

Large-volume injection in gas chromatographic trace analysis using temperature-programmable (PTV) injectors

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The use of programmed-temperature vaporising (PTV) injectors for large-volume injection in capillary gas chromatography is briefly reviewed. The principles and optimisation of large-volume PTV injection are discussed. Guidelines are given for selection of the PTV conditions and injection mode for specific applications. Relevant examples from the recent scientific literature serve as illustrations.

1. Introduction

Capillary gas chromatography (GC) is a very attractive separation method for trace analysis of environmental and biological samples. In addition to an efficient and fast separation it offers the analytical chemist a wide range of sensitive and selective detectors. Especially the good compatibility with mass spectrometric detection is important in this respect. A shortcoming of GC in trace analysis is that only volumes of a few microliters of organic solvent can be introduced into the gas chromatograph. As a consequence, sample preconcentration has to be carried out before GC analysis can take place.

The injection of much larger volumes, i.e. hundreds of microliters or even more, would (partly) eliminate the need for preconcentration prior to injection into the GC and therefore simplify the sample pretreatment procedure. Alternatively, large-volume injection is a means of further improving analyte detectability.

In gas chromatographic trace analysis, on-column and splitless injection are frequently applied sample introduction techniques. With these techniques injection of more than a few microliters of solvent causes band broadening and/or inadequate quantitative performance of the GC system. However, by modest adjustments in instrumental set-up and conditions it is possible to overcome these adverse effects. Already in 1979 Vogt and co-workers [1,2] described the introduction of sample extracts of up to 250 µl using a temperature-programmable split/splitless injector. Despite the promising results obtained by these authors there was hardly any interest in the programmed-temperature vaporising (PTV) injector for large-volume sampling in the decade following that publication. PTV injection did, however, receive considerable attention as a means of discrimination-free injection [3,4].

In the early 1980s large-volume injection techniques based on on-column injection were described by Grob as part of the development of systems in which liquid chromatography is coupled on-line to GC [5]. Large-volume on-column injection proved to be a very accurate technique. However, further experience also revealed certain limitations. The most important one is the deterioration of the system's performance upon introduction of involatile matrix constituents.

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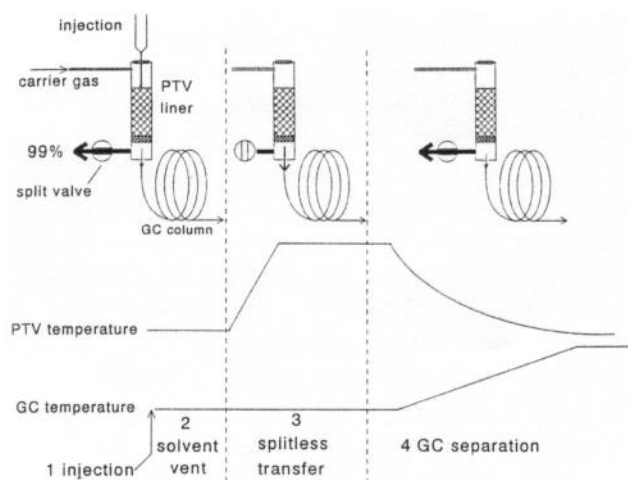


Fig. 1. Principle of large-volume PTV injection.

Unfortunately, in gas chromatographic trace analysis the sample extract often contains a substantial amount of in volatile compounds. This renders on-column based techniques less suited for large-volume injection unless a very efficient clean-up (as in coupled LC-GC) is performed prior to injection into the GC system. As a result, there has been a renewed interest in large-volume sampling techniques based on split/ splitless injectors, which are more tolerant to 'dirty' samples. For this purpose the use of conventional split/splitless injectors has been reported (vapour overflow injection [6,7]) but in general the use of PTV injectors is preferable because of the wider application range. This article describes recent developments in large-volume injection using programmed-temperature vaporising injectors. The principles and key parameters as well as the optimisation of the experimental parameters will be discussed and several applications will be given.

2. Principles of large-volume PTV injection

The large-volume injection technique described in this paper is usually referred to as solvent split or solvent vent injection. The principle of the technique is schematically depicted in Fig. 1. The procedure involves three subsequent steps: injection, solvent

venting, and splitless transfer. During injection and solvent elimination the split exit is open and the temperature of the PTV injector is well below the solvent boiling point (PTV temperature typically between 0 and 50°C). The solvent evaporates and leaves the system via the split exit while less volatile analytes are retained in the liner. After solvent elimination the analytes are transferred from the liner to the GC column in the splitless mode. This involves closing of the split exit and rapid heating of the injector. After the splitless transfer step, the split exit is re-opened to remove residual solvent vapour and high-boiling matrix compounds from the liner. Involatile matrix compounds remain deposited in the liner which, if necessary, can easily be exchanged. The temperature of the GC oven is below the solvent boiling point until splitless transfer is complete in order to facilitate refocusing of the analytes at the top of the analytical column.

2.1. Injection modes and optimisation

Upon injection it is important that the liquid sample is retained in the liner because otherwise part of the sample will be vented—in the liquid state— via the split exit and/or flood the analytical column. This would lead to loss of analytes and distorted peak shapes, respectively. The approximate volumes of liquid retained in different types of liners are given in Table 1. For sample volumes below the values given in Table 1 rapid injection (1-2 s) of the entire sample is possible. This so-called 'at-once' injection mode is the most user-friendly injection mode; optimisation is straightforward [8,9]. Optimisation starts with establishing the maximum volume of liquid that can be accommodated by the liner without flooding (V_{max}), i.e., verification of the values of Table 1. This can be done visually [8,9]. The next step is the determination of the solvent vent time, i.e. the time needed to evaporate and eliminate the solvent via the split exit prior to transfer of the analytes to the analytical column. To this end the above-mentioned maximum volume of solvent is rapidly injected under conditions that will be applied during subsequent analysis. Typical conditions are an initial PTV temperature of 30°C, a split flow of 250 ml/min, and a GC oven temperature of 40°C. Upon injection, approx. 99% of the solvent vapour is vented via the split exit while roughly 1% enters the column and reaches the detector after the column hold-up time. An increase in the detector background occurs until all solvent in the

Table 1
Volume of liquid retained in several types of liners

Empty liner	1–4 mm I.D.	< 5 μ l
Packed liner	1 mm I.D.	10–20 μ l
Packed liner	4 mm I.D.	100–150 μ l

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liner has been evaporated. The width of the solvent peak obtained in this way is the solvent vent time that is to be used in subsequent analysis. Typical vent times are 30 s to 2 min. Other ways to determine the solvent vent time are described elsewhere [8].

When the sample volume exceeds the value depicted in Table 1, the sample should be introduced either by repetitive (multiple) injection, or by speedcontrolled injection. With *repetitive injection* fractions of the sample smaller than V_{\max} are rapidly injected. The time between two injections is equal to the solvent vent time which is determined as described above. After injection and solvent elimination of the last fraction, all analytes accumulated in the liner are transferred to the analytical column in the splitless mode. Optimisation of this large-volume injection technique is as straightforward as described for the atonce mode.

With *speed-controlled injection* the sample is introduced at a rate which is equal to or slightly above the evaporation rate of the solvent. Lower injection rates will result in a lengthy sampling procedure and in higher losses of volatile analytes whereas (much) higher injection rates will result in flooding of the liner and, thus, in losses of liquid sample via the split exit. A speed-programmable syringe is needed for injection. After sample introduction has been completed, an additional vent time has to be applied for elimination of solvent that has accumulated in the liner during injection. Optimisation of speedcontrolled injection is less straightforward than atonce injection because now two interrelated parameters (i.e. injection speed and vent time after injection) have to be optimised. Strategies for optimisation of speed-controlled injection have been extensively discussed elsewhere [10-12].

In general, the at-once injection is the easiest and most user-friendly injection mode, both from the point of view of optimisation and instrumentation. The use of wide-bore packed liners is often advantageous because of their larger sample capacity (see Table 1). With certain applications, however, optimal performance requires the use of small diameter and/ or empty liners. This will be discussed below.

2.2. Packed liners

Due to their larger solvent capacity, the use of packed liners is attractive in large-volume PTV injection. The packing not only serves to retain the sample liquid, it also helps to prevent transfer

of high-boiling matrix constituents to the analytical column. On the other hand, the packing material may cause undesired adsorption or degradation of analytes in the liner due to the presence of active groups (e.g. silanol groups) on the surface of the material. As an example, glass wool, even when silanised, was found to cause adsorption/degradation of a number of polar and labile compounds [13,14]. In a recent study [14] several packing materials were tested as alternatives for glass wool. The packing was kept in place by a glass frit located in the bottom part of the liner. Apart from the inertness of the packings, also their thermostability and the ability to retain the liquid sample were evaluated. Chromosorb-750 coated with Dexsil, and uncoated Supelcoport (60-80 mesh) are two examples of thermostable and inert materials that substantially improve the performance of largevolume PTV injection in the determination of thermolabile or adsorptive analytes. Pressure programming can help to reduce possible degradation [15]: during splitless transfer a high inlet pressure is applied which reduces the residence time of the analytes in the liner at elevated temperatures. After transfer the inlet pressure is reduced to the optimal value for GC separation.

2.3. Volatile analytes

In large-volume PTV injection the analytes are retained in the liner during solvent elimination only if their vapour pressure is sufficiently low. This is generally the case if the initial PTV temperature is some 250°C below the boiling point of the analyte [8]. For *n*-alkanes this means that in order to quantitatively retain C₁₆ or C₁₃, the PTV temperature should be 30°C or -30°C, respectively. Although in the latter case sub-ambient cooling of the injector is required, this simple mechanism (cold trapping) is the easiest and most reliable and robust way of retaining the analytes.

When part of the simplicity of the procedure is sacrificed, it is possible to further extend the application range towards more volatile analytes. A first possibility is to close the split vent shortly before evaporation of the solvent has been completed. It was found that losses of volatile analytes occur mainly with evaporation of the last few microliters of solvent [8]. Up to that moment most compounds are efficiently retained in the liner as a result of solvation by the liquid and due to the fact that the temperature at the site of evaporation can be much lower than the initial PTV temperature (cooling by solvent evaporation).

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To quote an example, at 0°C, quantitative determination of C₉ in hexane is possible for a 100 µl at-once injection [8]. In this situation, however, the vent time is rather critical.

With repetitive and speed-controlled injection, solvent trapping of the analytes in the liner during solvent elimination is less efficient than in the at-once mode and, hence, the application range towards more volatile analytes is less favourable.

Another way of reducing losses of more volatile compounds in a PTV solvent split injection is to add a higher boiling solvent, a so-called co-solvent or keeper, to the main solvent. The analytes are trapped in this higher boiling solvent during and after evaporation of the main solvent. Termonia et al. [16] improved the recovery of biphenyl by the addition of octane (final concentration 15%) to hexane in a large volume injection using an initial PTV temperature of 70°C.

A third possibility to prevent losses of volatiles is to pack the liner with a suitable adsorption material (e.g. Tenax or Thermotrap) [11, 14]. A draw-back of this approach is that it does not really extend the application range because high-boiling analytes are too strongly adsorbed to be transferred to the analytical column. However, if the analysis does not involve high-boiling compounds, the use of an adsorbent-packed liner is a very attractive option. As an illustration a chromatogram obtained after injection of 100 µl of a solution of methyl esters of halogenated acetic acids (herbicides) in ethyl acetate is shown together with a 1 µl splitless injection (reference chromatogram) in Fig. 2.

Quantitative recoveries are obtained at an initial PTV temperature of 30°C despite the relatively low boiling points of the esters (144°C-183°C).

To summarise the above: large-volume PTV injection of sample volumes up to 100-150 µl is straightforward unless the compounds of interest are highly volatile. In the latter case a more careful selection of conditions and liner design is required. Speed-controlled injection is a good alternative if even larger sample volumes have to be injected. Also here, however, optimisation is slightly more complex. In Table 2 guidelines are given for the selection of the liner and injection mode in large-volume PTV injection. Basically, the volatility of the analytes and the sample volume determine the preferred injection mode and liner configuration. For very thermolabile and adsorptive compounds degradation or adsorption of the solutes in the liner may lead to low recoveries, even when inert packing materials are used. In this case the recoveries can be improved by using small I.D., and preferably empty, liners. In addition, it can be advantageous to increase the inlet pressure during the splitless transfer step in order to reduce the residence time of the analytes in the (hot) liner. In the unlikely case that recoveries are still unacceptable one should resort to on-column techniques for large volume injection. For this the PTV injector can be converted into an on-column injector by using a special on-column insert [17]. Alternatively, a standard on-column injector can be used.

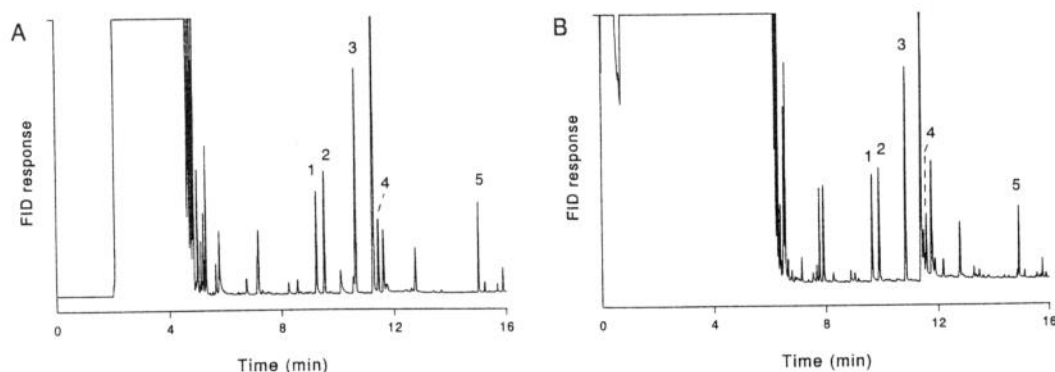


Fig. 2. GC-FID chromatograms obtained after (A) splitless injection of a 20 ng/µl standard of methylated halogenated acetic acids, empty liner (3.4 mm I.D.), (B) 100-µl injection of a 0.2 ng/µl solution in ethyl acetate. At-once injection at 30°C, liner packed with Tenax TA (35-60 mesh), split flow 250 ml/min, solvent vent time 2 min. Splitless transfer: from 30°C to 250°C (ramp 8°C/s), splitless time 2.5 min. GC column: 50 m x 0.33 mm I.D., 0.19-µm CP-Sil-19-CB, P_{in} = 135 kPa, temperature programme: 40°C (2 min) ↑ 4°C/min ↑ 84°C (0 min) ↓

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Table 2

Guidelines for the selection of liner and injection mode in large-volume PTV injection

	Analyte	
	Very labile/ adsorptive	Other
Sample volume (μl)	> 5	< 100–150 > 100–150
Liner I.D. (mm)	1	4 1–4
Packing	Empty	e.g., Supelcoport, Chromosorb-750 coated with Dextsil
Injection mode	Repetitive ($n \times 5 \mu\text{l}$) or speed-controlled	At-once Repetitive ($n \times V_{\text{max}}$) or speed-controlled
Volatility application range	$\geq C_{13}^a$	$\geq C_9^b$ $\geq C_{13}^a, C_{10}^c - C_{30}^c$

^aApplying sub-ambient initial PTV temperatures, otherwise ~ C16.

^bApplying sub-ambient initial PTV temperatures and solvent trapping (i.e., closing the split valve slightly before complete evaporation of the solvent).

^cWhen packing the liner with Tenax (application range is a rough indication as retention of the analytes depends on their structure).

3. Applications

3.1. Easier sample pretreatment

Prior to GC analysis the analytes usually have to be isolated from the matrix (e.g. soil, water, tissue). Soxhlet extraction or liquid-liquid extraction are still frequently employed to this end. A dilute extract of the analytes in typically 100–500 ml of an organic solvent is obtained after the extraction procedure. Therefore, evaporative concentration to 1–5 ml is often carried out using Kuderna-Danish or rotational evaporators, after which 1 μl is subjected to GC analysis. The concentration steps are not only rather laborious and time consuming, they are also prone to errors by evaporation or degradation of the solutes of interest. An obvious application of large-volume injection therefore is in the replacement of these off-line evaporative concentration procedures. Concentration carried out in the PTV injector is much faster, occurs under better controlled conditions and is easier to automate.

An example of this type of application is the use of large-volume PTV injection in the determination of polycyclic aromatic hydrocarbons (PAHs) in river sediment by GC-MS [9]. Instead of applying Kuderna-Danish concentration, 50 μl of the Soxhlet extract were injected into a PTV injector equipped with a packed liner (at-once injection). Because no sub-ambient cooling was used, losses due to coevaporation with the solvent occurred for naphthalene and, to a lesser extent, for acenaphthylene and acenaphthene. However, even the data for these analytes could still be used for quantitative determination as losses were reproducible. In water analysis the replacement of liquid-liquid

extraction by solid-phase extraction (SPE) has largely eliminated the need for evaporative concentration steps. However, also in this type of analysis large-volume injection can make sample pretreatment easier. By injecting a larger portion of the extract, the volume of water to be processed can be much smaller (e.g. 10 ml instead of 1 L) while the same detection limits are obtained. Apart from reduced transport problems and easier storage of the sample, this has two additional advantages: the sorption step will be much faster, and for polar analytes the extraction efficiencies will improve as breakthrough from the SPE cartridge is less likely to occur. The performance of large-volume PTV injection was recently described for the determination of 32 relatively polar nitrogen and phosphorus-containing pesticides [9]. Rapid injection of 60 μl of ethyl acetate extracts into a liner packed with a Dextsil-coated support was performed. Solvent elimination took 60 s at an initial injector temperature of 30°C. Severe adsorption or degradation in the liner occurred during splitless transfer for only three pesticides (phosphamidon, oxyde-metonmethyl and vamidothion). In agreement with observations in classical hot splitless injection by Erney and Poole [18], the extent to which this degradation took place was affected by the matrix. For standard solutions in a clean organic solvent degradation was most pronounced, while in acidic extracts degradation was almost absent. The explanation given for this phenomenon is that matrix compounds can shield active sites in the liner thereby preventing adsorption/degradation of the analytes. The shielding effect is strongest with acidic extracts because these often contain the highest level of matrix compounds (e.g. humic acids).

3.2. Improving analyte detectability

In this type of application sample pretreatment is generally carried out in the usual way but a larger aliquot of the (preconcentrated) extract is subjected to GC analysis. Provided that the selectivity of the GC detector is sufficient, the detectability of the analytes will improve proportionally with the volume injected. The amount of involatile matrix compounds introduced also will increase but this material is efficiently retained in the liner of the PTV injector and the performance of the analytical column does not deteriorate. Several authors have demonstrated that the detectability can be improved 10-25 fold by large-volume PTV injection. Stottmeister et al. [19] determined PCBs and toxaphenes in water. In order to improve the detection limits (in concentration units in the water sample), 10 μl of the extract obtained after SPE were injected. The study showed that the typical patterns of the PCBs and toxaphene standards used could still be recognised at the 10 ng/l level using electron capture detection (ECD). Szpunar-Lobinski et al. [20] used large-volume PTV injection for the determination of organotin compounds in environmental waters. The ionic organotin compounds were first preconcentrated by sorption on an LC- type precolumn packed with C_{18} -modified silica and, next, ethylated by pumping an aqueous sodium tetraethylborate solution through the pre-column. The derivatised compounds were desorbed with 250 μl of methanol. Aliquots of 25 μl were rapidly injected into the PTV injector (liner packed with Tenax). Detection limits down to 0.1 ng Sn/l were achieved using atomic emission detection (AED). Linkerhägner et al. [21] also applied large-volume PTV injection in combination with a GC-AED system. Nitro musks were determined in human adipose tissue. The lack of sensitivity of the AED nitrogen and oxygen channels was compensated by injecting 12.5 μl of the extract into a PTV equipped with an empty baffled liner (chromatogram is shown in Fig. 3). Detection limits were at the ng/g level.

In principle, an increase of the injection volumes from 10-25 μl to, e.g. 100-250 μl , should further improve analyte detectability, but in practice coeluting matrix compounds will become the limiting factor in quantification. This means that more selectivity will be required, either during sample

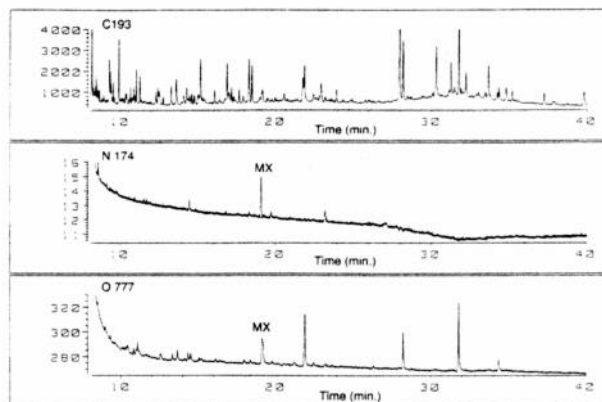


Fig. 3. GC-AED carbon, nitrogen and oxygen traces obtained after injection of 12.5 μl of a human fat extract (toluene-hexane). MX = musk xylene, 0.07 ng/ μl . Reprinted from [21].

pretreatment (clean-up, LC-GC, GC-GC) or during detection (GC-MS or GC-MS-MS).

3.3. On-line sample pretreatment-GC

Systems in which (part of) the sample pretreatment procedure is coupled on-line with the GC analysis offer great automation potential and enable us to increase sample throughput at low cost. Liquid chromatography, solid-phase extraction (SPE) and liquid-liquid extraction can all be coupled directly to a GC instrument provided that the latter can handle large volumes of liquid.

Several authors have reported the use of PTV injectors as an interface in on-line SPE-GC. The general procedure is that organic compounds present in water samples of typically 1-10 ml are first sorbed on an extraction column. Then, after drying the column with a gas at ambient temperature, the analytes are desorbed by an organic solvent (50-250 μl) which is directly introduced into the PTV injector. For automated operation the extraction column is connected between switching valves in a set-up such as depicted in Fig. 4; LC pumps are used for sampling and desorption. Staniewski et al. [22] determined pesticides in water samples this way. The analytes from 1 ml of water were sorbed in a cartridge packed with a copolymer (PLRP-S). For desorption/transfer to the PTV injector 50 μl of ethyl acetate were needed. In the PTV injector which was equipped with a liner containing a deactivated porous glass bed, the ethyl acetate was vaporised and vented after which splitless transfer of the pesticides to the column and GC analysis took place. When using FID detection, sub

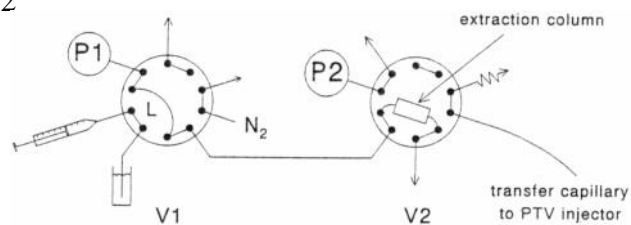


Fig. 4. Schematic representation of an instrumental set-up used for on-line SPE-GC. V 1 and V2 are switching valves, L is the sample loop, P 1 and P2 are LC pumps containing HPLC-grade water and an organic solvent, respectively.

$\mu\text{g/l}$ detection limits were achieved. A similar approach was used by Mol et al. [23], using opentubular extraction columns rather than packed cartridges. Organochlorine pesticides from 10-ml water samples were extracted into a 2 m x 0.50 mm I.D. capillary coated with a 5- μm dimethylsiloxane phase. Hexane (100 μl) was used for desorption. The same set-up, in this case with a 5 m x 0.32 mm I.D. extraction column, was also used for the determination of sulfur-containing pesticides. Here 250 μl of hexane were required for desorption/transfer to the PTV injector. As the desorption volume exceeded the maximum capacity of the liner (1 mm I.D., packed with Supelcoport), the desorption speed had to be adjusted to the solvent evaporation rate

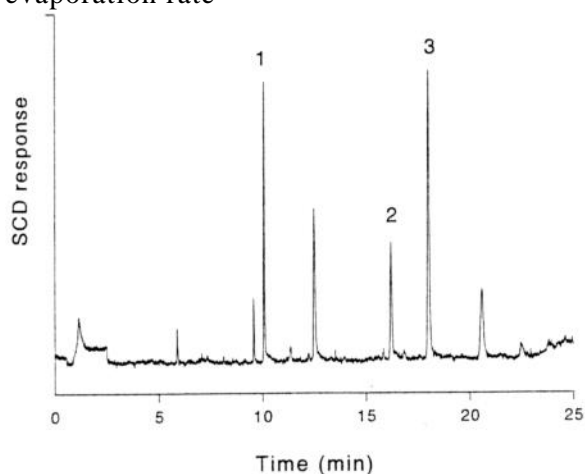


Fig. 5. GC-SCD chromatogram obtained after on-line extraction of 5 ml of river water spiked with sulfur-containing pesticides (0.1 ng/ml). Sampling procedure as described in Ref. [23]. Desorption/transfer to the PTV injector, 250 μl of hexane at 150 $\mu\text{l/min}$. PTV conditions, 1 mm I.D. liner packed with Supelcoport, 30°C, split flow 250 ml/min. Additional vent time, 15 s. Peak assignment: 1 = ethoprophos, 2 = promethryne, and 3 = parathion-ethyl.

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in the injector. At an initial PTV temperature of 30°C and a split flow of 250 ml/min, the optimum introduction/desorption speed was 150 $\mu\text{l/min}$. After completion of the desorption an additional vent time of 15s was employed. With the on-line extraction-GC system, detection limits down to 5-20 pg/ml could be achieved using sulfur chemiluminescence (SCD) detection (Fig. 5).

Clean-up procedures are another example of sample pretreatment that can be automated when the GC is capable of handling large volumes of liquid. The online clean-up of petroleum ether extracts obtained after liquid-liquid extraction of water samples was reported for the determination of organochlorine pesticides and PCBs [9]. clean-up was required because the selectivity of the electron-capture detector was insufficient to allow detection of the chlorinated species at low levels. The system consisted of one sixport valve with a 130 μl sample loop, a programmable syringe filled with petroleum ether, and a 20 mm x 2 mm I.D. stainless-steel column packed with aluminium oxide which was mounted in the transfer line between the valve and the PTV injector. Clean-up was performed by transferring the water extract through the aluminium oxide column into the PTV injector. A total of 400 μl of petroleum ether (speed 200 $\mu\text{l/min}$) were needed for quantitative transfer of the organochlorine compounds. The capacity of the aluminium oxide column for retaining contaminants was sufficient for ten analyses.

3.4. Direct injection of aqueous solvents

Water is a difficult solvent in GC analyses. In the GC column it can hydrolyse siloxane bonds which causes re-activation of silylated surfaces and deterioration of the stationary phase. In addition, water is not compatible with flame-based GC detectors. In large-volume injection the high boiling point and the large volume of vapour formed per volume of liquid complicate solvent elimination. These characteristics plus the poor wettability of deactivated retention gaps by water still render oncolumn based large-volume injection of aqueous samples extremely difficult or even impossible. In contrast, direct injection of large volumes of aqueous solvents (water samples, fractions from reversedphase LC systems) is possible by using a PTV injector. There is no need for wettability and waterresistant packing materials are available. Tenax is most frequently used for this purpose because it

combines good water resistance with a high temperature stability and chemical inertness [14]. As was already mentioned above, a limitation of Tenax is that high-boiling compounds can not easily be splitlessly transferred to the GC column as they are too strongly retained due to non-specific hydrophobic interaction. On the other hand, due to this interaction many compounds will be adsorbed on Tenax even when water is vented as a liquid which allows us to perform solid-phase extraction in the liner of the PTV injector. This set-up was first presented by Vreuls et al. [24]. These authors called the technique solidphase extraction/thermal desorption (SPETD). Up to 100 μ l of aqueous standard solutions containing chlorinated benzenes and phenols were injected. During injection and drying of the liner a backflush from the column to the injector was applied to prevent water from entering the GC column. Mol et al. [25] compared two ways of water sampling, the solid-phase extraction mode (SPETD) and the evaporative sampling mode in which water is introduced at a speed below the evaporation rate. The first approach was advantageous in case of non-polar analytes as sampling was faster. The second approach was more successful for more polar analytes (atrazine) as breakthrough was found to occur when sampling more than 100 μ l at SPE conditions. Sample volumes up to 1 ml of tap water were analysed. Muller et al. [26] used the PTV injector for direct water injection applying the evaporative sampling mode (Fig. 6). Spiked surface water was analysed. For chemically/thermally labile analytes (dimethoate, metamidophos) recoveries were below 50% which was attributed to accumulation of salts and suspended matter in the insert. Although the PTV injector in principle allows direct injection of aqueous solvents, further experience has to reveal its practicality for this type of application.

4. Conclusions

Programmed-temperature vaporising (PTV) injectors have proven to be suitable devices for large-volume injection in capillary GC. Recent improvements in injector design and the availability of inert packing materials have not only simplified the optimisation procedures but also extended the application range towards more labile and adsorptive analytes. Large-volume PTV injection can be implemented in analytical procedures in which splitless injection is

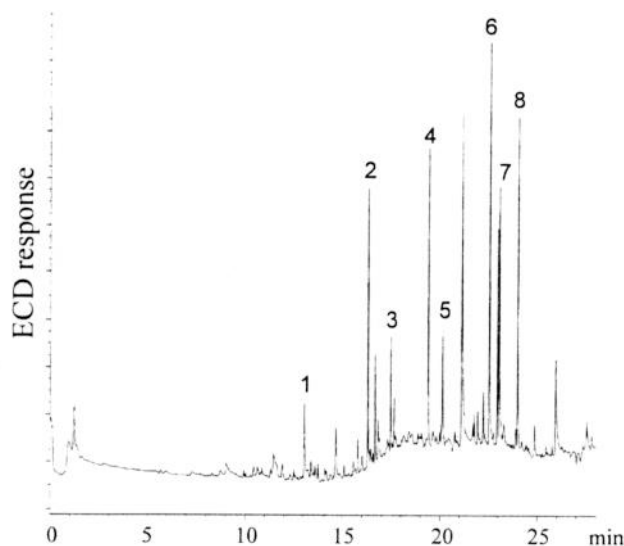


Fig. 6. GC-ECD chromatogram obtained after direct injection of a 500- μ l water standard. PTV liner packed with Tenax, 50°C, split flow 600 ml/min, introduction speed 12 μ l/min, inlet pressure ambient during injection. Peak assignment: 1 = dichlorvos, 2 = 2,6-dinitrotoluene, 3 = hexachlorobenzene, 4 = lindane, 5 = 2,4,6-trinitrotoluene, 6 = chlorfenvinphos, 7 = dieldrin, and 8 = nitrofen. Reprinted from [26].

currently used and it can be an attractive alternative for large-volume on-column injection, especially when regarding dirty sample extracts. The at-once and repetitive injection modes are very user-friendly and maintenance (periodical replacement of liner) is simple. PTV solvent split injection is, however, not a universal solution. For volatile or very labile/ adsorptive analytes large-volume on-column injection techniques are more accurate (although with the latter type of analytes this is only true for relatively clean samples). If the application of on-column techniques proves to be necessary, then the PTV injector can be transformed into an on-column injector by using an on-column insert. This, plus the possibility to handle aqueous solvents, makes the PTV injector a very versatile injection device.

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