Review

Vaporising systems for large volume injection or on-line transfer into gas chromatography: classification, critical remarks and suggestions

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Abstract

Techniques for large volume introduction of liquid samples into capillary gas chromatography (GC) follow a small number of principals. Vaporising systems, vapour discharge modes and methods for solvent–solute separation are classified and evaluated.

Presently, programmed temperature vaporising (PTV) solvent split injection is the preferred method if on-column techniques cannot be applied. Critical re-evaluation suggests, however, that solvent evaporation and solvent–solute separation should be performed in separate compartments and optimized individually. Permanently hot chambers offer the highest capacity for solvent evaporation. The preferred techniques for solvent–solute separation are stationary phase focusing in a coated capillary or solvent trapping in an uncoated capillary precolumn. The vaporising chamber–precolumn solvent split–gas discharge system is proposed for large volume injection and on-line transfer of water-containing solvent mixtures, the in-line vaporiser–precolumn solvent split–overflow system for most on-line transfer applications.

Keywords: Large-volume injections; Injection methods; Programmed-temperature vaporizer; Vaporiser–precolumn solvent split; In-line vaporiser–precolumn solvent split; Reviews

Contents

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1. Introduction

It seems promising that injection and on-line transfer of large volumes of liquid sample into capillary GC are becoming accepted as routine methods. Advantages for trace analysis are all too obvious. It is, however, often less obvious what technique to recommend to a routine analyst.

As recognized in the early sixties, even 1 μl of a liquid sample basically forms excessively large initial bands; it turns into several hundred microlitres of vapour which fill a capillary section of many metres in length. However, mechanisms were found that enable one to reconcentrate the components in the column inlet and form sufficiently sharp initial bands to avoid peak broadening. These mechanisms are so efficient that even several millilitres can be introduced (the record still stands at 20 000 μl [1]).

Literature describes numerous techniques for introducing large samples, with a nomenclature that makes these appear to be even more. Several recent papers gave a broad overview (e.g. [2–4]). On the other hand, there are options that have hardly been tested. This paper starts with a classification of the systems and techniques involved. The rich collection

Table 1
Sample introduction in GC

First choice: on-column injection/transfer
— 0.2–1.5 μl directly
— >1.5 μl with uncoated precolumn
— >50 μl with early vapor exit
— >100 μl with partially concurrent evaporation

Impossible for
— strongly "dirty" samples
— non-wetting samples (e.g. water)
— liquids attacking precolumn (e.g. water-containing samples)

Second choice: injection/transfer through vaporiser chamber

will lead to some evaluations and suggestions made on the basis of the authors' experiences and preferences.

The author's starting point is summarized in Table 1: the on-column injection–retention gap technique is considered first choice whenever applicable. It has been successfully used for large volume syringe injection and on-line high performance liquid chromatography (LC)–GC for over a decade and is summarized in [5,6]. Recently a system has been introduced that performs on-column injection of up to around 500 μl. It involves speed-controlled autosampler injection, partially concurrent evaporation, an early vapour exit, and software controlling conditions and closure of the vapour exit [7]. It has found rapid acceptance for the analysis of micropollutants in water (e.g. in-vial extraction [8]) and other trace analyses involving clean samples, but also for applications involving efficient clean-up. It is promising for off-line LC–GC: A sample is preseparated by the high efficiency of LC and with the accurate cuts enabled by on-line detection. The fraction containing the components of interest is collected in an autosampler vial at the outlet of the LC detector and is transferred to GC, where most of it is injected in order to obtain sufficient sensitivity. This efficiently cleans up the chromatograms, but also enables on-column introduction of originally "dirty" samples.

On-column injection is not applicable, however, if samples contain large amounts of involatile by-products, building up retention power and adsorptive sites in the column inlet. Substantial concentrations of water (or other aggressive by-products) attack the deactivation of the precolumn and renders it adsorptive [9]. Such problematic samples must be introduced through a vaporising chamber that acts as a filter retaining involatile material and prevents con-

densed water from getting into contact with surfaces of the precolumn or separation column (water vapours hardly have any deteriorating effect).

2. Classification of vaporisers

2.1. "On-column" and "vaporising" injection/ transfer

All sample introduction techniques for GC involve, of course, sample vaporisation and, hence, vaporising chambers. It is, however, appropriate to distinguish between "vaporising" and "on-column" injection/transfer techniques. The initial meaning of "on-column" introduction was injection directly into the separation column, but soon the use of uncoated precolumns became common. When an early vapour exit is used, there is often even a retaining precolumn, provoking the term "on-precolumn" injection. It seems more appropriate to define on-column injection/transfer through the vaporisation of the sample from a capillary wall at the oven temperature. In capillary GC, on-column injection means that the sample is introduced as a liquid, i.e. that the injector and the column inlet are at a temperature below the pressure-corrected solvent boiling point. To distinguish it from (hot) on-column injection into

packed columns, it was also termed "cold on-column" injection [10]. "Vaporising" techniques involve an oven-independently thermostatted chamber, being permanently at a temperature above that of the oven or temperature-programmed (PTV). This definition leaves open whether injection into precolumns installed in a separately thermostatted oven [11,12] or with directly applied heating [13] is an "on-column" technique.

2.2. Vaporising chambers

The principal design characteristics of the various vaporising systems in use is shown in Fig. 1. The classical as well as the PTV split/splitless injectors incorporate a glass tube, with the carrier gas entering at the top and a split outlet leaving at the bottom. In splitless injection, the split outlet is closed during injection and sample transfer into the column; it serves as a purge line afterwards. In PTV solvent split injection, the solvent vapours are discharged through the split outlet. The latter is closed before the chamber is heated in order to achieve splitless transfer of the solute material into the column. Usually there is a septum purge outlet leaving the injector just below the septum.

The direct injector is distinguished from the split/splitless injector by the absence of a split outlet; the
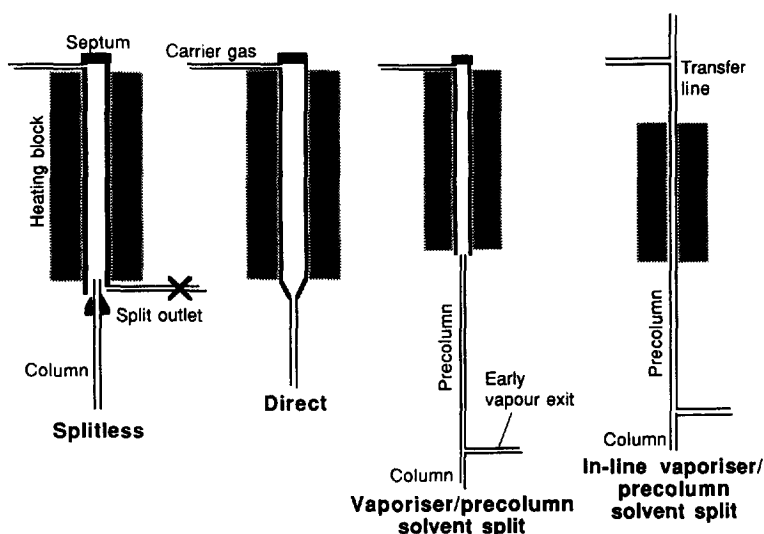

Fig. 1. Principal designs of vaporiser systems.

column inlet is directly connected to the vaporising chamber. The vaporising chamber may be considered as an elongation of the column inlet, reminding packed column GC analysts of "hot on-column" injection.

The vaporising chamber–precolumn solvent split system consists of a vaporising chamber connected to a precolumn in direct or splitless mode. The latter ends in a T-piece that splits the gas phase between the separation column and the early vapour exit (connected to an electric valve). This set-up is distinguished from the vaporiser–solvent split system by discharging the vapours through a precolumn. The latter serves to retain the solute material, i.e. solvent–solute separation is performed in a pre-column instead of in the vaporising chamber (see below). The temperature of the vaporiser may be programmed (PTV), but since solvent–solute separation occurs in the precolumn, it may also be permanently hot. The precolumn may consist of an uncoated precolumn (retention gap), a coated pre-column (retaining precolumn) or of a combination of both. A PTV–precolumn solvent split system has been described by Staniewski et al. [14].

The first three systems in Fig. 1 involve an isolated vaporising chamber equipped with a septum or an analogous entrance valve. The sample is introduced through a syringe needle or transfer line ending at the main evaporation site. In the in-line vaporiser–precolumn solvent split system, however, the vaporiser consists of a section of the transfer line (usually 0.32 mm I.D. fused-silica capillary tubing). The carrier gas enters the transfer line somewhere above the vaporising chamber through, e.g., a press-fit T-piece. The capillary tubing serving as the transfer line and the vaporiser chamber may also function as an uncoated precolumn. The system has become the most important LC–GC interface in our laboratory when no highly volatile components are to be analysed [15].

Vaporising injectors are applied for the techniques listed in Table 2. A first difference concerns the temperature; there are the classical techniques in-volving injectors kept isothermally at temperatures determined by solute evaporation. PTV injectors are regulated with an initial temperature adjusted for solvent evaporation, then heated for solute volatilisa-tion.

Table 2
Injection techniques performed with vaporising injectors

Isothermal, hot vaporising chambers
Classical split injection
Classical splitless injection
Splitless overflow [16]
Direct injection
Vaporiser–precolumn solvent split

Programmed temperature vaporisers (PTV)
PTV split injection
PTV splitless injection
PTV direct injection (SPI, [17])
PTV solvent split
PTV precolumn solvent split

For splitless injection of small (1–3 µl) volumes (conventional or PTV), the vaporising chamber is usually empty. For most other applications it is packed in order to retain the sample liquid, to support sample vaporisation, and to stop liquid "shooting" through hot chambers. The in-line vapor-iser contains a piece of wire (raw or deactivated) or fused-silica capillary with flame-sealed ends.

2.3. Discharge of solvent vapours

The large volumes of vapour generated by the sample, primarily consisting of solvent, are removed either by gas discharge or overflow. Gas discharge means vaporisation in a stream of carrier gas. Solvent evaporation is possible below the boiling point at a rate of up to that determined by the amount of vapour saturating the carrier gas at the actual injector temperature [18]. PTV solvent split injection is an example (Fig. 2). The same rules apply for recondensation in an uncoated precolumn; vapours from the vaporiser recondense in the column inlet if the carrier gas is oversaturated, i.e. if temperature is below the dew point of the vapour–gas mixture. Oven temperatures may, thus, be further below the solvent boiling point the more the vapours are diluted with carrier gas.

Overflow is performed in the absence of carrier gas flow; vapours leave the system by their expan-sion during evaporation, driven by a vapour pressure at least corresponding to the pressure drop from the evaporation site to the vapour outlet. Since there is no dilution with carrier gas, the temperature must at least equal the boiling point of the solvent at the
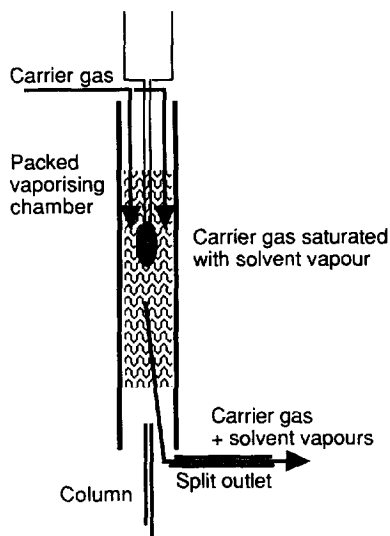
Fig. 2. Removal of solvent vapours by gas discharge: PTV solvent split injection as an example.

pressure required for discharging the vapours. If the sample is evaporated in a vaporiser, recondensation in the column inlet is governed by the same rule; to avoid recondensation, the temperature must be above the pressure-corrected boiling point. Below this boiling point, there is complete recondensation. There is no possibility of achieving partial recondensation, except if a higher boiling co-solvent is used (see below).

Fig. 3 schematically shows two overflow systems. The loop-type interface, primarily used for on-line LC–GC [19,20], performs on-column evaporation with pressure-regulated supply of the sample liquid. The oven temperature must be somewhat above the pressure-corrected boiling point of the solvent because the supply of the evaporation heat from the oven atmosphere into the region of solvent evaporation requires a temperature gradient. The LC–GC interface used by Cortes et al. [21] also involves on-column evaporation, but the supply of liquid is flow-regulated. Removal of the solvent vapours by gas discharge and overflow is used for the techniques listed in Table 3.

Table 4 compares characteristics of overflow and gas discharge systems. Gas discharge is more flexible concerning conditions, because temperature and gas flow-rate can compensate each other: The tem-

Overflow Technique

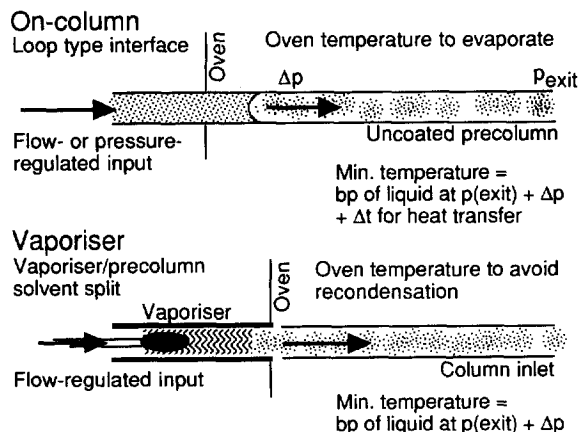Oven temperature above boiling point at the pressure needed for discharge of vapours

Fig. 3. Overflow involving on-column vaporisation (concurrent evaporation with the loop-type interface) and a vaporiser (vaporiser–precolumn solvent split); minimum oven temperatures avoiding flooding of the column inlet. Undiluted vapours are discharged, since there is no carrier gas flow during solvent evaporation.

Table 3
Injection/transfer techniques involving gas discharge or overflow

Gas discharge	Overflow
Split injection	Splitless/overflow [16]
Splitless/direct injection	PTV overflow [22]
On-column injection	Vaporiser/overflow [15]
PTV solvent split [23]	Loop-type LC–GC interface
On-column LC–GC	
interface [24]	Cortes LC–GC interface [25]
Vaporiser/gas discharge	

Table 4
Comparison of overflow and gas discharge systems

Overflow
  +Easy to optimize
  +Self-adjusting minimised flow-rate
  +Pressure drop over vaporiser packing is uncritical
  −Relatively high oven temperatures required
  −Fully concurrent evaporation only
    Solvent trapping not applicable

Gas discharge
  +Lower temperature, stronger retention of volatiles
  +Partial evaporation/recondensation possible
    Solvent trapping for retaining volatiles
  −More demanding for design and operation

perature for evaporation or recondensation in an oven-thermostatted precolumn can be lowered by stronger dilution of the vapours with gas (the dew point is lowered). Lowered oven temperatures may be of interest to obtain stronger stationary phase focusing (see below). Furthermore, gas discharge enables partially concurrent evaporation [26] or partial recondensation, which may be of interest to achieve solvent trapping. Overflow is more simple in use, since temperature is the only variable to be adjusted and is easy to estimate from the boiling point at the pressure required for vapour discharge. Closure of the vapour exit is not critical, because the flow collapses at the end of solvent evaporation; there is no carrier gas driving components out of the vapour exit. However, there is no possibility of achieving solvent trapping when the uncoated precolumn cannot retain the full amount of sample liquid, and there is less retention of volatile solutes by stationary phase focusing because of relatively high oven temperatures.

2.4. Solvent–solute separation

Introduction into GC of large volumes of liquid samples actually involves two steps: evaporation, first of all of the solvent, and separation of the solute material from the solvent vapours before the latter are discharged. Solvent–solute separation occurs by gas chromatographic retention power that keeps the sample constituents as sharp initial bands in the column inlet while the solvent vapours are released.

The basic possibilities for building up retention power are listed in Table 5. Retention power is a function of a stationary phase, the gas–vapour flow-rate and temperature. There are temporary and permanent stationary phases. Permanent stationary phases usually consist of packing materials inside liners of PTV injectors or stationary phase films in retaining precolumns. Stationary phase focusing means solute retention by permanent stationary phases, although the term has usually been used in the context of retention in separation columns or retaining precolumns. In splitless injection, cold trapping or thermal focusing is used for describing the same mechanism. A temperature that is as low as possible is chosen in order to maximise the retention

Table 5
Retention of volatile solutes

Increasing retention power →	**Stationary phase focusing/cold trapping** *Permanent stationary phase* Retention —in the packing of the PTV injector —in retaining precolumn **Phase soaking** Retention by stationary phase in retaining precolumn soaked with solvent **Solvent trapping (co-solvent trapping)** *Temporary stationary phase* Retention by film of sample liquid obtained by —partially concurrent evaporation —partial recondensation of the solvent in uncoated precolumn

power by the stationary phase, being limited, however, by evaporation or recondensation of solvent. At the end of solvent–solute separation, i.e. at the end of solvent evaporation, the retention power of a permanent stationary phase is overcome by increasing temperature. At that moment, strong retention power of permanent stationary phases easily turns into an obstacle for the desorption of high boiling and labile compounds.

Temporary stationary phases can be built up by the sample liquid, hence primarily consist of solvent. The mechanism involved is described by solvent trapping [27–29]. When occurring in a capillary tubing, the solutes are retained by the thick film (ca. 10 μm) of non-evaporated or recondensed sample liquid (solvent) on the wall of the column inlet. Since solvent evaporation proceeds from the rear to the front of the sample film, solute material released by the vaporised solvent is immediately trapped again in the sample film ahead of the evaporation site. The volatile solutes start chromatography at the moment when the last solvent is evaporated. Solvent trapping is, in fact, the most perfect solvent–solute separation mechanism available. It provides more powerful retention than stationary phase focusing, and the high retention power automatically disappears as soon as it is no longer required, i.e. at the end of solvent evaporation. Thus, a temporary stationary phase does not hinder the analysis of high

boiling solutes. If more than 1 μl of condensed solvent is involved, an uncoated precolumn is needed in order to refocus the initial bands of the components eluted substantially above the injection/transfer temperature.

Co-solvent trapping involves retention by a small amount (5–20%) of a higher boiling solvent added to the main solvent [30]. At least part of this co-solvent is recondensed or not evaporated, while most of the main solvent does not recondense or is evaporated. Trapping by a film of condensed co-solvent has the advantages of involving a relatively small amount of liquid, hence results in a short flooded zone in a capillary tube or occupies a small volume in a packed bed. Co-solvent trapping can, furthermore, also be applied in overflow systems (such as with the loop-type interface [31]).

Phase soaking [32,33] is a solvent effect taking place in the inlet of the retaining precolumn or separation column. At a temperature just above the recondensation point of the solvent, i.e. near the boiling point in an overflow system or dew point in gas discharge, the stationary phase film is swollen by solvent. This increases the retention power several fold, depending on the combination of solvent and stationary phase involved [34].

2.4.1. Solvent trapping in packed beds

Solvent trapping has been investigated for capillary GC. No doubt, there is an analogous process in a packed bed, e.g. of a PTV injector. Solvent trapping was found to strongly improve retention of volatile compounds after "at once" injection into a PTV chamber [35,36]. The effect of co-solvent trapping in a PTV injector has also been demonstrated [37]. The question has not been answered, however, whether such solvent trapping is as complete as in a capillary (pre)column. In a capillary tube, solvent evaporation is strictly organised, proceeding from the rear to the front of the flooded zone (Fig. 4). In packed beds, however, it also proceeds from the region close to the insert wall towards the centre; since evaporation consumes a large amount of heat (supplied from the insert wall), a temperature gradient is expected that causes the solvent in the centre of the packing to evaporate last. The solute material released near the insert wall is likely to be removed (possibly through
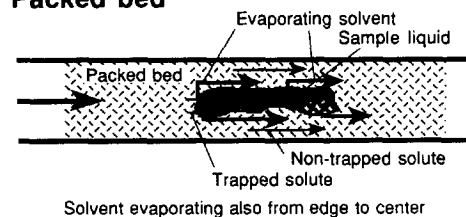
Open tubular precolumn
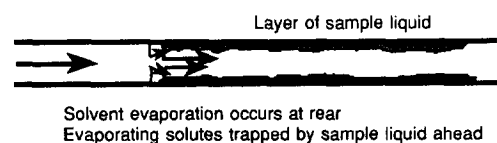
Packed bed

Fig. 4. Is solvent trapping in packed beds as efficient as in capillary tubes?

the vapour exit) before the end of solvent evaporation.

2.5. Evaporation and solvent–solute separation in the same compartment?

PTV solvent split injection vaporises the solvent and retains the solutes in the same packed bed, i.e. the packing material and the conditions must suit solvent evaporation as well as solvent–solute separation. Sample evaporation with solvent trapping, as obtained in on-column injection, also volatilises the solvent and retains the solutes in the same region. Other techniques perform the two steps in partially or totally separated compartments. Splitless injection, for instance, separates solvent and solute in the column inlet by means of cold trapping or solvent effects. Precolumn solvent split techniques evaporate in a vaporiser, the temperature of which can be set high because the chamber does not serve to retain the solute material. Solvent–solute separation is performed in the oven-thermostatted precolumn system.

Such classification demonstrates the many options for injection or transfer systems and techniques. Of course, practice requires selection of the one or two best options, i.e. best combination of the aspects outlined above.

3. Critical remarks concerning PTV solvent split injection

Presently, PTV solvent split injection is considered as the method of choice for large volume injection of "dirty" or water-containing samples. In fact, good results have been shown for a variety of samples (e.g. Refs. [38,39]). However, this should not stop the search for better alternatives.

3.1. Difficult temperature control

Performance of solvent evaporation and solvent–solute separation in the same chamber, as in PTV solvent split injection, has severe drawbacks. When large volumes are introduced at convenient rates (50–1000 μl/min), solvent evaporation consumes amounts of heat that result in strong cooling of the evaporation site and disturb thermostatting of the chamber [20,36]. As dichloromethane or water were introduced into a vaporiser at 200°C at flow-rates exceeding 600 and 100 μl/min, respectively, the whole chamber was cooled to the solvent boiling point (PTV injector for 5000 Series instruments, Fisons/CE Instruments, Milan, Italy; [40]). In fact, non-evaporated solvent ran into the column. This means that the chamber was cooled by some 100 and 160°C, respectively. Heat supply to the vaporiser chamber could certainly be improved, but hardly to the extent that massive temperature drops were avoided.

Even when samples are introduced at lower rates, temperature distribution over the longitudinal axis of the chamber becomes a problem. If the thermocouple used for thermostatting the chamber is positioned near the evaporation site, the system reacts rapidly by strong heating. This, however, overheats the sections of the injector that are not cooled and reduces the retention of the volatile components. A thermocouple positioned further away from the evaporation site (Fig. 5) results in slow reaction of thermoregulation. Temperature at the evaporation site drops, the evaporation rate falls, and the liquid floods further down the packed bed.

Drifting temperatures affect the stability of the evaporation rate. Since temperature, hence also the evaporation rate, drops during sample introduction, the initial temperature must be too high or the
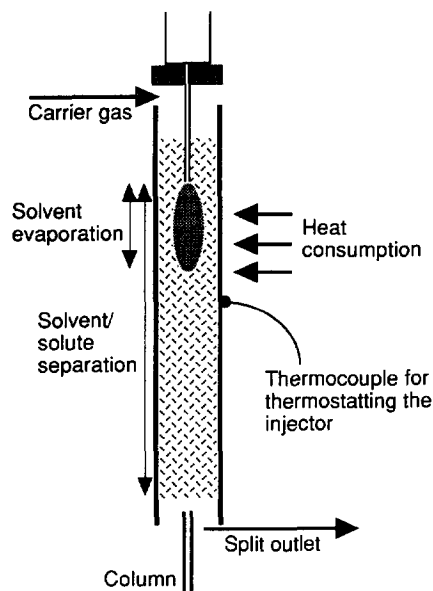

Fig. 5. In PTV solvent split injection, strong cooling by the evaporating solvent disturbs thermostatting of the chamber.

introduction rate lower than optimum, resulting in increased loss of volatile constituents at least in the initial phase. Reproducibility of the evaporation rate may also be a problem: When the sample liquid is driven deeper into the packed bed, it evaporates over a longer section of the chamber and extracts more heat. If it happens to cool the liner down to the position of the thermocouple, it initiates strong heating. Evaporation rates depend, in fact, on impenetrable factors, affecting the adjustment of the optimum injection rate as well as of the time for closing the split outlet.

3.2. Separation into two compartments?

It seems obvious that the PTV solvent split technique could be improved by dividing the system into two separately thermostatted compartments. Solvent evaporation would no longer disturb thermoregulation of solvent–solute separation and, secondly, solvent evaporation and solvent–solute separation could be optimized individually.

A high capacity solvent evaporator must provide large amounts of heat. This requires large temperature gradients, hence thermostatting often more than 100°C above the solvent boiling point. If solvent–

solute separation is performed separately, it no longer requires careful minimisation of the temperature of the vaporiser chamber. The chamber may, in fact, just as well be hot enough for the volatilisation of the solutes i.e. it could be isothermally thermostatted as a classical hot injector. Isothermal injectors can be constructed with a larger thermal mass than PTV injectors, readily providing the heat consumed and better levelling out temperature over the longitudinal axis of the injector as heat is consumed locally.

Solvent–solute separation could be performed in a second packed bed. The latter would be thermostatted slightly above the dew point of the solvent–carrier gas mixture when the solvent is not supposed to recondense, or slightly below it for improving solute retention by partial recondensation and solvent trapping. At the end of the injection or on-line transfer, the chamber is heated for thermal desorption of the retained solutes, i.e. this part of the system must be a PTV type injector. More accurate thermostatting of this chamber would render methods more reproducible and improve retention of volatile components.

Packed vaporising chambers are more robust towards "dirty" samples than open tubular systems. However, since the solvent evaporator retains the troublesome non-evaporating sample by-products, this no longer restricts our choices for solvent–solute separation, i.e. open tubular systems should be reconsidered. They offer advantages at the low, as well as at the high, temperature end of GC; solvent trapping is the most effective tool for retaining volatile solutes, and vaporisation in a well deactivated capillary provides the best conditions for high boiling and labile sample constituents.

4. The most promising vaporiser systems

The authors conclude that the packed vaporiser chamber–precolumn solvent split–gas discharge system is the most promising system for large volume injection and some LC–GC applications, and that the in-line vaporiser–precolumn solvent split–overflow system is best for on-line LC–GC with normal phase eluents, provided no solvent trapping is needed.

4.1. The vaporising chamber–precolumn solvent split–gas discharge system

The packed vaporising chamber–precolumn solvent split–gas discharge system is outlined in Fig. 6. The sample is introduced at regulated speed by an autosampler or through an on-line transfer capillary. The packed vaporiser is usually kept at a temperature also suiting solute volatilisation, i.e. isothermally at around 250–350°C. For thermally labile compounds it might be advantageous to evaporate the solvent at lower temperature than the solutes, i.e. to use a temperature-programmable injector. The vapours are discharged through a precolumn and an early exit. An uncoated precolumn is used if part of the solvent is recondensed for achieving solvent trapping. In this instance, there may or may not be a retaining precolumn, depending on whether the solvent vapour exit is closed before or after the end of solvent evaporation. When solvent trapping is not needed or not feasible (e.g. for water-containing solvent mixtures), only a retaining precolumn is used, i.e. a 2–3 m precolumn with a retention power similar to that of the separation column.

4.1.1. Design characteristics

This system is promising because the various parts fit well together. Packed vaporising chambers have a high capacity for retaining non-evaporating sample byproducts. There are, furthermore, packing materials resisting attack by water, such as Tenax or Carbofrit (Restek). Finally, their resistance against the discharge of gas and vapours can be kept low.
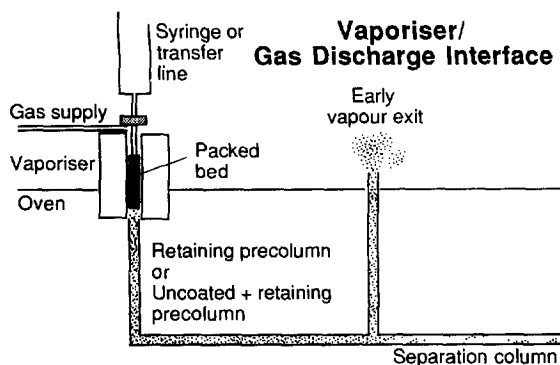

Fig. 6. The packed vaporising chamber–precolumn solvent split–gas discharge system.

Attention must be paid to violent evaporation, particularly at the beginning of sample introduction, when volatile sample liquid hits hot surfaces. Prerequisites for achieving smooth and complete evaporation have been investigated by visual experiments [40]. "Shooting" was observed when liquid accumulated at the exit of the syringe needle or transfer line and dropped onto hot packing material. The liquid sample must be brought into immediate contact with the packing material.

Gas discharge seemed preferable to overflow. The injector liners are of 1 mm I.D. at least, because their resistance against the discharge of the vapours must not become a factor limiting the introduction rate. This, however, renders the preparation of packed in-line vaporisers difficult. When the sample liquid is introduced by a syringe needle or transfer line, the top of the chamber becomes a dead volume. Flow of vapours into this part can be prevented by a gas flow introduced behind the introduction site. Gas discharge is, furthermore, advantageous for aqueous and water-containing samples/eluents: Since no solvent effects can be achieved, reduction of the oven temperature by dilution with carrier gas is important for enhancing stationary phase focusing.

Solvent and solutes are separated in the precolumn(s). Solvent trapping can be achieved as with on-column systems, with the difference that it involves recondensation. When the proportion of recondensed solvent is kept small, 800 μl at least can be injected into a 10 m×0.53 mm I.D. uncoated precolumn (as with partially concurrent evaporation practised in on-line LC–GC).

4.1.2. Vaporiser filtering "dirty" samples

The retention of non-evaporating sample by-products in the vaporising chamber was confirmed using OV-17 (a phenylmethyl polysiloxane) as a sample impurity. The left chromatogram in Fig. 7 was obtained by the on-column injection (100 μl) of a series of alkanes in heptane (10 m×0.53 mm I.D. uncoated precolumn, 12 m×0.32 mm I.D. separation column coated with an 0.2 μm film of PS-255). Then the same mixture was injected together with 1000 μg of OV-17 (10 mg/ml in the sample). As shown at the lower left, contamination of the uncoated precolumn completely ruined the chromatograph. Injection of an even more "dirty" mixture
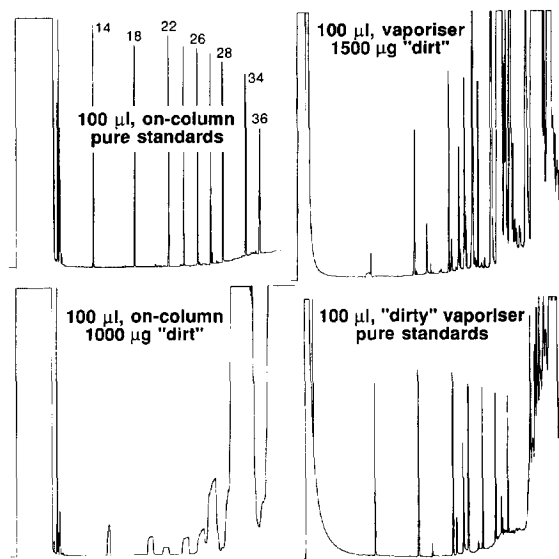

Fig. 7. On-column injection of a sample containing 1 mg of involatile "impurity" ruins the precolumn (lower left chromatogram). n-Alkanes as indicated in the upper left chromatogram. The vaporising chamber has a filtering effect and avoids such degradation (upper right, 1.5% of involatile material in the sample). The chamber firmly retains the "dirt", as observed by still perfectly shaped peaks (lower right, fifth injection of the clean solution after the introduction of the "dirty" sample).

(1500 μg of OV-17) at 100 μl/min through a vaporiser system produced a chromatogram crowded with material from the OV-17, but peaks remained well shaped (upper right chromatogram). The 1 mm I.D. vaporising chamber was packed with Carbofrit (3 cm) and thermostatted at 300°C. A 3 m×0.53 mm I.D. retaining precolumn was used, coated with 0.2 μm of PS-255. The oven temperature of 40°C during injection prevented solvent recondensation. Since there was no solvent trapping, the most volatile constituent of the mixture was lost. The fact that five additional 100 μl injections of the clean mixture did not result in peak distortion confirmed that no OV-17 was carried from the vaporising chamber into the precolumn, i.e. that the filter firmly retained the troublesome by-products.

4.1.3. Injection of non-wetting samples

Solvent evaporation in a vaporiser chamber also enables introduction of samples that are not suitable for on-column injection because of wettability problems. The left chromatogram in Fig. 8 was obtained
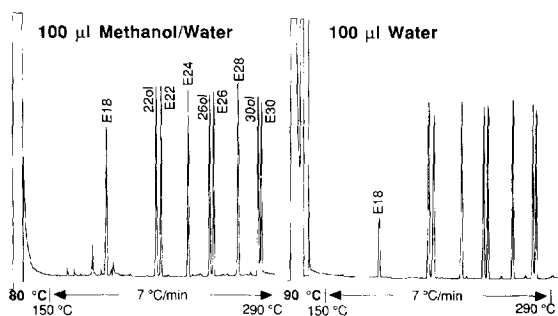
Fig. 8. 100 μl injections at 100 μl/min of the FAME (E) and alkyl alcohols (ol) indicated as solutions in methanol–water (1:1, v/v) and water, using a vaporising chamber–retaining precolumn system.

by injection of 100 μl of the fatty acid methyl esters (FAME) and alcohols indicated in methanol–water (1:1, v/v) at 100 μl/min. The above vaporiser–retaining precolumn system was used, with the vaporising chamber at 300°C and the oven temperature at 80°C (just above the dew point of the vapour–gas mixture, as determined by a visual experiment). For the chromatogram at the right, the same solute mixture was introduced in water with the oven at 90°C. Further experimental details will be given in a future paper.

Results from 500 μl injections of ten times diluted test samples are shown in Fig. 9. The carrier gas flow-rate through the open vapour exit before injection was 500 ml/min. The increased volume of vapor driving the solutes through the retaining precolumn increased the losses in the early part of the chromatogram. Introduction occurred at 150 μl/min, i.e. the high temperature of the vaporising chamber enabled more than ten times higher evaporation rates than with a PTV [41,42].

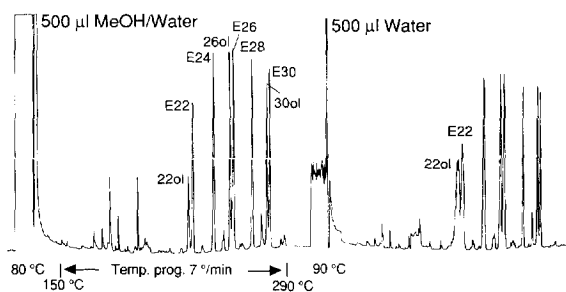Fig. 9. 500 μl injections at 150 μl/min. Samples as in Fig. 8.

4.2. The in-line vaporiser–precolumn solvent split–overflow system

The in-line vaporiser–overflow system shown in Fig. 10 was developed for online LC–GC with normal phase eluents [15]. Since overflow only gives the choice between no or complete recondensation, it is usually not suited for achieving solvent trapping (the flooded zone would be too long as soon as sample volumes exceeded about 100 μl). Hence, the technique substitutes the loop type interface, but not the on-column interface.

With the vaporiser, oven temperatures can be lower than with the loop type interface, since there is no need for a temperature gradient to transfer the heat for solvent evaporation into the uncoated precolumn and no pressure drop over an uncoated precolumn. This improves retention of the volatile sample components by phase soaking. For alkanes as solutes, an apolar stationary phase in the retaining precolumn, and pentane as solvent, the improvement corresponded to about four carbon atoms (e.g. undecane could be analysed instead of only pentadecane) [15]. This system also eliminated the need for a sample loop, which rendered it more flexible (e.g. for multitransfer) and avoided mixing at the beginning of the fraction window [43].

The vaporiser consisted of a part of the 0.32 mm I.D. fused-silica transfer line. A 5-cm piece of 0.21–0.27 mm steel wire or fused-silica was inserted for stopping the sample liquid and achieving complete evaporation. The wire was used raw or deactivated
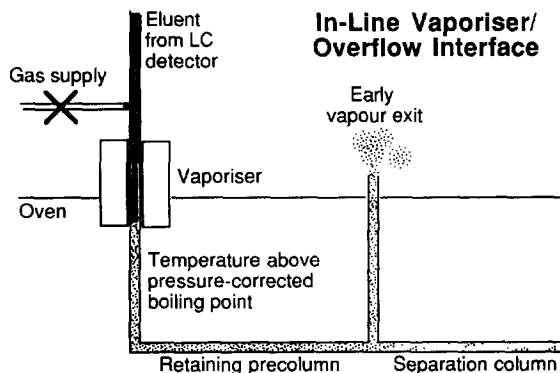

Fig. 10. In-line vaporiser–precolumn solvent split–overflow system for on-line systems, such as LC–GC.

by the Silcosteel procedure (Restek, applied for deactivating metal capillary columns). The surfaces in these chambers exhibited to the sample are small and well under control. The temperature of the vaporiser was 250–350°C.

Overflow is favoured because resistance against vapour discharge through the chamber may create substantial backpressure. There is no risk of back-flow into the gas supply system, however, when the line is interrupted. Overflow is simple regarding adjustment of conditions. Since pentane is the most important solvent for normal phase LC–GC (typically transferred at 42–50°C), there is little room for lowering oven temperature during transfer by a gas discharge system.

The in-line vaporiser–overflow system was successfully applied for routine LC–GC analysis of mineral oil paraffins in foods [15], for the analysis of stigmastenols in edible oils [44], and for the determination of mineral oil polyaromatics in foods [45]. It is less suited for water-containing samples or eluents, because "shooting" of liquids can only be suppressed by narrowing the gap between the wire and the capillary wall which, however, results in high backpressure [40].

5. Conclusion

The intention of this review was to stimulate discussions on the best vaporising systems for large volume sample introduction into capillary GC. A wide horizon should be kept open for some time to come, making sure that the best methods become standard.

On-column introduction of large sample volumes (10–2000 μl) has been used for many years and remains our first choice wherever applicable. However, for "dirty" samples and samples in non-wetting solvents (such as water), systems with a vaporising chamber are needed. The overview on the options available leads us to vaporiser–precolumn solvent split systems. They have a high capacity for solvent evaporation and perform solvent–solute separation by the best methods available. More experience will be needed to confirm these expectations.

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