Application Note No. 020

Original Research Papers

Environmental Applications of Large Volume Injection in Capillary GC Using PTV Injectors

Hans G.J. Mol*, Mariken Althuizen, Hans-Gerd Janssen, and Carel A. Cramers
Eindhoven University of Technology, Laboratory of Instrumental Analysis, PO Box 513, 5600 MB Eindhoven, The Netherlands

Udo A.Th, Brinkman
Free University, Department of Analytical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Key Words:

Large volume injection
PTV injector
Water analysis
River sediment
Pesticides
Polycyclic aromatic hydrocarbons (PAHs)

Summary

Temperature programmable (PTV) injectors with packed wide-bore *(ca.* 3.5 mm i.d.) liners are used for large volume injection in capillary gas chromatography with the aim to simplify and/or improve off-line sample pretreatment procedures. A simple procedure for optimization of large volume PTV injection is described. The system performance, *i.e.* linearity and repeatability, is evaluated for polar nitrogen/phosphorus containing pesticides (PTV-GC-NPD) and organochlorine pesticides (PTV-GC-ECD) in river water extracts as well as for polycyclic aromatic hydrocarbons (PAHs) in river sediment (PTV-GC-MS).

1 Introduction

In environmental analysis sample preparation techniques such as Soxhlet extraction, liquid-liquid extraction and solid-phase extraction (SPE) are widely used. Most of these procedures can be simplified or improved by injecting larger volumes into the capillary GC system, *e.g.* 100 µl instead of the common 1 µl. With sample preparation processes currently applied in most routine laboratories, dilute sample extracts have to be reconcentrated by (Kuderna-Danish) evaporation of the solvent in order to achieve the desired detection limits. Such time consuming and labor intensive evaporation steps can be replaced by large volume injection. Here the solvent is evaporated in the GC system, a process which is much faster and takes place under carefully controlled conditions. Besides, the risk of sample contamination is reduced. The reconcentration step can be easily automated by using large volume auto samplers. When solid-phase extraction is used for preconcentration of the analytes, *e.g.* in water analysis, large volume injection allows us to process much smaller sample volumes (e.g. 10 ml instead of 1 L) while keeping the detection limits (in concentration units in the sample) the same. Apart from reduced transport problems and easier storage of the samples this has two advantages: the sorption step will be faster and the extraction efficiencies for polar analytes will improve because breakthrough from the SPE cartridges is less likely to occur.

Large volume injection can of course also be used to improve analyte detectability. If the sample extract is sufficiently clean and/or the detector selectivity sufficiently high, the detection limits will improve proportionally with the volume injected.

The techniques used for large volume sample introduction in capillary GC can be divided into two categories: techniques based on oncolumn injection and techniques based on split/splitless injection. In general, with the on-column techniques the solvent is vaporized in a few meters of uncoated deactivated capillary (retention gap) and vented *via* a so-called early vapor exit [1]. On-column techniques are very accurate, especially when thermo labile analytes or volatile analytes are concerned. On the other hand, the robustness is less than with split/splitless techniques, because the performance can rapidly deteriorate upon introduction of non-volatile material or traces of water [2,3]. On-column injectors with retention gaps have been extensively used as interface in on-line systems, *i. e.* in coupled LCGC [1,4,5], and in on-line extraction-GC systems [6-8]. Although the advantages that large volume injection offers are also applicable to off-line sample preparation-GC, only few applications have been reported so far [9-13]. Large volume injection obviously is still considered to be a complex technique [14], an impression that may well be due to the fact that in most applications large volume injection is presented as part of a sophisticated on-line system.

With large volume injection based on split/splitless injection the solvent is vaporized in the liner and vented v*ia* the split exit of the injector. The use of a conventional split/splitless injector has been reported for this purpose [15], and also for large volume injection using the vapor overflow technique [16]. In general, however, programmed temperature vaporizing (PTV) injectors are most suited. The use of the PTV injector for large volume sample introduction is especially useful for the analysis of relatively dirty samples. Nonvolatile matrix constituents remain in the liner which can easily be exchanged, and will not contaminate the GC (pre)column. In most applications of large volume PTV injection reported so far the sample volumes injected were relatively small (10-25 µl) [17-19]. Such volumes can be rapidly injected without overloading the liner (typically 1 mm i.d.) with liquid. The introduction of larger volumes of extract is possible by performing speed-controlled injection. Speedcontrolled injections require careful optimization [20-22] and for introduction into the PTV injector a pump or speed programmable auto sampler is needed.

Recently we described the use of PTV injectors equipped with packed wide-bore liners (3.5 mm I.D.) for large volume injection [23]. These packed liners can retain up to 150 µl of liquid. This means that extract volumes up to 150 µl, which is sufficient for most applications, can be rapidly injected. This in turn greatly simplifies both optimization and instrumentation compared to the situation for speed-controlled sample introduction. As was to be expected, for optimum performance with polar analytes the inertness of the packing material was found to be an important aspect. This was evaluated in a subsequent study and several promising materials were proposed [24]. In the present contribution the applicability of PTV injectors equipped with packed wide-bore liners for large volume injection is evaluated for real-life environmental samples. Three examples are given: the determination of (i) polar nitrogen/phosphorus containing pesticides in river water, (ii) organochlorine pesticides in river water and (iii) PAHs in river sediment, using NPD, ECD and MS detection, respectively. The system performance, i.*e.* linearity and repeatability, is evaluated for each application. In addition, the effect of the sample matrix on the (NPD) response of the nitrogen/phosphorus pesticides is examined. For the organochlorine pesticides, a system for on-line clean-up of the extract is presented.

2 Experimental

2.1 *PTV-GC -NPD*

The extracts of river water, in ethyl acetate, were kindly supplied by KIWA (Nieuwegein, The Netherlands).The extracts had been 1,000-fold enriched by solid-phase extraction (C_{18}) of neutral and acidified river water samples from several locations in The Netherlands. For 60 µl injections the extract was diluted 60 times in ethyl acetate (Baker, Deventer, The Netherlands) which had been distilled before use. The amount of matrix now introduced with each injection is equivalent to that present in 1 ml of river water. Extracts were spiked with a nitrogen/phosphorus containing pesticide standard (obtained as a gift from KIWA). Large volume injection-GC analysis was performed using an ATI **U**nicam GC (Model 4600, Cambridge, UK) equipped with a nitrogen/phosphorus detector (NSA-25) and a PTV injector (liner I.D. 3.4 mm) (Optic, Ai Cambridge, Cambridge, UK). A Nelson 1020 data system (Perkin Elmer, Norwalk, CT, USA) was used for data handling.

2.2 *PTV-GC -MS*

Sediment samples were taken from the river Dommel in The Netherlands. The sediment was dried at room temperature for 2 days. Soxhlet extraction using 50 ml of hexane/acetone (1:1) Was carried out with 10 g of sieved (1 mm) sediment for 8 hours. The extract was further treated using two different methods as will be discussed in the next section. Hexane p.a. and acetone p.a. were obtained from Baker and were distilled before use. The PAH standard (16 PAHs. SRM1647c) was obtained from Schmidt B.V. (Amsterdam. The Netherlands). For fractionation 0.4 ml of the extract in hexane was sampled onto an amino cartridge (Bond elut NH_2, 3 ml, Analytichem Intern., Harbor City, CA. USA) which was preconditioned with hexane. After washing with 0.6 ml of hexane, elution was performed with 2% v/v dichloromethane in hexane. The extracts were analyzed using a GC system (Autosystem, Perkin Elmer) with mass spectrometric detection (Q-mass 910) and a PTV injector (PSS, liner I.D. 2.3 mm). Data handling was done using the Q-mass 910 Analytical Workstation software.

2.3 *PTV-GC-ECD*

River water extracts (Lekkanaal, The Netherlands) obtained after liquid-liquid extraction of 1 L of water with 200 ml of petroleum ether (40-60 °C, nanograde, Malinckrodt, Germany) were kindly supplied by WRK (Nieuwegein, The Netherlands) as were the organochlorine pesticide/PCB standards. The aluminum oxide (basic, W200, ICN Pharmaceuticals, Eschwege, Germany) used for clean-up was first activated overnight in an oven at 150 °C. Then 1.1 g of water was added to 8.9 g of Al_2O_3 and the mixture was allowed to homogenize for 24 hours. The system used for on-line clean-up-GC consisted of a 6-port valve (Valco, Houston, TX, USA), a 20 mm x 2 mm i.d. stainless steel LC-type precolumn which was (dry) packed with Al_2O_3, and a speed-programmable syringe (Gerstel, Mülheim a/d Ruhr, Germany). GC analysis was carried out using an ATI Unicam GC equipped with a PTV injector (liner I.D. 3.6 mm) and an ECD (make-up gas, 50 ml N_2/min; detector temperature 300 °C). For data handling a Unicam 4880 chromatography data handling system was used.

For all three applications home-made liners with a glass frit in the lower part were packed with Dexsil-coated Chromosorb-750 (mesh 80-100, Chrompack, Bergen op Zoom, The Netherlands). The length of the packed bed was 25-30 mm in all cases. Liners were conditioned as described elsewhere [24]. All but the speed-controlled injections were carried out manually using a 100 µl syringe. For speedcontrolled injections a speed-programmable syringe was used (Gerstel). Gas chromatographic conditions are given in the legends to the figures.

3 Results and Discussion

The principle of PTV large volume injection in the solvent split mode is schematically depicted in Figure 1. The procedure consists of three steps, injection, solvent venting, and splitless transfer. During injection and elimination of the (bulk of the) solvent the split valve is open and the temperature of the PTV injector is below the solvent boiling point (typically between 0 °C and 50 °C). The latter ensures maximum retention of the analytes inside the liner by cold trapping and solvent trapping, while the solvent is released *via* the split exit [23]. After solvent elimination the analytes retained in the liner are transferred to the GC column in the splitless mode. This involves

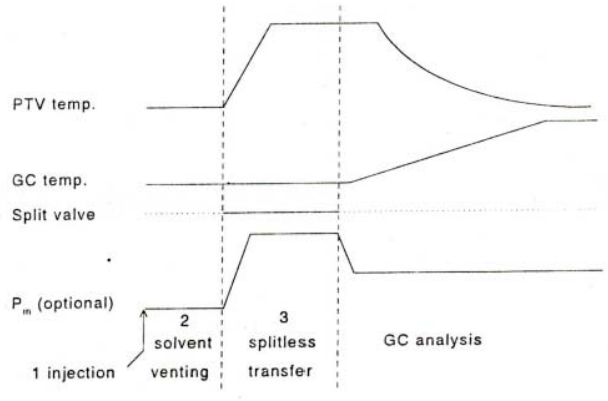

Figure 1. Principle of large volume PTV injection.

ATAS GL INTERNATIONAL B.V.
De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 Fax. +31 (0)40 254 97 79
E-mail: info@atasgl.com Internet: www.atasgl.com
Web shop: www.atasgl.com/shop

closure of the split valve and a rapid increase of the injector temperature. After the splitless transfer step the split valve is opened again to remove residual solvent vapor from the liner. The PTV injector is maintained at the high temperature for some time to remove high-boiling matrix constituents from the liner; next the heating is switched off and the injector temperature decreases. During splitless transfer the temperature of the GC oven is below the solvent boiling point to facilitate refocusing of the analytes at the top of the analytical column after the splitless transfer. Although not strictly necessary, it can be advantageous to use pressure programming if the GC is equipped with this option. In this case the inlet pressure is low during injection and solvent elimination (increases evaporation speed), high during splitless transfer (for efficient transfer and minimal thermal degradation [23,25]) and finally optimal for GC separation.

Large volume PTV injection can be optimized in three steps:

(i) *Selection of packing/determination Vmax.* For large volume injection with PTV injectors the liner has to be packed in order to prevent the sample from being pushed to the base of the injector. This would result in losses of liquid sample *via* the split exit and/or in flooding of the column inlet. The choice of packing material depends on the volatility and the polarity of the analytes. A support coated with Dexsil was earlier found to be a good general purpose packing material [24] and is used throughout this work. To keep the packing in place, liners with a glass frit in the lower part are used. A plug of glass wool is less suited for this purpose because of its activity and because there is a risk that the packing will be pushed downwards. The length of the packed bed is typically 25-30 mm.

Vmax is the maximum volume of liquid sample that can be rapidly injected without flooding the liner. To determine this volume the packed liner is inserted into the PTV injector. The column is not yet installed, *i.e.* when the carrier gas is supplied, it will leave the injector at the base. The carrier gas flow rate measured at the base of the injector is adjusted to, e.g., 250 ml/min, *i.e.* to the split flow to be applied in subsequent analyses. Now *Vmax* is determined by rapid injection of increasing amounts of solvent. Flooding of the liner is easily observed visually at the bottom of the injector. To create a safety margin, usually 10 µl less than the limiting volume found is injected. Liners packed with the same amount of packing material have been found to have rather similar *V*max values.

(ii) *Optimization of solvent elimination time.* Optimization of this parameter is straightforward [23]. A large volume injection of the pure solvent (volume < *V*max, rapid injection) is performed under conditions that will be applied during subsequent analyses. The GC oven temperature is kept above the PTV temperature and the split exit is open. After injection the solvent evaporates and the vapor is discharged v*ia* the split exit. Approx. 1% of solvent vapor will enter the column and reach the detector after the hold-up time (assuming the solvent is not retained in the column). A solvent peak is obtained with most GC detectors. The width of the solvent peak (see **Figure 2)** is a good estimate of the time needed for solvent elimination.

(iii) *Splitless transfer.* The splitless transfer is optimized by performing standard 1 µl cold splitless injections. Splitless times will generally be longer than with conventional hot splitless injection because it takes some time for the injector to reach the final temperature.

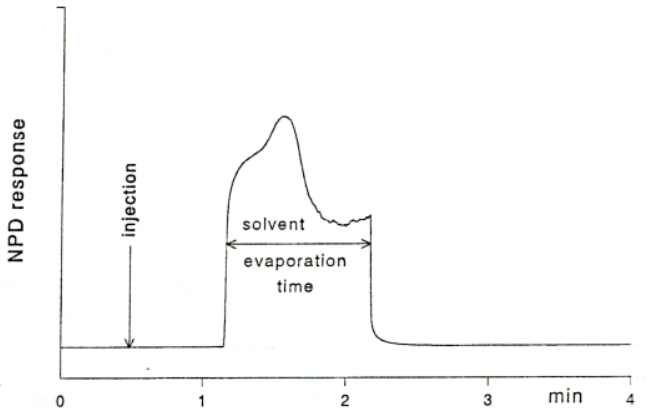

Figure 2. Determination of the solvent elimination time by using the GC detector as a monitor detector. Detector, NPD; PTV, 30°C; split flow, 250 ml/min: GC oven, 40°C; injection, 60 µl ethyl acetate.

After diluting the standard used for splitless injection *e.g.*100 times and carrying out a 100 µl injection (assuming V_{max} ~ 100 µl) the experimental analyte recoveries obtained under large volume injection conditions can be evaluated. If the sample contains volatile analytes and losses of these solutes are unacceptable, the solvent vent time should be stepwise decreased. This can be repeated until peak distortion, caused by excessive recondensation of solvent vapor in the column, occurs [23]. Optimum conditions with regard to minimum losses of volatiles exist slightly before this point.

3.1 *PTV-GC -NPD: Nitrogen and Phosphorus Containing pesticides in River Water*

Many nitrogen and phosphorus containing pesticides are relatively polar analytes and therefore sensitive to adsorption or degradation in packed liners. These analytes are therefore interesting for an evaluation of the performance of large volume PTV injection. Degradation of the pesticides in the liner was first studied by comparing 1 µl cold splitless injections with 1 µl on-column injections (standards in ethyl acetate) **(Table 1).** Pesticides sensitive to adsorption/degradation include metamidophos, mevinphos, dichlorvos, phosphamidon, metamitron, oxydemeton-methyl, and - as expected [26] - the carbamates dimethoate and vamidothion. Next, a 60 µl volume of a dilute standard in ethyl acetate was injected. The solvent vent time used was 60 s. The vent time was not very critical, not even for the more volatile pesticides. Varying the vent time from 45 to 150 s decreased the recoveries of dichlorvos and mevinphos by less than 25%. The recoveries of the polar/labile pesticides obtained with large volume injection were genera1ly higher than for the 1 µl splitless injection, despite the fact that the amount of pesticides introduced was more than ten times lower. An explanation for this is that after large volume injection part of the pesticides is located in the lower part of the packed liner which may we1l reduce thermal degradation during splitless transfer to the GC column. The relative standard deviations (RSD) were below *10%* for 22 out of the 32 polar pesticides. Not surprisingly, the ten pesticides with high RSD values included most of the above mentioned labile pesticides. It should be emphasized here that GC analysis of thermo labile compounds such as vamidothion can cause problems even when applying on-column injection.