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Video-taped sample evaporation in hot chambers simulating gas chromatography split/splitless injectors I. Thermospray injection

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Abstract

The processes in devices imitating vaporising injectors were visualised and video-taped using perylene as a fluorescent marker for non-evaporated samples. The observations in the context of thermospray injection are summarised. Partial evaporation inside the needle turns the solvent into a propellant which nebulises the sample liquid at the needle exit. Evaporation in the vaporising chamber occurs from fine droplets suspended in the gas phase. Empty injector liners are best suited; packings with glass wool or obstacles in the liner, like the cup, have no significant effect on the process observed. Non-evaporated (matrix) material forms aerosol particles which may enter the column together with the vapours, but most of them are transferred to the liner wall. Since solute material may be carried along, this is a possible source of matrix effects.

Keywords: Sample evaporation; Vaporising injection; Split/splitless injection; Thermospray injection; Injection methods; Perylene

1. Introduction

1.1. Sample evaporation in hot injectors

Quantitative analysis by capillary GC is often confronted with impenetrable deviations, such as generally high standard deviations, deviations from day-to-day, and systematic differences between calibration solutions and samples, often termed ''matrix effects''. Many analysts have their ideas about possible sources and try to find better conditions, but frequently the results change in the unexpected direction or turn out inconsistent, adding to the confusion. For instance, in a streak of luck their measures may be honoured by three well repeated results, but on the next day it all too often turns out that this was not the real remedy. Systematic investigation of parameters and mechanisms through chromatographic experiments is difficult because of the many interacting parameters.

Sample evaporation in the injector is a major source of such problems and it may easily proceed in an unpredictable way, as visualised by the experimental observations summarised below.

1.2. Solvent evaporation

For sample evaporation in a hot vaporising chamber, solvent evaporation is the first obstacle to

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overcome: there is hardly any solute evaporation before the solvent is fully vaporised since non-evaporated solvent forms a cool site in the hot injector (in the neighbourhood of the droplets, temperature corresponds to the solvent boiling point) and exerts a strong retention power on the solutes. After solvent evaporation, the surrounding area must first be heated again before high boiling components can be vaporised.

It may appear easy to vaporise 1–3 μl of solvent with a boiling point below 100°C in a chamber at, e.g., 250°C, but this overlooks that the real problem is the heat consumption of the evaporation process and the short time available for heat transfer [1].

The carrier gas in the vaporising chamber contains such a small amount of heat that around 0.05 μl of a commonly used solvent, such as hexane, is sufficient to cool it from 250°C to the solvent boiling point [1]. Even a packing material, such as glass or fused-silica wool, only contains a small amount of heat compared to what is consumed. Hence, most of the heat must be provided from the liner wall. A layer of glass of 0.3 or 1.4 mm thickness is cooled by 20° if 2 μl of hexane or water, respectively, are injected (calculated results [1]).

Heat transfer from the liner wall to the sample liquid is more time-consuming than intuition suggests. When cooling by 20°C is accepted, the heat transport for vaporising 2 μl of hexane is calculated to take 0.3–9 s, among other factors depending on the heat conductivity of the carrier gas (nitrogen being the worst). In reality, solvent evaporation is faster, primarily because the injector chamber is cooled by more than 20°C.

It was concluded that sample evaporation is slower than one might assume and that the nature of the solvent and the sample volume injected have a strong influence on the real temperature in the vaporising chamber during the time this temperature is important, i.e., during sample evaporation.

1.3. Previous work

In the 1960s, work aimed at achieving complete sample evaporation in specially designed unpacked chambers (e.g. [2]). Typically undiluted samples, such as mineral oil fractions, were injected with extremely high split ratios. In the 1970s, the dilute solutions in volatile solvents became the common sample, which might have had a greater impact on the vaporisation process than recognised. Jennings introduced the ''inverted cup'' liner with an obstacle forcing the gas to change its flow direction twice [3]. The major concern was mixing of the sample vapours with the carrier gas before the diluted vapours reached the column. Schomburg suggested the use of glass wool [4], while German and Horning [5] packed the liner in a similar way as a packed column.

In the meantime, many more types of liners were proposed, but since there was no direct evidence on their effect, evaluation was merely based on repeatability tests; inevitably results remained rather speculative. They neglected that performance is fundamentally different depending on whether injection is performed by the hot needle technique or through a fast autosampler. In fact, the fast autosampler did not exist at that time and all injections were performed with a more or less heated needle, i.e., with thermospray. Stopping a band of liquid was a problem merely for samples with high boiling matrices.

1.4. Visual observation

Direct visual observation of evaporating sample liquid (solvent) was first reported in 1981 by Munari and Trestianu [6]. They used a GC oven with two windows into which a transparent (glass) vaporising chamber was built. Recording by high speed camera enabled the observation of nebulization of pentane as well as of band formation for higher boiling solvents (5 μl, 250°C).

Direct observation is difficult since the amounts are small and the movements are fast. It is facilitated when perylene, a polyaromatic hydrocarbon, is added: when irradiated by a strong UV lamp (366 nm), the liquid fluoresces and can be sensitively observed in a dark room [7]. Fluorescence of perylene in solution is strong, but that of crystals is weak; fluorescence in the molten state is not relevant since the melting point is 278°C. No fluorescing vapours have been observed, maybe because of the low vapour pressure. Hence, fluorescence is a sensitive indicator for a non-evaporated liquid, i.e., incomplete solvent evaporation.

Visual observations with perylene were described in Refs. [8,9]. The injector was imitated by a Pasteur pipette bent to a U-shape, equipped with a gas supply and heated in a silicone oil bath. The processes were followed by eye. The most intriguing observations included the band of liquid rushing from the syringe needle through the vaporising chamber, passing also through many of the liners with obstacles or the droplets of liquid jumping around and exploding. This revealed that vaporisation is often not the smooth and well controlled process hoped for.

1.5. Summary of videos

The experiments described below and in Part II were performed in the same way, but a video camera was used. This greatly improved the observations and helped the clarification of numerous points of conjecture. Around 500 videos were taken and some 80 collected on a CD-ROM, commented, and made available through Restek (Bellefonte, PA, USA [10]).

This paper summarises the observations referring to thermospray injection. In the previous visual experiments, samples were sometimes nebulised, but left the needle as a band of liquid other times. The difference was tentatively attributed to solvent properties [8]. This interpretation must be modified: nebulisation is the result of partial evaporation inside the syringe needle.

Part II of the present report [11] summarises observations on injection with the liquid forming a band and the effectiveness of the various techniques to stop such liquid above the column entrance. The sample liquid leaves the needle as a band if solvent evaporation inside the needle is suppressed, e.g., using a fast autosampler as marketed by Hewlett-Packard.

Part III [12] confronts advantages and drawbacks of the two approaches, discusses the matrix effects to be expected, and draws the conclusions regarding injector design and method validation.

2. Experimental

Hot needle injections into air at ambient temperature were performed using a block of brass of 5 cm height with a 1 mm I.D. boring through which the needle passed. This block was brought to 200°C on a heating plate before performing injections. Alternatively an aluminium block of 15 mm height was used, equipped with two heating cartridges and a thermocouple (gift from Brechbühler, Schlieren, Switzerland). These were connected to the power supply and the regulation of a Carlo Erba Model 2150 gas chromatograph. The block was thermostatted at temperatures ranging between 200 and 300°C and had a 1-mm boring through which the syringe needle was passed, protruding by some 2 mm.

Most experiments with a gas flow-rate (imitating split injection) were performed using a Pasteur pipette with the broad (5 mm I.D.) section imitating the vaporising chamber and the tip bent upwards (U-shape) simulating the split outlet (Fig. 1). Gas was fed through a silicone tube, which also served as septum [8].

Splitless injection was imitated in 4–5 mm I.D.

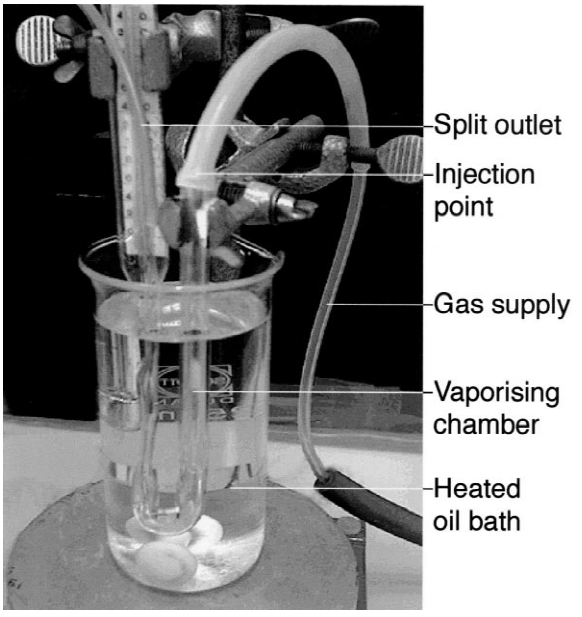

Fig. 1. Device imitating a split injector: pasteur pipette bent to a U-tube with the broad part serving as a vaporising chamber (containing some glass wool) and the tip simulating the split outlet (connected to a plastic tubing and finally a flow meter). The device was thermostatted in a silicone oil bath on a heating plate, regulated by the thermometer. A magnetic stirrer improved the homogeneity of the temperature. Experiments were performed in a dark room using a UV lamp (not shown).

glass tubes with flame-sealed bottom ends or a 20 mm I.D. centrifuge tube, using no gas-flow. For the nebulisation of the sample, the syringe needle was introduced into the hot tube 2 cm deep at least or through the thermostatted aluminium block placed above the tube.

The experiments were performed in a dark room irradiating the device with a UV lamp at 366 nm. Videos were taken at 24 frames per second using a Sony DCR-PC7E digital camera and transferred to a computer for further processing.

3. Summary of observations and discussion

3.1. Thermospray upon injection through a hot needle into ambient air

The first experiments served to prove that nebulisation of the sample liquid at the needle exit is the result of partial solvent evaporation inside the syringe needle (thermospray). Injection into ambient air (no injector chamber) through a heated 5-cm needle nebulised the liquid, while injection through a cool needle formed a band of liquid (Fig. 2). This behaviour was checked for solutions in hexane, chloroform, dichloromethane, ethanol, toluene, and dimethylformamide (DMF).

The band of liquid formed a straight, bright line with sharp edges that covered more than 20 cm

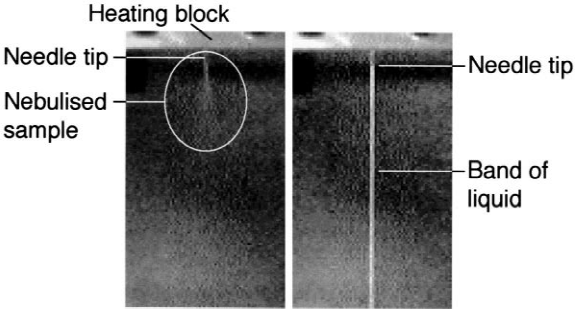

Fig. 2. Injections into ambient air with the syringe needle passing through an aluminium heating block of 15 mm height (partly visible at the top) with the needle protruding about 2 mm (standard 10-μl syringe). Perylene solution in toluene (5 μl). Left: heating block at 300°C, nebulising the liquid near the needle tip (circled zone of some 20 mm height). Right: sample liquid leaving as a band.

without being broadened. Its width was around 0.3 mm. Since this exceeds the internal diameter of the syringe needle (0.11 mm), the band probably consisted of droplets moving in a row at a velocity exceeding time resolution of the video (as suggested by Qian et al. [13]).

3.1.1. Diffuse cone of weak fluorescence

Under conditions nebulising the liquid, a core of bright fluorescence left the needle, usually 1–5 mm long. Further away, fluorescence rapidly lost intensity. It formed a cone, sometimes with rather clear boundaries at the side, other times diffuse, without clear contours. Often it seemed that some fine droplets were squirted away for a distance of 5–20 mm (a kind of spreading jet, see Fig. 2).

Shapes and dimensions of the cone varied. A 2-μl aliquot of a perylene solution in chloroform injected into ambient air through a 5-cm needle at 220°C once produced a broad cone, visible up to 2 cm from the needle exit and some 3 cm wide at the front. Another time, the same injection resulted in a sharper jet which was visible for 4 cm and only some 4 mm wide at that point. A 5-μl aliquot of the chloroform solution covered a distance of 8 cm and reached a width of 4–6 cm. Solutions in other solvents performed similarly.

The fog of nebulised perylene solution was visible in 1–2 frames of the video, i.e., during 40–80 ms at most. Its disappearance suggests that the solvent evaporated in such a short time, consuming heat from ambient air.

Extrapolation from this to what happens inside the vaporising chamber may not be straight forward: there is little room for expansion, i.e., far less gas to extract heat from while temperature is higher.

3.1.2. Proposed mechanism

The sample enters a pre-heated syringe needle at high velocity (some 10 m/s). Vaporisation on the needle surface forms bubbles of solvent vapour which build up high pressure and expel the liquid through the center of the needle (Fig. 3). Pressure inside the needle causes the liquid to be overheated (increased boiling point). On leaving the needle, the liquid explodes and fragments into small droplets. Hence, partial evaporation inside the needle turns the

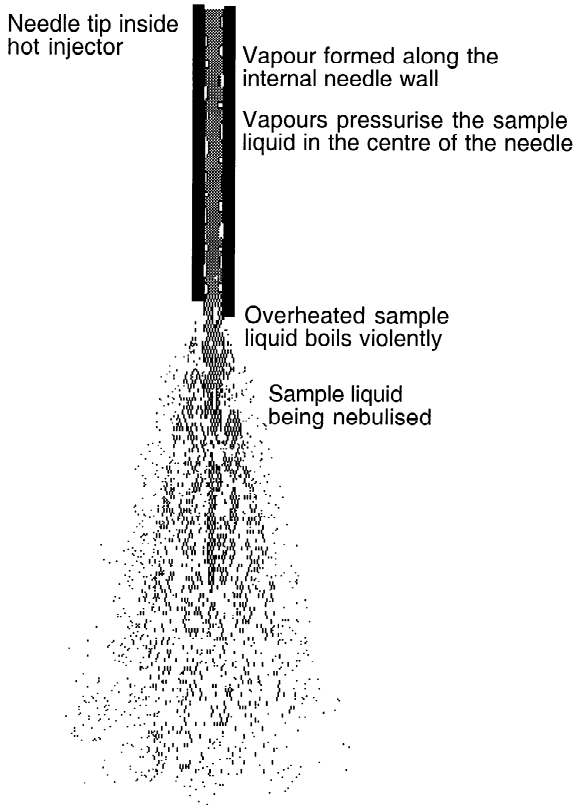

Fig. 3. Thermospray of the sample liquid after hot needle injection. The length of the cone is typically in the range a few centimetres.

solvent into a propellant and produces a thermospray effect.

Friction with the gas rapidly slows the resulting particles to the gas velocity. While suspended in the gas, there is enough time to evaporate the solvent. When solvent evaporation is completed, the temperature of the droplets rises to that of the injector and the solutes evaporate.

3.1.3. Limits to the nebulisation

Under critical conditions the first part of the sample liquid was nebulised whilst the rest left the needle as a band. A 5-μl injection of a DMF solution through a 5-cm needle, a 1.5-cm section of which was heated to 250°C, was an example. Apparently the evaporating liquid extracted that much heat from the needle surface that temperature dropped to the solvent boiling point (153°C).

A 51-mm gauge 26S needle consists of about 60 mg of steel and has a thermal capacity of some 7 mcal/°C (1 cal=4.184 J). Complete evaporation and heating of 2 μl of hexane to 230°C consumes 340 mcal. Since this heat is extracted in a short time (20–50 ms), the concurrent supply of heat from outside is not significant and the needle should be cooled by about 50°C. For the vaporisation of the same amount of water, 1520 mcal are required, cooling the needle by 217°C – or rather to the boiling point, vaporisation remaining incomplete.

Such a calculation does not properly reflect reality. Solvent evaporation inside the needle is incomplete (the proportion being unknown) and heat consumption is lower. On the other hand, the injection process is so fast that not the whole heat capacity of the needle is exploited (heat transfer within the needle wall). The data is sufficient, however, to show that cooling by solvent evaporation is substantial and that under certain conditions temperature may drop to such an extent that the nebulisation process is stopped.

Table 1 summarises the observations on nebulisation by examples either considered typical or borderline. Injection of solutions in the solvents commonly used (b.p. up to 100°C) through a 51-mm needle at 220°C always nebulised the liquid (volumes tested, 5 μl, lengths of visible jet in ambient air, 2–8 cm). Toluene (b.p. 110°C, injection No. 4) was nebulised, but not DMF (153°C, No. 5). At this point it should be reminded that in real injectors the needle temperature may remain far below the temperature regulated since the head of the injector is cooler than its centre. At an injector temperature set at, e.g., 350°C, the septum cap of an Hewlett-Packard instrument hardly reaches 150°C [14], whereas that of a ThermoQuest instrument exceeds 250°C [15].

Heating the needle to 250°C for a length of merely 1.5 cm still nebulised 5 μl of the low boiling solvents. A 5-μl portion of toluene left as a band (No. 10), whereas 300°C resulted in the borderline situation (No. 11): initial nebulisation ceased and elution turned into band formation. This weaker thermospray effect reflects the stronger cooling of a smaller amount of needle wall material. So it was found that 350°C was not sufficient to achieve thermospray of 2 μl of DMF (No. 13).

For some experiments, a gauge 32 needle (for

Table 1
Sample liquid exiting a heated needle under various conditions

No.	Solvent	Volume (μl)	Needle temp. (°C)	Length heated[a] (mm)	Time visible (frames)[b]	Result: spray vs. band (length of cone)[c]
26 S gauge needle						
1	Chloroform	2	220	50	1	Spray (4.0 cm)
2	Chloroform	2	220	50	1	Spray (2.0 cm)
3	Chloroform	5	220	50	2	Spray (8.0 cm)
4	Toluene	5	220	50	2	Spray (5.0 cm)
5	DMF	5	220	50	2	Band
6	Hexane	5	250	15	2	Spray (4.0 cm)
7	Dichloromethane	5	250	15	2	Spray (2.5 cm)
8	Chloroform	5	250	15	2	Spray (4.0 cm)
9	Ethanol	5	250	15	3	Spray (8.0 cm)
10	Toluene	5	250	15	2	Band
11	Toluene	5	300	15	2	Spray/band
12	DMF	5	300	15	2	Band
13	DMF	2	350	15	1	Band
32 gauge needle						
14	Hexane	2	250	15	1	Spray (8.0 cm)
15	Hexane	5	250	15	2	Spray/band
16	Chloroform	2	250	15	1	Spray (0.5 cm)
17	Chloroform	3	250	15	1	Band

[a] Length of the needle heated in the metal block.
[b] Time the band or spray was visible (number of frames of 40 ms).
[c] Observed spray (with length of the cone) versus band formation.

manual on-column injection) was used. Its outer diameter is 0.23 mm, the inner is 0.11 mm (same as the gauge 26S needles) and, thus, its thermal capacity is more than five times lower than that of the gauge 26S needle. In fact, 5 μl of hexane cooled it to such an extent that part of the liquid left as a band (15 mm section heated to 250°C), roughly 3 μl being at the limit for complete nebulisation. If the whole needle wall was cooled to the boiling point of hexane, the amount of heat extracted was sufficient for vaporising almost half of the hexane. For chloroform, the transition from full nebulisation to partial band formation occurred at 2.5 μl. This experiment confirms the importance of the thermal capacity of the needle and also indicates that the wall thickness is not only important for the robustness of the needle.

3.2. Thermospray in empty liners

Injection through a hot needle into a hot (200°C) chamber produced essentially the same nebulisation as observed upon injection into ambient air, except that the fog could not expand as freely because of the narrowness of the space.

3.2.1. Transfer as aerosol

When perylene concentrations were high (around 0.1%, requiring a suitable solvent, such as chloroform or dichloromethane), the fog remained visible beyond the end of solvent evaporation. In the absence of a gas-flow through the tube, it was stationary and kept its fluorescence for many minutes. When a gas-flow was switched on, it was discharged like wind blows away clouds or smoke. No fluorescent material remained on the liner wall, confirming the stability of the aerosol.

Upon solvent evaporation, the fine droplets of dilute solutions shrink by a factor of about ten (assuming 0.1% solute in the solution) and form an aerosol. These particles are too small to settle by gravity and too large for diffusing towards surfaces and condensing there.

Perylene is widely analyzed in GC, e.g. as internal

standard for the determination of the benzopyrenes. The visual experiment showed that nebulised perylene can be introduced into the column under conditions far from providing complete evaporation (200°C, despite Fp. of 270°C), namely as aerosol. In fact, the fog readily reacted to gas-flow and seemed to behave like the vapours. Hence injection with thermospray does not presuppose evaporation in the injector. Transfer as aerosol at low temperature is particularly attractive for the analysis of thermolabile compounds.

3.2.2. Glass wool improving evaporation?

It is often believed that a plug of glass wool would improve solute evaporation. Either it is assumed that wool brings heat to the particles or that it retains them on the fibres and gives them more time for evaporation (larger volume of gas). The visual observations did not confirm this. Fog formed by a hot needle injection (needle heated in the heating block or inserted some 3 cm into the heated tube) was driven through a 15 mm long, dense plug of glass wool without noticeably losing fluorescence. The wool neither retained the perylene particles nor helped the vaporisation.

3.2.3. Homogenisation across liner

In split injection, elevated standard deviations are often explained by non-homogeneous distribution of the sample vapours within the vaporising chamber: during one injection, a trail of concentrated vapours hits the column, another time it passes by it. This is the background for the assumption that mixing devices are needed, such as obstacles built into the liner. Reproducibility testing confirmed this, e.g. [16,17], but also cast doubts [18].

The perylene aerosol seemed to homogeneously fill the cross-section of the 5 mm I.D. liner within 1–2 frames of the video (less than 40–80 ms, injections without gas flow). Even for an unrealistically wide tube of 20 mm diameter, spreading seemed to be completed within only four frames or 160 ms. This suggested that mixing through thermospray injection is fast compared to the process of sample splitting, which takes 500–1000 ms when the split flow-rate is 60 ml/min. Maybe there is turbulence through the high initial velocity of the sample material and the violent evaporation.

3.2.4. Effect of matrix material

If nebulisation forms stable aerosols also of the non-evaporating sample by-products, splitless injection would transfer them into the column, resulting in serious contamination of the column inlet. This does not correspond to practical experience. Thermospray injection of matrix-loaded samples into empty liners forms a ring of dark brown deposits on the liner wall which extends from some 5 mm above the tip of the inserted syringe needle to 15 mm below. The amount of matrix material accumulated there by far exceeds the contaminants carried into the column. Hence, this seems to contradict the observations made for concentrated perylene solutions.

The behaviour of matrix material was investigated with perylene solutions containing 1–5% edible oil. Injection through a hot needle into ambient air formed a cloud of diffuse fluorescence that remained stable like smoke for a long time (determined by ventilation of the room), i.e., the oil formed micro particles containing dissolved perylene.

In a 20-mm I.D. tube at 200°C, the same kind of fog was formed and was stable until displaced by a stream of gas. No fluorescence remained on the wall after the removal of the fog, indicating that little if any oil was deposited there. These two results suggest that virtually the complete amount of the oil imitating a sample matrix would have been driven into the column.

Injections into an empty liner of only 5 mm I.D. provided a fundamentally different result: within a single frame of the video (40 ms), immediately after fog formation, nearly all of the fluorescence was transferred to the liner wall, resulting in an oil film. The oil did not form a patch with clear-cut edges, as when a larger drop splashes against a surface, but appeared to have clouded over the surface (Fig. 4). With a gas flow-rate of 40 ml/min (ca. 3 cm/s), a small amount of fog was driven onwards and left the chamber. It seemed that droplets and particles not immediately deposited onto the wall would remain suspended. With a flow-rate of 2 ml/min (1.6 mm/s), simulating splitless injection, deposition of the oil on the liner wall was virtually complete.

The fast transfer to the liner wall presupposes the action of strong forces (incidental contact with the wall would result in far slower deposition). Only electrostatic forces, maybe arising from charge sepa-

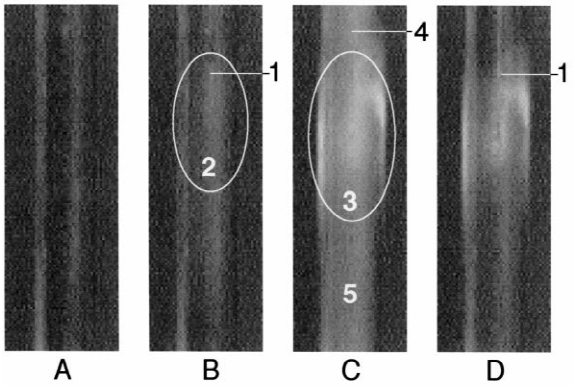

Fig. 4. Hot needle injection of a perylene solution (2 μl, dichloromethane) containing 5% of sunflower oil. Liner at 200°C; gas flow-rate=40 ml/min. (A) Liner before injection; (B) the first nebulised sample (2) leaves the needle exit (1); (C) 40 ms later, most of the oil is transferred to the wall (3), (4) pointing to oil having been driven backwards above the needle exit, (5) to some light fog of nebulised material which is driven away by the gas-flow; (D) shows the situation after 3 s: the liner is contaminated by the perylene-containing oil.

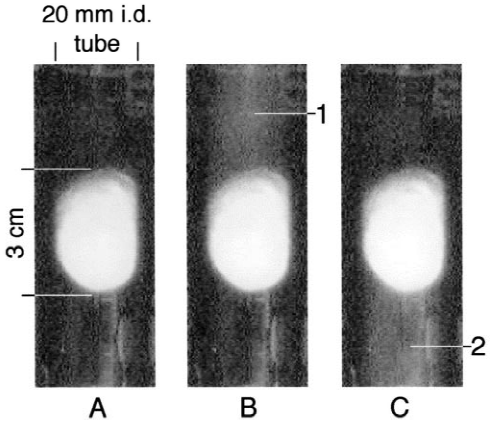

Fig. 5. Filtering nebulised sample contaminants through a dense plug of glass wool? (A) Tube before injection (wool is weakly fluorescent with bluish colour, different from perylene, and the video seems sensitive to reflected UV light). (B) Injection (needle outside of the picture), (1) fog of nebulised oil. (C) Fluorescence of the fog leaving the plug (2) has not lost in intensity. During the slow movement through the wool (200 ms between B and C), no significant amount of aerosol was filtered out.

ration during thermospray, seem to be strong enough. The different behaviour of the 20- and 5-mm I.D. tubes would have to be explained by rapid loss of effectiveness with increasing distance. As the commonly used liners are of 4-mm I.D. only, this might explain why column contamination is far less of a problem than could be expected after nebulisation.

3.2.5. Wool preventing column contamination?

The effectiveness of a dense plug of glass wool for filtering out nebulised matrix material was tested in the 20-mm I.D. tube which did not attract the fog to the wall. The chloroform solution (5 μl) containing perylene as well as 5% oil was sprayed into the tube at 180°C packed with a dense 3-cm plug of wool some 20 mm below the needle tip (Fig. 5). A 15-mm section of the needle was heated to 250°C in the thermostatted aluminium block located above the photographed region. The nebulised edible oil slowly passed through the wool without significant retention: the intensity of fluorescence above and below the wool was not noticeably different (B and C, although more easily observed on a moving video), nor was there a deposition of fluorescing material on the wool. Hence filtration of a sample through glass wool is as inefficient as that of smoke from a waste incinerator.

The oil was more efficiently retained in the packing when the tip of the syringe needle entered the plug of glass wool: far less fog left the wool at the bottom than when the nebulised sample entered the plug as a fog. Apparently injection into the plug largely hindered the formation of a fog.

3.2.6. Solute evaporation from matrix-loaded samples: matrix effects

Transfer of difficult solutes into the column as aerosol under gentle conditions (empty liner, evaporation from suspended droplets, relatively low temperature) is an excellent feature of thermospray injection. Attraction of contaminants to the liner wall is another. However, the combination of the two is bound to create problems.

(i) Injected as a clean, concentrated (0.1%) solution, perylene formed a fog without being attracted to the liner wall (also in the 5-mm I.D. liner). Inside a real injector, transfer into the column would have occurred as aerosol and been quite complete despite the temperature being as low as 200°C.

(ii) When injected as a solution contaminated with oil, the perylene was pulled to the liner wall together

with the oil. To reach the column, it would have had to evaporate from the oil film, which was quite impossible at 200°C. Hence hardly any perylene would have reached the column.

This drastically illustrates what is often termed a ''matrix effect'', the essence of which is that the sample composition influences the quantitative result of the analysis. The clean perylene solution (as commonly used for calibrating the response) would have produced a satisfactory peak, whilst a sample contaminated with oil had yielded hardly any signal for the same amount or concentration of perylene. Performed in this way, the results of a hypothetical perylene analysis would have been systematically far too low. We called it ''reducing matrix effect'' [19], as opposed to the ''matrix-induced chromatographic response enhancement'' termed by Erney et al. [20] and described as a process by Müller and Stan [21].

4. Conclusions

For the vaporisation of the solutions in volatile solvents most commonly injected into capillary GC, there seem to be two alternatives of strongly differing characteristics. The first involves partial evaporation inside the needle, nebulisation of the sample liquid at the needle exit (thermospray), and evaporation in the gas phase. It is preferably performed by hot needle injection, manually or by an autosampler imitating manual injection. The second approach suppresses evaporation in the needle, e.g., using a fast autosampler, and releases a band of liquid which is stopped by a packing or trapped in an obstacle. It is followed by evaporation from surfaces (see Part II of this paper). Analysts must select the appropriate way and optimize injection parameters correspondingly. A discussion on what to prefer will follow in Ref. [12].

4.1. Characteristics of thermospray injection

After nebulisation, a fairly clean sample hardly gets into contact with the liner wall or other surfaces. The aerosol even passes through a dense plug of glass wool or liners with obstacles, i.e., packings or obstacles have little effect on solute vaporisation. Droplets containing low boiling material (solvent) are repelled from hot surfaces, and the low mobility of the aerosol particles renders contacts with surfaces improbable.

Evaporation from droplets suspended in the gas starts with the solvent. If, for instance, the total of the sample material in the solution amounts to 1 $\mu g/\mu l$, at the end of solvent evaporation the diameter of the droplet shrinks by a factor of ten. Then temperature increases and the solutes evaporate from this material, i.e., from their own matrix.

Evaporation from droplets suspended in the gas phase has the following positive characteristics.

(1) Adsorptivity and chemical activity of surfaces in the injector (liner wall, packing) have little effect. Non-deactivated, rather dirty liners can be used.

(2) Extremely high boiling components may reach the column, even though maybe as micro particles rather than vapours.

(3) The non-evaporating matrix material of previous injections is out of the way of the solutes: an accumulation on the liner wall has little effect on components evaporating in the gas phase. In particular, the resulting increase in retention power does not hinder the vaporisation of high boiling components.

(4) The distribution of the solutes within the sample vapours is homogeneous; there is no preseparation by a stepwise evaporation from a surface. This is advantageous for split injection where a fluctuating split ratio causes non-linear splitting when different components reach the split point at different times [22].

On the other hand, thermospray injection has the following negative characteristics.

(5) Non-evaporating by-products form an aerosol potentially reaching the column and contaminating its inlet. Fortunately, most of this material is attracted to the liner wall and deposited there.

(6) There are reducing matrix effects: samples loaded with substantial amounts of matrix material form particles which are transferred to the liner wall. The higher boiling solutes are carried along. Hence, the process is fundamentally different for a clean mixture (e.g., calibration mixture) and a contaminated sample, potentially giving rise to systematic errors.

4.2. Non-linear splitting

In splitless injection it is hardly relevant whether the solutes are transferred into the column as vapours or as micro particles.

In split injection, diffusion speeds may influence the split ratio. During the splitting process at the column entrance, the high-molecular-mass vapours and the particles tend to maintain their direction (e.g., into the column) while small molecular weight vapours are easily diverted (to pass by the column). When different components are split by varying ratios, splitting becomes non-linear and the composition of the sample analysed is distorted. This is the reason why the need for ''isokinetic splitting'' has been postulated [23], i.e., that the gas velocities into and past the column entrance should be equal. The concept is convincing in its logic, but hardly any data is available to substantiate its relevance for practical analysis. Further studies should include the question whether solutes reaching the column in aerosol particles are split by significantly different ratios. They should also take into consideration that the face of the column entrance disturbs the flow anyway.

Before further conclusions are drawn, particularly regarding splitless injection (Part III, [12]), the alternative approach involving band formation should be described more closely (Part II, [11]).

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