Review

Programmed temperature vaporiser-based injection in capillary gas chromatography

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Abstract

The application of programmed temperature vapourisation (PTV) in capillary gas chromatographic analysis is reviewed. The development of the different strategies as well as the state of the art are described. As the analytes are normally enriched in the PTV insert, the quoted papers are subdivided depending on whether the enrichment was carried out from organic solvents, from water or from gaseous media. Furthermore, the possibilities of PTVs for on-line coupling with sample preparation methods or other separation techniques and their use as thermoreactors are mentioned. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Programmed temperature vaporisers; Large-volume injection; Injection methods

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PII: S0021-9673(99)00723-2
1. Introduction

In the past few years, programmed temperature vaporisation (PTV) has developed into an important injection technique of capillary gas chromatographic analysis, and hyphenated gas chromatography (GC) systems use especially the potential of PTV-based large-volume injection (LVI). The targets of LVI set are clear: by increasing the sample volume, the detection limits of analytical methods can be decreased. Sample preparation steps can be simplified or can, to a large extent, be integrated into instrumental analytical work. Furthermore, LVI is used for the coupling of GC with sample preparation methods or other separation techniques such as liquid–liquid extraction (LLE), solid-phase extraction (SPE) or supercritical fluid extraction (SFE). Even though the first investigations in the field of LVI were at least 20 years ago, it seems that the introduction of large sample volumes is still not common practice in many routine laboratories.

Efforts to enable the largest possible sample volumes to be introduced into the GC system were realised by the development of suitable sample introduction techniques. Part of this was, on the one hand, the development of corresponding inlets or sampling devices whilst, on the other hand, the handling of the devices had to be adapted to the situations given in LVI. Large-volume sample introduction techniques are known under the names of loop-type injection [1], vapour-overflow technique [2], large-volume on-column injection [3] and LVI using a vaporising chamber-pre-column solvent-split–gas discharge system [4–7] or PTV-based LVI.

Usually, GC injection techniques are subdivided into evaporating injection techniques where the liquid sample is evaporated in a special unit before the chromatographic column, and into on-column injection where the sample enters the chromatographic column as a liquid. Large-volume on-column injection techniques, the so-called retention gap techniques, are very accurate, but, unfortunately, they fail if “dirty” samples with a considerable amount of non-volatile components or water-containing samples have to be investigated. In these cases evaporating sample introduction is much more suitable. PTV injection is one of the evaporating injection techniques where, as a rule, the sample is injected at a temperature below the boiling point of the solvent. Only after the injection is the PTV, with a defined speed, heated up to the necessary temperature for complete evaporation of the sample and for the transfer of the analytes into the column.

The development of PTV injection can be subdivided into several stages. After Vogt had presented a PTV system for the first time in 1979, the groups of Poy and Schomburg, at the beginning of the eighties, explored the possibilities of cold injection and the development of universally applicable types of inlets. After that, there was not much interest in PTV injection until the end of the eighties, when a number of authors did methodological investigations into the use of PTV injection, especially for LVI. This phase partly coincided with the introduction and improvement of systems capable of routine operation and the application of PTVs for on-line coupling with sample preparation techniques or other separation process.

Fig. 1 shows this development by means of the number of publications on PTV injection. The continuous interest in this injection technique is mainly due to the high degree of flexibility and its applicability in the injection of large sample volumes.

In this contribution, a survey will be given of the papers on PTV injection. Because of the great number of publications, only those papers that we considered to have made a considerable contribution to technical development, to the understanding of the processes taking place or to practical applications will be commented upon. When arranging the contributions according to certain topics, some compromises were inevitable.
2. Temperature-programmed vaporisation

The PTV consists of the same elements as a classical split/splitless inlet (see Fig. 2), but is equipped with an efficient heating and cooling system, in which cooling is realised by means of air, liquid nitrogen, CO$_2$ or electrical systems. During injection of the sample, the temperature control in the PTV is time-programmed; sample components with different volatilities are evaporated in succession. While in the case of conventional split/splitless inlets, the thermal mass needs to be large in order to prevent a decline in temperature during evaporation process, it should be as small as possible with the PTV in order to enable the changes in heating capacity to be quickly transmitted to the sample.

The concept of temperature-programmed sample introduction was described by Abel [8] as early as in 1964. In 1979, Vogt and co-workers [9,10], for the first time, presented a PTV injection system, which could be used to inject up to 250 µl volumes. Even...
at that time, Vogt et al., in their first publications, explained the principle of LVI with elimination of the solvent via the split outlet (see Fig. 3). The authors recognised the potential to the injection system and used it for the examination of samples from the areas of medicine [11], environment and foodstuffs [12].

Poy et al. [13–15] and Schomburg and co-workers [16,17] examined or developed PTVs with special emphasis on cold injection, however, under the viewpoint of a precise and discrimination-free sample introduction, if possible with universal injection systems. In this, the possibility of injecting large-volumes did not play any role.

3. Large-volume PTV injection techniques

Using PTVs, various techniques are available for the injection of large-volume samples (see Table 1).

3.1. PTV splitless injection

PTV splitless injection was described by Grob and
Table 1
Large-volume PTV injection techniques

<table>
<thead>
<tr>
<th>Large-volume injection techniques</th>
<th>Method-oriented papers</th>
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<tbody>
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<td>PTV splitless injection</td>
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<td>PTV as interface for on-column LVI</td>
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</tr>
<tr>
<td>PTV solvent-split</td>
<td>[25,26,29–31,33,36,37]</td>
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</table>

Li [18] in 1988. The maximum sample volume was 20 to 30 μl. In the following period, this injection technique did not play any great role in LVI.

3.2. PTV vapour overflow technique

Later, Grob [19] showed the possibilities and influences of the PTV vapour overflow technique for the introduction of large sample volumes. Here, the sample is injected at a temperature above the solvent’s boiling point, and the solvent vapour leaves the inlet via a septum purge line. The flow arises from the expanding vapour and it stops on its own after evaporation of the solvent. As this variant is not necessarily attached to PTVs, it was later carried out mainly with conventional split/splitless inlets [2,20,21].

3.3. PTV as an interface for an on-column LVI

In 1993, Staniewski et al. [22] showed a system in which the PTV, equipped with a special on-column insert, was virtually used as an interface for an on-column LVI. Using a double-oven GC system, separation of solvent and analytes did not take place in the PTV itself but in the pre-column of the first GC oven. The initial temperature of the PTV was equal to or slightly above the initial oven temperature. By means of a multi-column switching device, the solvent vapour was eliminated after the pre-column. The analytes were separated after cryofocusing in the chromatographic column of the second GC oven. Bosboom et al. [23] used a similar system that worked with one GC oven. After injection of a 100-μl volume, evaporation of the sample took place in the retention gap and the solvent was eliminated before the separation column, whereas the analytes were kept in a retaining pre-column. In direct comparison, the results obtained for volatile and thermolabile analytes corresponded to those of on-column injection using a conventional on-column inlet. The investigations mentioned are not really PTV injection techniques, but a set-up was presented, which, when using a PTV, enables one to choose between different injection modes without any great effort.

3.4. PTV solvent-split injection

PTV solvent-split injection has achieved some special importance. This technique makes use of the fact that different operating modes (split or splitless) can be assigned to the individual temperature conditions in the PTV. In addition to cold sampling, it is possible to separate sample components with differing volatilities even during sample introduction, and the solvent can be eliminated, for example, via the split outlet while the higher-boiling analytes are retained and, subsequently, transferred to the separating column in splitless mode. Thus, it is possible to increase the injection volume far above a volume of about 1 μl, which is usual in the case of hot sample injection. PTV-based LVI with elimination of the solvent (solvent-split or solvent-vent mode) can be described by means of three approaches that are based on each other:

(1) In the case of cold injection, i.e., if the initial inlet temperature is below the solvent’s boiling point, the sample, as a liquid, gets into the insert all at once (‘‘at-once injection’’) and is evaporated in a controlled way. The solvent vapour is eliminated via the split outlet so that, at any given time, only a part of the developing gas volume of the entire sample is in the insert. This prevents a so-called overflow of the insert due to the developing gas volume. Depending on the volume and design of the insert, the quantity to be injected can be increased up to about 150 μl.

(2) The process of cold injection with elimination of the solvent can be repeated several times. In the case of repetitive injection (multiple injection), the injection and evaporation of the solvent take place several times consecutively and only then is the PTV heated up to its necessary final temperature.

(3) In the case of speed-controlled injection, the repeated introduction of small portions is replaced by a continuous process. Using suitable samplers, the sample is injected at a defined speed so that an
equilibrium is maintained between the liquid injected and the eliminated solvent vapour. Injection and evaporation no longer take place in succession but simultaneously. Here, the injection volume can be increased to about 1000 μl.

Adaptation of the conditions for the separation of solvent and analytes in the inlet in PTV solvent-split injection proved a complex and many-faceted problem, the solution of which requires careful optimisation. Since the late eighties, a great number of authors have been dealing with this problem.

3.4.1. Insert packing

Packing materials and adsorbents are used in the insert to accommodate the liquid sample and to retain the analytes during solvent elimination. Herrariz and co-workers [24–27] described the use of various packing materials (e.g., Volasphere A-2, Tenax, glass wool, Chromosorb) in order to minimise the losses of highly volatile compounds during the elimination of solvents. Good results were obtained with Tenax. Furthermore, the influence of such parameters was studied in terms of the duration of solvent elimination, the length of packing, temperature, type of solvent, sample volume, etc.

Mol et al. [28] used various materials as alternatives to glass wool packing materials. Polymer materials (PTFE, polyimide), Dextil-coated support and Tenax TA were studied. The inertness of packing materials, the volume of liquid retained in the insert and suitability in terms of enrichment and desorption were tested. For the LVI of a standard solution of 27 compounds, over a wide range of volatilities, polarities and thermostabilities, the Dextil-coated support, PTFE wool and Tenax A showed good retention capacity. With Tenax TA, incomplete desorption of higher-boiling compounds (T_{b.p.}>T_{b.p.} endrin) was observed.

3.4.2. Enrichment of analytes by the solvent effect

In addition to the use of adsorbents, the solvent effect, i.e., the trapping of volatile compounds in a film of solvents, can be used to enhance the enrichment of analytes in the insert. Termonia et al. [29] discussed the addition of higher-boiling co-solvent to the solvent. In this case, 15% n-octane in n-hexane extracts of polycyclic aromatic hydrocarbons (PAHs) from aqueous samples result in a more effective enrichment of the early eluting compounds in speed-programmed LVI with solvent venting. Staniewski and Rijks [30] used inserts with a porous bed of sintered glass and compared these with packing materials like Tenax TA and Thermostatrap. Obviously, in the liner with a glass bed, a stable solvent film is formed in the porous bed, which results in a higher retention power. In comparison with the adsorbents, there were no problems at high desorption temperatures (decomposition of analytes, thermal decomposition of the adsorbent).

Mol et al. [31] stated that, for quantitative retention of analytes in an insert filled with glass wool, in the case of complete solvent elimination, the PTV temperature should be at least 250°C below the boiling point of the analyte. When a hexane solution (100 μl) was injected and the PTV temperature was 0°C, n-alkanes from C_{14} could be quantitatively retained by cold-trapping. The retention power by cold-trapping is supported by the temperature decline in the liner during solvent evaporation. Using an elimination flow of 1000 ml/min when hexane was injected, a temperature decline of 40°C was measured. By closing the split outlet before complete evaporation of the solvent, the retention power can be enhanced using the solvent effect. Under optimised conditions, 95% of an injected sample of nonane was retained at 0°C (see Fig. 4).

3.4.3. Liner diameter and injection mode

According to the initial concept of PTV injection, liners with a small internal diameter should be used in order to minimise the thermal mass an the purge volume. However, nowadays, several PTV injectors are equipped with so-called wide-bore purge volume. Mol et al. [31] discussed the influence of the diameter of the liner in PTV-LVI. PTV inserts with internal diameters of 1.2, 2.3 and 3.4 mm were studied. Inserts with smaller internal diameters (and with smaller volumes) result in faster transfer. The residence time of analytes in the insert is shorter, so that, during heating, they leave the PTV at lower temperatures. The consequences of this effect on thermally labile compounds were shown by means of the recovery of silylated fatty acids in splitless injection mode.

A further possibility for shortening the transfer time to the separating column is to use an increased head pressure during the splitless time (pressure...
Fig. 4. GC–FID chromatogram obtained after injection of 100 μl of a n-alkane standard (C₆–C₃₀, 0.2 μg/ml) in hexane. A PTV insert with an I.D. of 3.4 mm and an initial temperature of 0°C was used. Solvent vent time, 2.5 min at ambient pressure; split flow, 250 ml/min. Splitless transfer, PTV 0°C–4°C/s–325°C; splitless time, 1.5 min. Further conditions are given in Ref. [31].

pulse injection). At an internal diameter of 1.2 mm, some 20 μl of liquid can be accommodated in the insert. For larger volumes, the sample needs to be injected in a speed-controlled manner (or repeatedly). Using 3.4 mm inserts (wide-bore liner), sample volumes of up to 150 μl could be injected at once. The rapid injection of this sample volume is easier than speed-controlled injection because it can be carried out without a programmable sampler, and the injection speed need not be optimised.

By comparison, speed-controlled injection showed a lower retention for volatile analytes on the basis of the chosen conditions. Using these studies, Mol et al. [31] developed guidelines for the selection of suitable PTV injection modes for certain applications.

In order to increase the injection volume above the value in at-once injection in wide-bore liners, the sample should be introduced by repetitive injection or by speed-controlled injection. Mol et al. [32] showed that speed-controlled injection leads to better results than repetitive injection.

3.4.4. Further approaches to parameter optimisation

Villen and co-workers [33,34] and Senoráns et al. [35] studied various parameters, such as injection volume, elimination flow, initial PTV temperature, type of adsorbent and quantity or injection speed by means of mathematical optimisation procedures.

Staniewski and co-workers [36,37] took a systematic approach on the basis of calculating the evaporation rate of solvents from thermodynamic values (vapour pressure of a liquid at a given temperature). Using this method, the maximum injection rate of speed-controlled injection can be estimated for different solvents. However, based on the recovery of n-alkane standards, it was also shown that the calculated values are higher than the experimentally determined optimum injection rates. Temperature measurements in the PTV during the injection clearly show the limits of the theoretical approach. The calculation did not consider any temperature reduction due to evaporative cooling.
during solvent evaporation or incomplete saturation of the carrier gas with solvent vapour. The work also showed the influence of liner design (packing with glass wool) and head pressure reduction in speed-controlled injection of sample volumes of up to 1000 μl.

4. Application of PTV injection

4.1. Enrichment of the analytes from organic solvents in the PTV insert

At present, the injection of large volumes of organic solvents in capillary GC is performed mainly by means of on-column, loop-type and PTV techniques.

With PTV injection, the sample evaporates in the inlet. Therefore, in contrast to on-column injection, the non-volatile sample components do not reach the separating column because they are retained in the insert. Using the example of a PTV splitless injection with the addition of DC-200 (polydimethylsioxane) and olive oil, Grob et al. [38] showed that matrix influences in the case of dirty samples are comparatively small. When comparing hot-splitless, on-column and PTV injection for the determination of sulphur pesticides in spinach, Müller and Stan [39] found the highest long-term stability using PTV injection.

Using carbamate pesticides as an example, Müller and Stan [40] demonstrated the potential of PTV injection for thermally labile compounds. Using empty inserts, similar results were achieved to those obtained with the very gentle on-column injection. Yinon [41] used PTV-based cold sample introduction for the determination of thermally labile explosives such as HMX (octogen) and RDX (hexogen). The results obtained by Hinshaw and Seferovic [42], using PTV injection for the gas chromatographic determination of triglycerides, were comparable to those obtained in on-column injection.

The advantages to PTV injection, i.e., retention of non-volatile components in the inlet and the situation given in cold sample introduction, can also be utilised in LVI. In addition, incompatibility or stress caused to the separation column and detector by the solvent are avoided in the solvent-split mode. This fact was made use of by MacNamara and Hoffmann [43] for the determination of ethyl carbamate in alcoholic beverages. On this occasion, 30 μl of the samples (ethanol–water matrix) were directly injected and, after eliminating the solvent using a multi-column switching device (MCSD), analysed. Staniewski et al. [44] injected 100 μl (4×25 μl, repetitive injection) of a solution of pesticides and polychlorobiphenyls (PCBs) in methylene chloride. Complete elimination of the solvent using a multidimensional GC system with an MCSD allowed for the direct investigation of methylene chloride samples using electron-capture detection (ECD).

The papers quoted in the following will make clear the goals of LVI, as mentioned already. First, by increasing the sample volume, the detection limit of analytical methods is reduced. A limiting factor is increased deterioration of the signal-to-noise ratio, especially when non-selective detectors are used, as well as a higher load of the entire GC system by the sample. Second, by enrichment of the analytes in the insert, it is possible to simplify sample preparation for trace analysis considerably and avoid errors connected with it. For example, it might be possible to avoid evaporation steps for extracts from external pre-concentration methods (LLE, SPE).

Stan and Christall [45] studied organophosphorus pesticides at injection volumes of up to 50 μl. Results obtained by Villen et al. [46], for injection volumes of 25 μl with concentration in the PTV insert, were more precise than in the case of external concentration. Braunstein and Spengler [47] used multiple injection (4×25 μl) for the concentration of pesticides from SPE extracts. On injecting 100 μl of an SPE extract from water samples, Müller et al. [48] were able to determine metamidophos up to a concentration of 0.05 μg/l [GC–nitrogen–phosphorus detection (NPD)]. Staniewski et al. [49] described the use of PTV-LVI with solvent venting for the determination of herbicides and PAHs after LLE from water samples. Using 100-ml water samples, after the speed-controlled injection of 125 or 250 μl of organic extract, detection limits in the sub-ng/ml range were achieved. David et al. [50] used the PTV injection of 10-μl samples with solvent venting for the determination of polychlorodibenzodioxins and polychlorofurans using a multidimensional GC system. Linkerhängner et al. [51] injected 12.5 μl of an
extract in PTV solvent-split mode into an empty insert and, by means of GC–atomic emission detection (AED), determined nitromusk compounds in human fat tissue. Stan and Linkerhängen [52] showed the possibilities of using a PTV-GC–AED system for the examination of pesticide residues in food samples. By combining LVI (12.5 μl) with the element-specific detection of AED, the method can be used in screening tests for pesticide residues at trace levels. The detection limits for 385 pesticides are presented after an optimisation of AED conditions [53]. Charreteur et al. [54] presented a method for the simultaneous determination of triazines and phenylcarbamide derivates in water. After LLE and derivatisation with heptafluorobutyric acid (HFBA), a 100-μl sample was speed-controlled injected with elimination of the solvent. For the pesticides investigated, the authors achieved detection limits of below 0.1 μg/l (GC–ion trap detector (ITD)).

Mol et al. [32] described the use of PTV-LVI (wide-bore liner) in the determination of organic trace compounds in environmental samples. They were mainly concerned with the possibilities of simplifying and improving sample preparation and the reduction of matrix influences. Nitrogen- and phosphorus-containing pesticides from river water were analysed after SPE using NPD and 60 μl at-once injection (see Fig. 5). In the case of a 50-μl at-once injection for the determination of PAHs from sediment by means of GC–mass spectrometry (MS), the detection limit was found to be 0.75 ng/g. For the determination of organochlorine pesticides and PCBs in river water using LLE, the authors used a GC–ECD system and speed-controlled injection

![Graph](image-url)
(400 μl at 200 μl/min) after preceding on-line clean-up.

Ceulemans et al. [55] described a simple method for the determination of organotin compounds in water samples. After in situ ethylation with sodium tetraethylborate (NaBEt₄) and LLE, 25 μl of the extract were injected into a PTV packed with Tenax. In the gas chromatographic determination with AED, the authors achieved detection limits of 0.1 ng Sn/l.

In conjunction with LVI, miniaturisation of the LLE has gained in importance. For example, the in-vial extraction [56], i.e., LLE carried out in the vial of an autosampler, is an uncomplicated form of sample preparation for aqueous samples. Using LVI, there is the potential, in principle, to transfer the total amount of the analytes from the sample into the GC system. Thereby, it is possible, using 1-ml sample volumes, to obtain the same detection limits as in external enrichment methods which, with a sample demand of 1 l and an injection volume of 1 μl, will analyse only an aliquot of the extract by GC [57] (see Table 2). In addition to a clear simplification in sample preparation, miniaturisation of the LLE procedure, combined with LVI, is also of interest for applications where only small sample volumes are available.

Teske et al. [58] used in-vial extraction for the determination of triazines in water samples. A 450-μl amount of tert.-butyl methyl ether (TBME) was added to 700 μl of a water sample in the autosampler vial. After shaking and centrifugation of the vial, 300 μl of the organic phase were automatically withdrawn by the sampler and, in a speed-controlled manner, injected into a PTV insert packed with Tenax TA (see Fig. 7, Section 4.2). For the compounds studied, the detection limits were in the range 0.02–0.01 μg/l (GC–NPD).

Steen et al. [59] discussed the combination of SPE with extraction disks and PTV-LVI for the determination of pesticides from the marine environment. By increasing the injection volume up to 40 μl, they were able to minimise the sample volume to 200 ml. Thus, it was possible to avoid blocking the extraction bed when examining water samples with large amounts of suspended matter. In MS–MS detection, the detection limits of the examined pesticides were in the range 0.2–5 ng/l.

### 4.2. Enrichment of analytes from water samples in the PTV insert

The direct injection of aqueous solutions in GC systems is especially attractive for the transfer of aqueous eluents from liquid chromatography (LC) fractions (see also Section 4.4.1) and in the GC investigation of analytes in water samples. It is known, however, that water as a solvent causes damage to the chromatographic column and that it possibly has a negative effect on the detector so that direct injection is not possible straightforward.

A suitable concept would be to enrich the analytes on adsorbents, which would involve a drying step, and subsequent thermal desorption of the analytes. Various authors having been using such methods since the beginning of the seventies for the off-line enrichment of analytes from water samples [60–66].

In 1990, Braunstein and Spengler [47] followed the same concept using a PTV injection system. A

| Table 2 Comparison between conventional extraction and micro-extraction, according to Ref. [57] |
|-------------------------------------|--------------------------|
| **Conventional extraction**         | **Micro extraction**     |
| **Water sample**                    |                          |
| Volume                              | 1000 ml                 |
| Analyte concentration               | 1 μg/l                   |
| **Extract**                         |                          |
| Volume                              | 1 ml                     |
| Analyte concentration               | 1 μg/ml                  |
| **Injection**                       |                          |
| Injection volume                    | 1 μl                     |
| Quantity of analyte                 | 1 ng                     |
|                                     | 1000 μl                  |
Tenax-packed PTV insert was used for the off-line concentration of PAHs and pesticides from 50-ml water samples. After reinstallation of the insert in the PTV, the analytes were thermally desorbed. In 1991, Vreuls et al. [67] described the first system in which enrichment was performed on-line in a PTV (see Fig. 6).

During the past few years, two variants of direct water injection have been developed on the basis of PTV. Enrichment of the analytes is either by SPE from the aqueous phase [SPE–thermal desorption (TD)] or the analytes are enriched on adsorbents after evaporation of the water in the PTV insert from the gas phase [which will be called gas-phase adsorption (GPA–TD)].

Vreuls et al. [68] used a system for SPE–TD in a PTV and investigated different packing materials. The Tenax phases showed the widest application range and gave good recoveries for chlorobenzenes and chlorophenols from 100-μl water samples. Mol et al. [69] discussed the direct injection of water samples into a packed PTV insert with elimination of the water, and looked into the various modes of enrichment. The authors used the SPE–TD mode because this enabled them to achieve clearly higher recovery rates for highly volatile compounds (e.g., methoxybenzene, ethylbenzene), and sample introduction takes less time. The GC system was provided with a back-flush device and a cryotrap. Quantitative recoveries were obtained on injection of 1000-μl spiked water samples. Louter et al. [70] presented an improved system for SPE–TD in the PTV. A new liner design made it possible to wash the injection system after enrichment with high-performance liquid chromatography (HPLC)-grade water. Thus, any possible decomposition processes caused by the interaction of analytes with retained matrix components were avoided and the otherwise inevitable pollution of the injection system in SPE–TD mode was prevented. In the case of real samples (manual injection of 100 μl, enrichment on Tenax GR) the authors, using MS–MS detection, reached detection limits of 0.1 to 0.2 μg/l for alachlor and metolachlor.

Fig. 6. GC–FID chromatogram obtained after SPE–TD of 500 μl of an aqueous standard solution of 12 fatty acids methyl esters on silylated C₃-silica. PTV, 80°C (5 min) –→ 250°C (15 min). Other conditions as given in Ref. [67].
Fig. 7. GC–NPD chromatograms of triazine herbicides obtained after speed-controlled injection and enrichment on Tenax TA using (A) direct water injection and (B) in-vial extraction with TBME. Initial PTV temperature, 50°C; split flow, (A) 600 ml/min and (B) 350 ml/min; solvent vent time, (A) 2 min and (B) 0.6 min. Splitless transfer, PTV 50°C→120°C/s→300°C (5 min). Splitless time, 1.5 min. Further conditions and peak identification as given in Ref. [58].
Müller et al. [71] described the direct injection of water samples into the PTV with evaporation of the water and enrichment of the analytes from the gas phase (GPA–TD). Because the enrichment was not performed according to the partition coefficient between water and adsorbent, water-soluble compounds might also be enriched. In addition, the non-volatile sample components remain in the easily interchangeable insert. Here, however, because the water is completely evaporated, sample introduction takes longer than in SPE–TD, because of the relatively high enthalpy of vaporisation of the water (the injection rate is only about 10 μl/min). After the determination of the breakthrough volumes for various analytes on different adsorbents, pesticides and nitroaromatics in water samples were investigated. In the case of enrichment on Tenax TA from 500 μl samples, the detection limit for dieldrin, for example, was 0.01 μg/l (ECD) and for aldimorph, it was 0.5 μg/l (NPD). Applications of the system with MS detection in scan mode, in screening investigations of surface water samples [72], showed detection limits of up to 0.01 μg/l; using this method, 21 compounds were identified in the water of river Elbe. Teske et al. [73] investigated the process of evaporation and elimination of water vapour in the direct injection of water samples in GPA–TD mode. For this, coloured water samples were injected by means of a transparent model injector. Maximum injection rates were determined at which the sample evaporates in the insert in front of the adsorbent bed, so that enrichment of the analytes takes place from the gas phase. A special liner design and the use of an inert dead-volume free back-flush device resulted in a system adapted to the requirements of water injection. When using the method for the determination of triazine herbicides in water samples [58], detection limits in the range of 0.01–0.02 μg/l (500 μl sample, GC–NPD) were reached. In water samples from the river Elbe, six triazines and triazine decomposition products were determined in the range of 0.01–0.1 μg/l. Fig. 7 shows the GC–NPD chromatograms of triazine herbicides obtained after direct water injection and in-vial extraction using TBME as the extracting agent. The potential of GPA–TD for quite water soluble compounds, such as hexazinone (peak 12), can be recognised.

Table 3 gives a summary of papers on the direct enrichment of organic water pollutants in the PTV insert; further works are mentioned in Section 4.4.

4.3. Enrichment of analytes from gaseous samples in the PTV insert

The use of PTVs in the determination of analytes in gaseous samples can, in principle, be classified as a variant of adsorptive enrichment with thermal desorption. However, the adsorption takes place in the insert of the PTV and the sample volumes are in the millilitre range. Nitz et al. [74] showed the determination of compounds from gaseous samples that were concentrated, after enrichment in thermal desorption tubes and subsequent thermal desorption, in the filled PTV insert at −150°C. Relevant on-line systems will be dealt with in Section 4.4.4.

Poy and Cobelli [75] described headspace injection with cryo-enrichment of the analytes in the PTV. The authors tested various packing materials (Carbotrap, Tenax TA and Gas Chrom Q coated with SE-30) and reached, for volatile pollutants in water samples, detection limits in the ng/ml range (GC–FID) or ng/l range (GC–ECD). Tabera et al. [76] looked into the enrichment of volatile compounds from grapefruit juice on Tenax GC in PTV by means of dynamic headspace analysis. Using the Simplex method, the parameters for sample introduction were optimised. Efer et al. [77] used the enrichment of ethylene in a PTV for the indirect determination of the pesticide ethepon in drinking water. In an alkaline environment, ethepon forms ethylene which,
after the injection of 12 ml of the headspace volume (static headspace analysis), was concentrated in the insert on Carbosieve. The detection limit for ethylene in water was at 0.05 μg/l. Russo [78] used a PTV to provide evidence of solvent residues in pharmaceutics using headspace analysis.

Tuan et al. [79] discussed the determination of sulphur compounds in natural gas. With the GC systems described, the analytes were concentrated on adsorbents in a PTV insert and were detected after thermal desorption using sulphur chemiluminescence detection (SCD). When various adsorbents were examined, Chromosorb 104 showed the highest selectivity for the sulphur compounds so that, for sample volumes of 13 ml, and a detection limit of 3 μg S/m³ was reached. Lewis et al. [80] investigated volatile organic compounds in air samples. By means of a mobile station, they studied, for example, biogenous emissions after direct concentration on active carbon in the PTV insert. Using a 600-ml sample volume, for C₂–C₆ hydrocarbons, they found detection limits for the single compounds of between 50 and 70 ng/l.

A PTV-GC–AED system was used by Lewis and Cooke [81] to determine volatile organic compounds in gaseous samples varying from a few millilitres to litres. These authors investigated headspace samples of foods such as garlic and onion as well landfills. The PTV, equipped with a Tenax TA sorbent trap, acted as a cryotrap device.

Eiden et al. [82] used in situ derivatisation employing sodium tetraethylborate as reagent for the determination of organotin species in water. The ethyl derivatives were purged from the sample on-line using helium and were trapped from the gaseous phase in a Tenax-filled insert of a PTV. Detection limits of about 1 ng Sn/l were reached using sample volumes of 800 ml and MS detection.

4.4. PTVs as an interface for on-line couplings

PTVs in solvent-split mode were often used as an interface for on-line couplings as they enable the transfer of large sample volumes in a GC system. Here, the PTV works as in LVI, with the separation of solvent and analytes usually taking place in the insert. However, in some applications, the PTV is only used as a vaporiser or cryotrap.

4.4.1. LC–PTV-GC

Senoránas et al. [83] described an on-line LC–GC coupling by means of PTV and studied various parameters, such as sample volume, packing material, rate of sample introduction and temperature of solvent elimination. Via a fused-silica transferline, the respective LC fraction was transferred through the septum into a Tenax-packed PTV insert. During the transfer of the LC eluent (methanol–water, 99:1 v/v), the GC column had been disconnected from the PTV and it was connected to the PTV after solvent elimination. The authors used the system for the determination of cholesterol and stigmasterol (see Fig. 8). In a further study [84], various kinds of liner packing were optimised. When examining real samples for sterols, 1050 μl of the eluent (methanol–water, 75:25, v/v) were transferred into a Tenax-packed PTV in 45 s.

Recently, an interface on LC–GC coupling was described in which the eluent moves through a special flow cell from which an LC fraction can be removed by means of a sampler. The flow of the mobile phase and the filling rate of the syringe are synchronised. In speed-programming, the removed fraction is injected subsequently into a PTV in solvent-split mode. Sandra et al. [85] used such a system for the determination of phenylurea pesticides from tobacco leaves. David et al. [86] described the determination of dibenzothiophenes from crude oil after HPLC pre-separation.

The principle of the hot vaporising chamber (vaporising chamber-pre-column split–gas discharge system) for on-line LC–GC coupling, which was discussed by Grob and co-workers [4–7], among others, was occasionally realised by means of PTVs. However, this technique is different from the one in PTV in the injector. The eluent is evaporated in a permanently hot chamber and the separation of solvent and analytes takes place subsequently in a pre-column.

4.4.2. SPE–PTV-GC

Staniewski et al. [49] used a short LC column as an SPE cartridge in on-line SPE–PTV-GC coupling. From a 1.1-ml water sample, the analytes were concentrated on styrene–divinyl benzene copolymer (PLRP-S) and, after elution with 50 μl of ethyl acetate, passed to the PTV via a transfer line. The
authors used an insert with a porous glass bed. The system was used for the determination of herbicides in water and for the investigation of plasticiser in table and mineral water from plastic bottles. Detection limits in the ng/ml range were reached.

4.4.3. Open tubular trapping column (OTTC)-PTV-GC

A further possibility for the extraction of analytes from water samples or aqueous eluents is enrichment with an OTTC in the stationary phase of a thick-film capillary GC column. After removal of the water or the eluent and drying with nitrogen, the analytes are eluted by means of organic solvents and transferred into the PTV.

Mol et al. [87] used OTTC for the on-line enrichment of organic compounds from water samples. Extraction of the analytes from water samples of up to 5 ml took place in a nonpolar GC column (2 m \( \times 0.32 \) mm I.D., 5.4 \( \mu \)m film; CP-Sil-5-CB), the retention power of which was considerably increased by treatment with polar solvents (phase-swelling effect) such as chloroform or methylene chloride. The double-oven GC system was equipped with a PTV and a short wide-bore column in the first oven. The methylene chloride extract was evaporated in the PTV and the solvent--analyte separation took place in the pre-column. After elimination of the solvent vapour, the analytes were refocused by means of a cryotrap and separated in the analytical column of the second oven. When examining spiked river water, the authors obtained detection limits in the low ng/ml range (GC-FID) for most compounds from a mixture of priority pollutants. In addition, Mol et al. [88] used OTTC as an interface in the on-line coupling of reversed-phase (RP) LC-GC systems. The retention power of the column was enhanced by treatment with \( n \)-hexane (phase-swelling effect). After investigations to select suitable operating conditions, the authors used the system for PAH analy-
sis. From 300 µl of an LC fraction (methanol–water, 50:50, v/v) at a flow-rate of 100 µl/min, 16 PAHs were enriched in a trapping column (2 m×0.32 mm I.D., 5.4 µm film; CP-Sil-5-CB). Desorption was carried out with 80 µl of hexane, which was transferred into the GC system at a flow-rate of 25 µl/min and a PTV temperature of −30°C. Under the chosen conditions, the recoveries were between 80 and 102%. Another paper by the authors [89] describes the use of geometrically deformed capillaries by which the sampling flow-rate can be clearly increased.

4.4.4. Adsorption/thermal desorption–PTV-GC

In on-line coupling of thermal desorption systems with gas chromatographs, PTVs are used as cryotrap devices for refocusing the analytes.

Various authors described the use of a thermal desorption system in connection with refocusing in a PTV for the determination of analytes in gaseous samples such as car exhaust gases and cigarette smoke [90] or in breathing air for medical diagnosis [91]. In addition, the thermal desorption system was used in the thermal extraction of compounds from solid samples [92,93]. A system working on the same principle was used by Castello et al. [94] for the GC determination of organic compounds in the ng/ml and ng/l range in air.

Recently, the application of on-line thermal desorption units for the determination of biogenic emissions was described by Heiden et al. [95]. After enrichment in thermal desorption tubes, refocusing was performed at −100°C in the PTV. The detection of analytes took place continuously as the time of GC separation was used for enriching the subsequent sample.

Baltussen et al. [96] used polydimethylsiloxane phases (PDMS) in thermal desorption tubes to examine air and natural gas samples. The PDMS phases excelled due to their high inertness, very good thermostability and low affinity for water. Due to the lower sorption energies and the possibility of using high desorption flow-rates, the desorption could be carried out at relatively low temperatures. In addition, thermal desorption tubes with PDMS were used for the off-line pre-concentration of PAHs and organochlorine pesticides from 100 ml water samples [97]. Because of the enrichment mechanism, the authors classified this technique as LLE. After a drying step with nitrogen, the analytes were desorbed in the thermodesorber and refocused at −150°C in the PTV. Recently, Baltussen et al. [98] used polydimethylsiloxane and polybutylacrylate for the enrichment of amines from water after derivatisation with pentafluorobenzoyl chloride. By means of GC–NPD the detection limits were in the sub-ng/ml range even if 1-ml samples were used.

4.4.5. SFE–PTV-GC

Houben et al. [99] described the application of a PTV in the on-line coupling of SFE and GC. The PTV served as an interface to the GC, in which the analytes were concentrated during elimination of the fluid (CO₂). For this, the authors used a glass-wool-packed insert at −20°C and showed the applicability of the method by examining carbon black filters and cigarette tobacco. Blatt and Ciola [100] used a device in which the analytes reached the PTV from the restrictor of the SFE apparatus via a stainless steel needle through the septum. The system was used to examine substances contained in vetiver roots. Lou et al. [101] studied the parameters of SFE–GC on-line coupling for PAH-containing samples and polymeric materials. A fused-silica capillary, as a restrictor, was connected to a packed PTV (Dexsil 300, coated on Chromosorb 750). For samples with high analyte concentrations, the PTV was used as a conventional split inlet with an empty insert.

When investigating plant material, Blanch et al. [102] used a SFE–GC coupling in off-line mode. A PTV insert was used as an analyte trap in the SFE apparatus and installed subsequently in the PTV for thermal desorption.

4.5. PTV as a thermoreactor

Occasionally, PTVs served as thermoreactors, in which a decomposition reaction is used in order to obtain defined compounds that can be examined by GC. Here, there is the possibility of using the PTV as a pyrolizer. In addition, thermal decomposition can be combined with pre-concentration of the analytes and matrix separation.
For the examination of solid substances, van Lieshout et al. [103] used a PTV, supplemented by a cryotrap, as a TD unit and as a pyrolizer. By means of multi-step temperature treatment up to about 600°C, the system was successfully used to characterise polymer compositions [103] and for examination of geological samples [104].

In 1993, Müller et al. [48] used a PTV as a thermoreactor for determination of the herbicide buminafos. After repetitive injection (10×10 μl) of a SPE extract and solvent elimination at 50°C, the PTV was heated to 250°C. The decomposition product (di-n-butylphosphite), formed in the PTV, was determined using GC–NPD.

Various authors have described pyrolytic methylation with derivatisation reagents such as methylammonium or methylsulphonium salts. At room temperature, the reagents, together with acidic groups (e.g., OH and NH), form an ionic compound that can be thermally transformed into their respective methyl derivates. Juárez et al. [105] used the method for the determination of free fatty acids in cheese by methylation with tetramethylammonium hydroxide. As a result of the investigations, however, the applied PTV was used as a hot inlet.

Färber et al. [106] dealt with pyrolytic methylation in the determination of pesticides in water. After extraction of the analytes from the aqueous phase (LLE or SPE), a methanolic solution of trimethylsulphonium hydroxide or trimethylanilinium hydroxide was added. An aliquot of the extract (7–10 μl) was injected in the solvent-split mode into a glass-wool-packed PTV insert. After increasing the injector temperature from 60 to 250°C, the corresponding methyl derivatives were analysed by means of GC–MS. In the case of LLE from 1 l of water, for example, the authors achieved detection limits of 25 ng/l for various chlorophenoxy carboxylic acids [106], and of 25–50 ng/l for urea herbicides [107]. For the determination of carbamate pesticides [108], detection limits between 25 and 50 ng/l are reported after SPE enrichment on C18 cartridges.

Recently, Zapf and Stan [109] described pyrolytic methylation of organic acids and phenols in water after LLE using trimethylsulphonium hydroxide. A 100-μl volume of the extract was injected in a glass wool-packed PTV. The method was applied to the investigation of batch cultures of bacteria.

In our laboratory, a method was developed [110] in which pyrolytic methylation is combined with direct water injection. The derivatisation reagent, trimethylsulphonium hydroxide (TMSH), is stable in the aqueous phase and, together with the chlorophenoxy carboxylic acids 2,4,5-T and 2,4,5-TP, forms an ionic compound which, because of its low volatility in LVI of water, can be well concentrated in the PTV insert. Because of the hydrophilic properties of the ionic compound, a clean-up step using in-vial extraction can be integrated into the method, so that impurities from the reagent and further sample components are partly removed with hexane whereas the analytes fully remain in the aqueous phase. After that, an autosampler with a programmable submergence depth of the injection needle withdraws the aqueous phase and, in a speed-controlled manner, injects 500 μl at 10 μl/min into a Tenax-packed PTV insert. After elimination of the water vapour, the enriched ionic compound is thermally decomposed at 300°C and the methyl esters are transferred into the separation column. Fig. 9 shows a GC–ECD chromatogram obtained using 800 μl of a spiked sample, 60 μl of a methanolic solution of TMSH (0.2 M) and, for in-vial clean-up, 400 μl of hexane.

![Fig. 9. GC–ECD chromatogram of the methyl esters of 2,4,5-trichlorophenoxy propionic acid (1) and 2,4,5-trichlorophenoxy acetic acid (2) after speed-controlled injection and enrichment on Tenax TA. Initial PTV temperature, 50°C; split flow, 600 ml/min; solvent vent time, 2 min. Splitless transfer: PTV (CIS3), 50°C→12°C/s→300°C (10 min); splitless time, 1.5 min. Column, SPB-5, 30 m ×0.25 mm, 0.1 μm film thickness; hydrogen head pressure, 0.7 bar; oven, 70°C (3.5 min)→15°C/min→280°C (10 min). Ref. [110].]
5. Conclusions

Today PTV, especially the PTV-based LVI, is a powerful tool in capillary GC systems. In recent years, LVI has become of considerable importance. Several techniques (on-column injection, PTV etc.) are available, but careful selection of an appropriate technique is necessary, depending on the nature of the analytes (volatility, polarity, thermolability) and the sample matrix. Several recent papers [4,11–116] are, among other things, concerned with this problem.

In the majority of cases, PTV-based LVIs are carried out in the solvent-split mode. A feature of this technique is that non-volatile components remain in the insert and do not enter the column. The analytical column and the detector will not be attacked either by the large volume of solvent vapour or by aggressive additional components since they leave the system via the split outlet. The separation of solvent and analytes occurs in the PTV insert, eventually assisted by adsorbents. This mechanism is not very suitable for analytes of higher volatility. In such cases, better results should be obtained using stationary phase focusing or solvent-trapping with a retaining pre-column (e.g., with an on-column interface). If thermolabile compounds are being investigated, PTV injection produces intermediate results compared to other injection techniques.

The number of publications illustrates the continuous interest in PTV injection and its potential in GC-hyphenated systems. The application of micro-extraction techniques, for instance, or combination with derivatisation procedures leads to simplified sample preparation. PTVs were successfully used as interfaces for on-line coupling of GC with sample preparation methods or other separation techniques, and allow the direct injection of water samples and aqueous eluents. Occasionally, the injectors serve as a cryotrap or thermoreactor. Actually, PTV is not simply a sampling device for capillary GC, but an element of sample preparation as well. However, as already mentioned, the technical possibilities provided by PTV are still not routinely applied in many laboratories. Therefore, further developments in this field should be concerned with automation as well as simplification of parameter optimisation. The systems should be easier to handle and made more rugged.

References
