimethylformamide (DMF) through a cool needle into ambient air released a band of liquid which covered a distance of several tens of centimetres until it was split up and fluorescence disappeared (probably because of solvent evaporation). The band had a width of about 0.3 mm, which exceeds the internal diameter of the needle (0.11 mm) and suggests that it actually consisted of a series of droplets which were not resolved by the video (see Qian et al. [7]).

No difference was observed whether this band moved through ambient air or a bent tube of 15 cm length heated to 220°C. Hence the release of liquid from a cool needle results in band formation also in a hot injector. This confirms the observations by Qian et al. and shows that suppression of solvent evaporation inside the needle, e.g. by a fast autosampler, is the source of band formation.

3.1.2. Velocity of the liquid

The band of liquid covers long distances through empty, hot chambers because it moves so fast that no significant amount of heat for evaporation is absorbed. Manual depression of the plunger of a 10-μl syringe from the ''10 μl'' to the ''0 μl'' position occurred within two frames of the video, i.e., less than 80 ms, which indicates that the liquid left the needle at more than 125 μl/s and its velocity at the exit of a gauge 26S needle exceeded 8.9 m/s. Qian et al. determined that a 2-μl injection by a fast autosampler took 61 ms. Since the autosampler did not withdraw the liquid from the needle into the barrel, this included the time for accelerating the plunger. It remains that manual depression of the plunger is faster than that by the autosampler.

If the liquid is ''shot'' through the vaporising chamber at 10 m/s, it covers the 4-cm distance between the exit of the syringe needle and the entrance of the column in 4 ms, which is at least a hundred times shorter than the time needed for picking up the energy required for solvent evaporation [12].

3.1.3. Deformed needle tip

A slight deformation of the (bevelled style) needle tip (point bent slightly inwards) caused a mechanical spray of the liquid (injection through a cool needle into ambient air). The liquid running against the small obstacle was split into small droplets, forming

two broader jets squirted away somewhat sideways. Fluorescence disappeared some 6 cm from the needle tip. The deformation was hardly visible by eye, but felt when passed over by a finger.

As thermospray, mechanical spray fundamentally changes the evaporation process in the injector chamber since the small droplets are rapidly slowed by the friction with the gas (depending on how fine the droplets are). This may provide the time required for heat transfer to evaporate the sample, first of all the solvent, from the suspended droplets.

Mechanical spray resulting from a deformed syringe needle could be one of the reasons why injections with different syringes often produce differing results. Well controlled mechanical spray might, however, also be promising for substituting thermospray, with the advantage of avoiding the side effects of partial evaporation inside the needle.

3.1.4. Wiping droplets from needle tip?

Sometimes it is argued that the needle tip should penetrate a packing inside the injector in order to wipe off a droplet of liquid hanging there at the end of the injection. For manual injection at normal speed, both at ambient temperature and at 200°C, visual observations did not confirm such a requirement: the exiting velocity is so high that the liquid is ruptured from the needle tip. The same has been observed for on-column injection [13].

Slow injection (1 μl/s) may, indeed, end with a droplet adhering to the needle tip, but it should anyway be avoided for split or splitless injection because of the excessive discrimination against high boiling sample components thus obtained [2].

3.2. Band of liquid in empty liners

To observe the performance of a band of liquid in an empty liner, perylene solutions were injected into glass tubes heated to 200°C in an oil bath. Band formation was achieved inserting the needle into the hot zone by merely some 10 mm.

Injection under conditions of splitting mostly caused the band of liquid to rush through the 5 mm I.D. part of the pipette, imitating the vaporising chamber, around the bend and up the narrow tip simulating the split outlet (Fig. 2). It passed the tube of more than 20 cm length in less than 80 ms (two

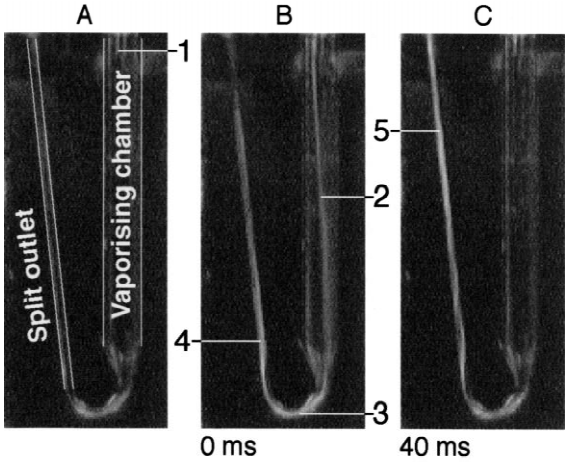

Fig. 2. Band of sample liquid (5 μl of hexane solution) passing through a Pasteur pipette with a bent tip, heated at 200°C. (A) Before injection, showing the device; (1) tip of the inserted needle. (B) Frame including the injection; (2) band of liquid shot through the vaporising chamber; (3) liquid passing the bend without contacting surfaces; (4) band leaving through the split outlet. (C) Subsequent frame of the video (times below the pictures indicate the beginning of a frame), showing the last liquid leaving the split outlet (5). After 80 ms, no sample was left in the ''injector''.

frames of the video), did not touch the hot wall, and took the curve in the bend without a sign of slowing. In fact, it was shot through the device virtually without evaporation.

Sometimes the liquid was slowed in the vertical outlet, the tip of the pipette of some 0.8 mm I.D. It formed a long droplet and fell backwards into the bend. In the funnel-shaped region between the wider bore chamber and the more narrow outlet, it hovered between the hot surfaces, moved back and forth, sometimes jumped against the gas stream into the vaporising chamber, and other times exploded. Explosions probably result from delayed evaporation and resulting overheating. The process was not reproducible.

3.2.1. Duration of evaporation

Solvent evaporation from a droplet dancing between or above hot surfaces or sitting in a packing material is slower than often assumed. Durations were estimated visually, determining the moment when bright fluorescence disappeared.

Table 1 lists results for injections with band

Table 1
Durations of solvent evaporation, as time for fluorescence to extinguish[a]

Liner	Solvent	Time (ms)
Empty	Chloroform (5 μl)	3500
	Chloroform (2 μl)	880
	Hexane (5 μl)	600
Glass wool	Hexane (2 μl)	1500
	Hexane (5 μl)	3900
Frit	Hexane (1 μl)	480
	Ethanol (3 μl)	240
	Chloroform (3 μl)	720
Carbofrit	Chloroform (2 μl)	4200
	Chloroform (5 μl)	5600
Chromosorb	Hexane (5 μl)	440
	Chloroform (5 μl)	1500
Cup liner	Chloroform (1 μl)	280
	Chloroform (2 μl)	600
	Dichloromethane (2 μl)	1000
Cyclo liner	Ethanol (2 μl)	320[b]
	Chloroform (1 μl)	640[b]
	Hexane (2 μl)	1500
	Chloroform (2 μl)	800
Laminar liner	Hexane (2 μl)	350
	Hexane (5 μl)	480
	Chloroform (2 μl)	500
Minilam liner	Hexane (1 μl)	800
	Hexane (5 μl)	400

[a] Injections with band formation; 190–200°C; gas flow-rate, 40 ml/min.
[b] With some breakthrough through the obstacle.

formation into chambers at about 200°C and with a flow-rate of 40 ml/min. Durations varied widely, from 240 ms to more than 5 s. Under most conditions, they were poorly reproducible (often varying within a factor of three for identical injections). They tended to be short when droplets jumped backwards into the empty vaporising chamber and exploded there, while they were long when most of the liquid remained sitting at the bottom, extracting the heat from a small area. Complex and non-reproducible behaviour also explains why durations were often proportional neither to the sample volume, nor to the evaporation heat of a solvent. Evaporation from glass wool was the exception, as the process was smooth and reproducible (see below).

3.2.2. Transfer to the liner wall

It is often assumed that the sample liquid is transferred to the liner wall and vaporised from there. The chamber is, in fact, a long, narrow bore channel, and the probability that the liquid is ''shot'' to the wall appears high. For solutions in volatile solvents, this is not true, however. Even upon injection vertically against the liner wall, using a side port hole needle, hardly any liquid adhered to the surface. The liquid was rejected by the vapours, deviated and flung through the chamber as with shots to the bottom of the chamber.

Transfer to the liner wall is possible only for high boiling solvents (boiling point not more than 50–100°C below the injector temperature), and solvents consuming a large amount of heat for their evaporation. At 200°C, it was reliable for DMF, often occurred for ethanol (large evaporation energy) and sometimes for toluene.

A 1-μl sample of DMF solution remained stationary at the spot on the liner wall it was transferred to. A 2-μl sample formed a tear with a tendency to flow downwards for a few millimetres. With 5 μl, the tear was so heavy that it immediately flew down the tube; in a real injector, it would have passed the column entrance into the split outlet. Hence, the capacity of the liner wall for retaining a wetting liquid, such as DMF, is 2–3 μl.

Transfer to the liner wall seemed to be complete and reliable with a side port hole needle. With a standard needle, there were occasional ''shots'' directly to the bottom of the chamber, particularly with samples/solvents boiling below the liner temperature (such as DMF). When the liquid approached the wall at an acute angle, it was commonly deviated by some vapours. Another problem concerns small droplets split from the bulk: little repulsion may be sufficient to prevent contact with the liner. The liquid squirted from the main stream, e.g., because of a slightly deformed needle exit easily drops to the bottom.

3.2.3. Rejection from bottom surface

Another set of videos was recorded using a 4 mm I.D. glass tube with a flame-sealed bottom, heated at

about 200°C. As there was no gas flow, the situation resembled that of splitless injection with an empty liner.

The process following injection through a cool needle was often dramatic and, again, not reproducible. The band of liquid shot to the bottom was usually rejected, easily 5 cm high (Fig. 3), hence almost to the top of a standard 8 cm chamber. Once it was flung straight upwards, but more often it coiled upwards along the liner wall, without touching the latter. Sometimes a larger droplet exploded in the middle of the chamber, forming small particles which largely evaporated while suspended in the gas. Mostly, however, the liquid fell back to the bottom and formed a ball dancing above the hot surface, carried by a cushion of vapour. Often it exploded again, maybe after 500 ms of slow and unspectacular evaporation, and squirted liquid several centimetres high, returned to a single droplet and evaporated during the following 1–4 s.

When a piece of fused-silica capillary was mounted into the vaporising chamber, imitating the column inlet protruding into the chamber, sample liquid sometimes wetted it from outside, perhaps because of its small thermal mass. As any other higher boiling solute, the perylene deposited onto the polyimide had no chance of reaching the column entrance since this would have presupposed a gas flow upwards.

3.2.4. Fate of the solute material

The probability that the solute material reaches the column entrance in the way expected by the injection technique is described in following scenarios, since these enable to categorise the observations.

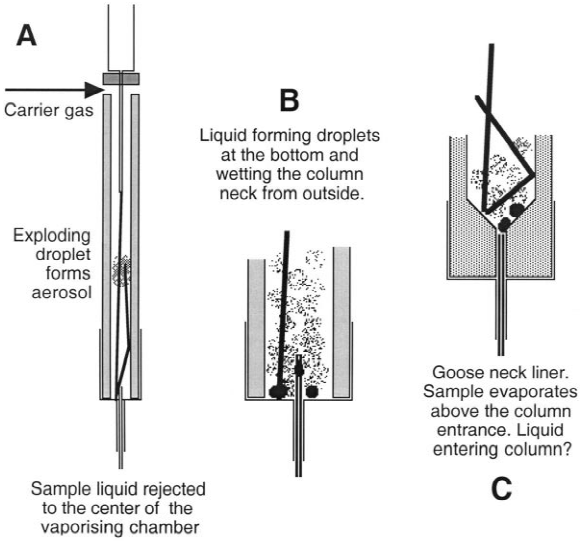

Fig. 4. Band of sample liquid hitting the bottom of the vaporising chamber: probable scenarios of subsequent processes.

1. After hitting the bottom surface of the vaporising chamber, the band of liquid is rejected above the column entrance (A in Fig. 4). An explosion splits it into small particles which evaporate there, suspended in the gas or driven upwards by expanding solvent vapours. Finally, the resulting vapours are driven to the column by the carrier gas and correctly enter it in split or splitless mode.
2. The liquid accumulates to one or a few droplets at

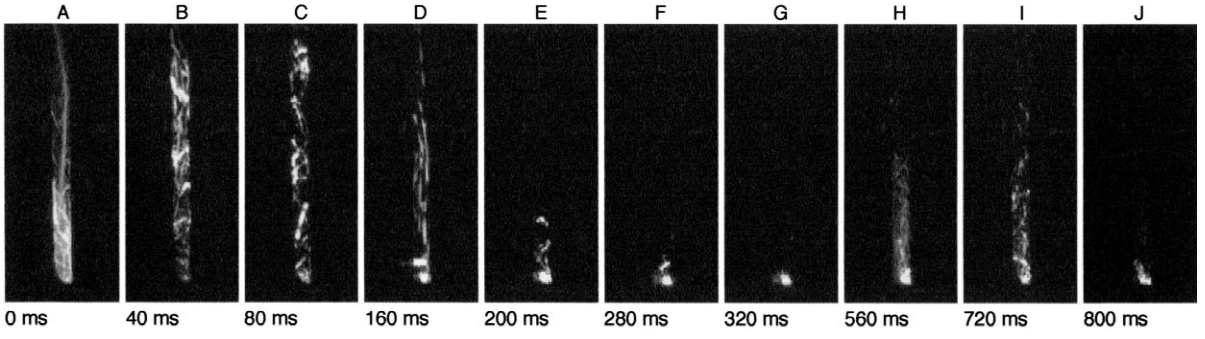

Fig. 3. Injection of an ethanol solution (5 μl) into a tube with a flame-sealed bottom. (A) The band of liquid approaches the liner wall, but is deviated, hits the bottom, is fragmented and is rejected. (B) Subsequent frame of the video. Droplets curl up the tube well 6 cm high. (C–F) Droplets fall back and are again rejected, but finally accumulate at the bottom (two frames omitted). (H) 560 ms after injection, the droplet explodes and sends liquid at least 4 cm high.

the bottom of the chamber. Either it always remains there or the droplets flung into the chamber return. Usually the droplets nervously hover on a cushion of vapour above the metallic surface (B in Fig. 4). The solvent produces a volume of vapour sufficiently large to expand above the column entrance (assumed to be installed 5 mm above the bottom) and may, therefore, enter. The solutes are vaporised only after solvent evaporation is completed (temperature remains low until all solvent is evaporated). Since 10 ng of a component forms a vapour cloud of around 0.001 μl only, it does not reach the column entrance and is lost for the analysis (immediately removed in split injection or rinsed through the split outlet upon purging the injector in splitless injection).

3. Usually the bottom of the vaporising chamber is littered with pieces of septum and other dust. Such particles are rapidly cooled to the solvent boiling point and suck up the sample liquid (like packings of wool, see below). In fact, with around ten septum particles deposited in the chamber, the liquid almost immediately disappeared in them, without any squirting around. The particles remained strongly fluorescent for an unlimited time: perylene was unable to evaporate from such strongly retaining material. Even at temperatures enabling vaporisation of the solutes, this process ends as Scenario 2. The solvent vapours expand above the column, while the solute vapours remain below the column entrance and are discharged through the split outlet.
4. It may seem preferable to install the column entrance below the bottom of the chamber, such that the solutes evaporate above the column, ruling out losses as in Scenarios 2 and 3. Surfaces of glass are preferred to those of metal because at the final stage of evaporation, the droplets with the higher boiling solutes are deposited onto them. Thus a goose neck liner is used with the column entrance positioned within the constriction (C in Fig. 4). The band of liquid was rejected and whirled through the chamber as described above. For the final evaporation, droplets formed which tended to glide towards the orifice of the constriction and probably occasionally dropped into it. Sometimes some liquid was shot straight into the column or past the column into the outlet channel. Another problem of this arrangement is that all the solute material must pass through possibly strongly retaining dust or septum particles which easily ''filter out'' high boiling or adsorptive compounds.

The first scenario was clearly the least important, though the only resulting in the process envisioned. It is concluded that the band of liquid must be stopped above the column entrance, i.e., that injection with a fast autosampler should not involve an empty liner.

3.3. Packed liners

3.3.1. Glass wool

In 1977, Schomburg et al. [14] proposed packing the liner with glass wool in order to improve results in split injection. Only the visual experiments explained the effects involved. In fact, a small plug of silylated glass wool positioned below the needle exit had a striking effect: it seemed to suck up the sample and no droplets flew around.

The approaching liquid rapidly cools the nearest fibres of the wool and then enters the packing. Guided by vapour cushions formed in the hotter zones around, the rest of the liquid follows to the same spot (Fig. 5). Fibres have a minimal thermal mass, as their diameter is in the order of 5–10 μm.

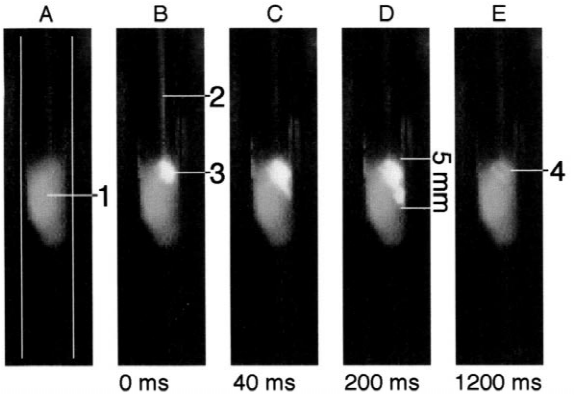

Fig. 5. Injection into a liner packed with glass wool; 2 μl of hexane solution. (A) Frame before injection; 1, glass wool. (B) Injection; band of liquid (2) and fluorescing zone in the wool (3). (D) Maximum extension of the wetted zone, 200 ms after injection. (E) Shortly before the end of solvent evaporation, 1.2 s after injection, with weakly fluorescing perylene in the boundaries of the wetted zone.

Evaporation takes a few seconds (Table 1), since all the heat must be drawn from a small region.

A volume of 5 μl of liquid was usually spread within a zone of the packing of a few millimetres in diameter, not necessarily over the whole cross section of the plug and no deeper than about 5 mm. The example shown in Fig. 5 is extreme as 2 μl of hexane entered 5 mm deep. There is no risk of liquid dropping from the bottom of the packing. Therefore, a small plug, representing a few milligrams of wool, is all which serves the purpose. The packing does not need to be dense, but just to ensure that there is no major gap. Any additional amount merely enhances adsorption, degradation, or other negative effects, as well known from deactivated glass, quartz, or fused-silica wool.

The effect was entirely different when the sample was nebulized above the wool. The fog passed through the packing without noticeable effect. Neither was evaporation improved, nor were particles retained (no fluorescence on the wool and no reduction in fluorescing fog below the wool), which also suggests that there is little interaction (adsorption or chemical activity) with the solutes. When introduced as a band, no liquid or fog left the wool, i.e., retention was complete. The solutes evaporated from the wool and were, hence, in closest contact with it. This might explain common experience that the negative effects of wool strongly depend on how the sample is injected.

3.3.2. Glass frit

As it is difficult to thoroughly deactivate glass or fused-silica wool and to shape a plug of homogeneous and reproducible density, liners with a glass frit were proposed (Fig. 6). Frits are made of glass particles of a few hundreds of micrometres diameter sintered to a block.

Their performance after injection with band formation was disappointing. Solutions in hexane and ethanol wildly danced above the frit. They touched it at best towards the end of solvent evaporation. The liquid was rejected by the high thermal mass of the sintered particles. At temperatures higher than 200°C, as normal in GC, the frit might behave like a solid surface.

Another surprising observation was that regularly a large proportion of the chloroform solution went through the frit (Fig. 7), apparently driven by the initial thrust immediately after injection. Small droplets must have made their way through the narrow channels, guided by vapour cushions. Hence, in contrast to a loose plug of wool, the more dense frit was not capable of stopping a band of liquid.

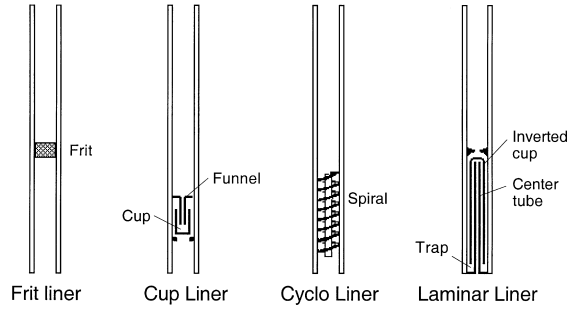

Fig. 6. Injector liners with various types of obstacles.

3.3.3. Carbofrit

Carbofrit (Restek), a filigree network of a carbon-type material treated at high temperature, behaved more like glass wool, sucking up the liquid without visible resistance and no liquid whirled around. With concentrated solutions, some fine fog was observed to leave the plug at the bottom right after injection,

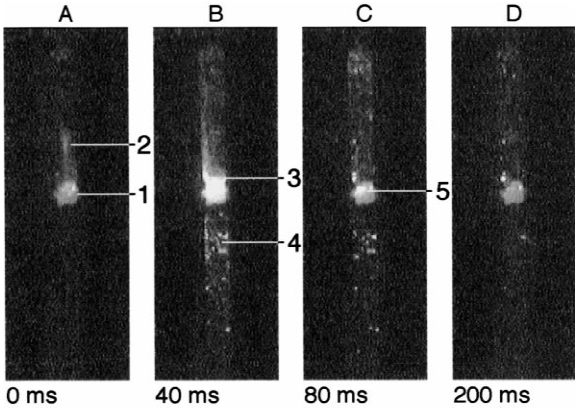

Fig. 7. Performance of a liner with a frit. (A) Injection (3 μl of chloroform solution), with the band of liquid hitting the liner wall (2), but not wetting it, and some first droplets on the frit (1). (B) The majority of the liquid dancing above the frit (3), but some liquid must have passed the obstacle (4). (C) Droplets rejected about 3 cm above the frit and some liquid wetting the sintered particles (5). Evaporation was nearly complete after 200 ms. (D) It was some ten times faster than with wool.

which suggests that some liquid was nebulized upon hitting the hot surface before the latter was cooled.

3.3.4. Column packing

Packing materials for GC columns, like deactivated Chromosorb, tend to be more inert than glass or fused-silica wool. They must be supported by wool, but, as mentioned above, wool has less detrimental effects if the vapours pass through it rather than if the solutes evaporate from its surface.

Using a 1-cm plug of Chromosorb above a 1-cm plug of dense wool, the band of liquid stirred up the packing well 5 mm deep. The liquid dug into the packing and the vapours whirled particles up 2–3 cm high. After about 100 ms, the packing re-settled and fell onto the part soaked with sample. Hence the sample ended up evaporating in the middle of the bed. There was no rejection of liquid, i.e., the thermal mass of the (porous) particles is sufficiently low to avoid repulsion.

Mixing into the packing may be advantageous in so far as the samples get into contact with more fresh material. Stirring up the packing could be avoided by a plug of wool on its top. However, doing so, the packing material below could just as well be left away since the wool would determine the process.

3.4. Liners with obstacles

Numerous designs of obstacles built into the liners were advertised to improve sample evaporation. Usually the improvement was demonstrated through standard deviations of peak areas, but was seldom really conclusive. Visual observation provides more specific information.

3.4.1. Cup liner

The most widely used liner with a built-in obstacle is commonly called ‘‘Jennings tube’’ or ‘‘inverted cup’’ liner. Since the cup is not really inverted, we prefer ‘‘cup liner’’ (Fig. 6).

Most of the liquid was stopped on the horizontal surface of the funnel, from where it was often rejected up to several centimetres high and performed wild movements (Fig. 8). Sooner or later some of the liquid poured into the cup. Sometimes it formed a droplet and smoothly evaporated there. Other times (depending on the amount entering the cup), this droplet boiled over or exploded. Liquid splashed against the bottom surface of the funnel and partly escaped the device, dropping to the bottom of the liner and past the column. With a (split) flow-rate of 40 ml/min, regularly some liquid broke through the device also upon the first thrust by the injection.

3.4.2. Baffles

Baffled liners have indentations protruding beyond the center of the chamber in order to prevent a straight shot from the needle exit to the column entrance. Such liners seemed to offer no advantage. The band performed perfect slalom and rushed past the position of the column entrance as if the liner

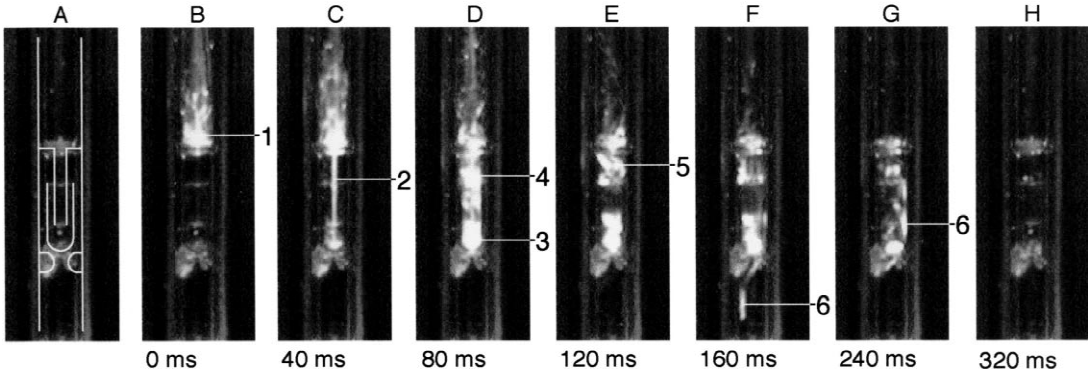

Fig. 8. Chloroform solution (2 μl) evaporating in a cup liner. (A) Before injection, pointing out the structure of the obstacle. (B) Band of liquid coming in (needle tip outside of picture) and hitting the horizontal surface of the funnel (1). (C) Liquid being rejected, but also pouring into the cup (2). (D) Violently boiling liquid in the cup (3) and liquid pushed upwards against the bottom surface of the funnel (4). (E) Liquid about to leave the cup (5). (F–G) Continuing wild boiling in the cup and liquid dropping towards the column (6).

were straight. The cushion of vapour formed upon approaching a hot surface guides the liquid and prevents contacts.

3.4.3. Cyclo splitter

The cyclo liner forces the sample through a narrow channel which is wound like a spiral along the liner wall (Fig. 6). The band of liquid usually passed this obstacle with little hindrance. Sometimes one or several droplets remained hanging on a spot within this channel and evaporated from there, presumably because of a dust or septum particle that caught the liquid.

3.4.4. Laminar liner

The videos also confirmed the previous positive results [10] concerning the laminar liner. The obstacle consists of an inverted cup sitting above a center tube, into which the column inlet is mounted (Fig. 6).

A highly varying proportion of the liquid evaporated at the entrance of the obstacle (on the bottom of the inverted cup), jumping around at first. The other part glided through the narrow space between the inverted cup and the liner wall to the bottom (Fig. 9),

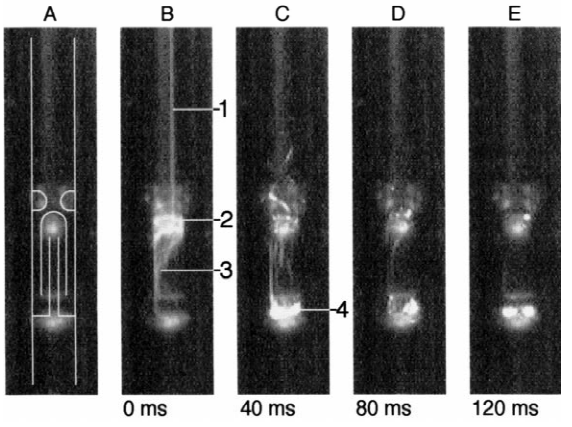

Fig. 9. Minilaminar liner during a 1-μl injection of a hexane solution. (A) Structure of the obstacle. (B) Incoming band of liquid (1), stopped on the bottom of the inverted cup (2), and liquid passing through the narrow space between the liner wall and the inverted cup (3). (C) Some liquid continues to dance on the bottom of the inverted cup, but the major portion (4) is trapped at the bottom of the liner. (D) Liquid accumulated to a droplet. (E) Droplet split into two, evaporating during the next 720 ms.

where it was trapped: it could neither return, nor enter the narrow channel conducting upwards into the inverted cup. Liquids are hindered to enter a narrow space because the hot walls accelerate evaporation and the vapours formed repel them. The laminar and the mini laminar liner (same design but the obstacle was only 15 mm high) were the only chambers which reliably stopped a band of liquid from travelling directly to the column inlet.

4. Discussion

Suppression of sample (solvent) evaporation inside the syringe needle eliminates the problems regarding inaccurate sample volumes and discrimination resulting from selective solute evaporation in the needle, but also fundamentally alters the starting conditions for the evaporation process inside the injector. In fact, the introduction of the fast autosampler had consequences reaching far beyond the problem it intended to solve. They have not been properly recognized and solved (despite the work published in 1992 by Qian et al. [7]).

4.1. Stopping the liquid by wool

There are two options for stopping the band of liquid above the column entrance. Transfer into a packing material of low thermal mass, such as deactivated glass or fused-silica wool, results in a smooth process and prevents uncontrolled squirting of the sample liquid. This appears to be the most perfect and simple method, but relies on well deactivated wool. Deactivation is not as simple as it might appear since the well elaborated procedures for deactivating glass or fused-silica columns cannot directly be applied to thin fibres. Furthermore, there is the problem that the deactivation should be chemically stable and resist attack by aggressive sample components, such as water present as humidity in the samples. Silylation provides high thermostability, but poor chemical stability. This is why the introduction of improved deactivation is crucial for this approach.

Carbofrit or supports for column packings are also suitable and maybe more inert, but frits or other

materials of relatively high thermal mass cannot be cooled by the sample liquid and do not serve the purpose.

4.2. Stopping the liquid by obstacles

Appropriate obstacles built into the liner are the alternative. They have a high thermal mass and the liquid cannot touch them as long as solvent evaporation is not completed. Hence obstacles cannot catch the liquid by their surfaces, but must guide it without direct contact. The liquid is, furthermore, highly mobile since vapour cushions enable it to glide through complicated structures requiring strong changes in direction.

So far, the laminar liner is the only way to reliably stop the liquid. There is still room for improvement, since the dancing of the liquid on the horizontal surface at the entrance is not sufficiently controlled – liquid may be rejected and jump several centimetres high, i.e., almost to the top of the liner. The obstacle should act as a trap for liquid, with a funnel type entrance inviting the band to pass into a small chamber from where it can neither go onwards not backwards. Narrow channels act as a barrier against liquid (but allow vapours to pass), provided their orifice is designed such that the liquid is not driven into them (no funnel).

Evaporation above or inside obstacles or a trap proceeds through two steps. First, the volatile material evaporates, i.e., the solvent and the volatile solutes, while the liquid ''dances'' above the hot surfaces. This cools the surroundings, while the boiling point of the droplets (shrunk to the higher boiling material) increases. The second step starts when the liquid is no longer repelled. Owing to their relatively large size, the droplets are deposited onto the surface and evaporate from there. Thus, evaporation of the volatiles occurs from droplets suspended in the gas phase, like that following thermospray, but then it is more difficult for high boiling solutes to evaporate from surfaces.

On the basis of present knowledge, it is not obvious whether wool or well designed obstacles provide better performance. Reports on practical experience with various samples would help in this matter.

4.3. Characteristics of evaporation from surfaces

Sample evaporation from surfaces has the following characteristics:

1. Clean vapours are formed and involatile material remains on the surface.
2. The surfaces have varying properties: sample by-products may deactivate or activate them, but also build up retention power hindering solute evaporation.
3. Particularly in trace analysis (splitless injection), inertness of packing materials or liners with obstacles is critical. Inertness can no longer be influenced, of course, when it is determined by deposits of sample matrix material.
4. All but the most volatile solutes evaporate after the solvent and are, therefore, less affected when the split ratio is disturbed by the expansion of the solvent vapours or by recondensation in the cool column inlet or split outlet [15].
5. In splitless injection, overfilling of the vaporising chamber is often less critical since primarily the vapours of the solvent and volatile components expand and escape through the septum purge outlet, while those of higher boiling solutes remain near the evaporation site. This is made use of by the overflow technique [16,17].

These observations should contribute to a better understanding of the puzzling results often obtained from split and splitless injection and enable more purposeful optimisation of conditions. They might also stimulate new ideas on injector design.

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