Original Research Papers

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

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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.

Application Note No. 020

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

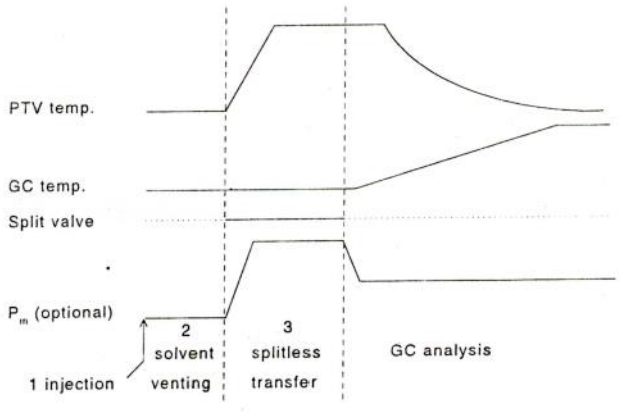

Figure 1. Principle of large volume PTV injection.

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.

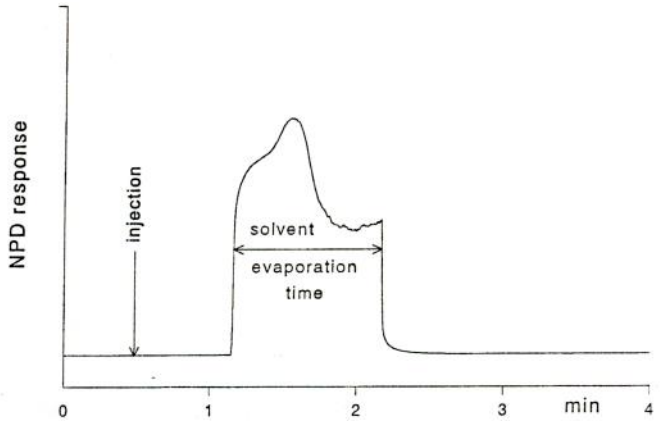

Figure 2. Determination of the solvent elimination time by using the GC detector as a monitor detector. Detector, NPD; PTV, 30°C; split flow, 250 ml/min: GC oven, 40°C; injection, 60 µl ethyl acetate.

After diluting the standard used for splitless injection *e.g.*100 times and carrying out a 100 µl injection (assuming $V_{max} \sim 100$ 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.

Table 1. Performance of large volume PTV injection in determination of nitrogen and phosphorus containing pesticides.

Compound		ng inj[c]	Rec. (%) rel. to on-column inj.[a] 1 µl	60 µl	RSD[d]	Response rel. to 60 µl standard[b] matr. 1	matr. 2	R^2 [e]
18*	degradation product of 18	–	–	–	13	(1.2)	1.9	0.9963
1	metamidophos	0.650	31	75	30	(1.2)	1.6	0.9991
2	dichlorvos	0.182	45	61	9.4	(1.1)	1.3	0.9929
3	mevinphos (*trans* + *cis*)	0.166	43	74	13	(1.2)	1.7	0.9994
4	ethoprophos	0.044	74	112	2.8	(1.0)	1.3	0.9998
5	chlorpropham	0.089	79	82	4.9	(1.0)	1.3	0.9994
6	desisopropyl atrazine	0.217	110	[f]	[f]	[f]	[f]	[f]
7	desethyl atrazine	0.217	88	98	11	(1.1)	(1.2)	0.9999
8	dimethoate	0.182	58	65	22	(1.3)	2.5	0.9994
9	simazine	0.243	93	96	3.1	(1.1)	1.1	0.9992
10	atrazine	0.220	96	100	5.7	(1.2)	1.2	0.9999
11	propazine	0.230	100	100	6.3	(1.0)	(1.1)	0.9999
12	terbutylazine	0.217	96	98	7.4	1.2	1.2	0.9998
13	phosphamidon (*trans*)	[g]	21	35	43	2.4	4.8	0.9991
14	pirimicarb	0.269	93	102	1.9	(1.0)	1.1	0.9999
15	desmetryn	0.218	100	103	4.5	(1.1)	1.2	0.9999
16	metribuzin	0.218	89	92	3.9	1.1	1.5	0.9999
17	phosphamidon (*cis*)	[g]	91	115	21	(1.5)	3.0	0.9997
18	oxydemeton-methyl	0.632	16	12	60	4.5	18	0.9981
19	prometryn	0.218	92	95	5.8	(1.2)	1.3	0.9994
20	terbutryn	0.222	99	109	3.1	(1.1)	1.2	0.9999
21	bromacil	1.020	80	91	4.7	2.0	1.2	0.9998
22	parathion-ethyl	0.110	92	132	6.0	(1.1)	1.3	0.9998
23	triadimefon	0.852	92	100	6.6	(1.0)	(1.0)	0.9999
24	cyanazine	0.217	101	91	18	(1.0)	(1.0)	0.9999
25	benzolin-ethyl	0.935	87	101	4.0	1.1	1.1	0.9999
26	penconazole	0.874	91	101	4.8	(1.0)	(1.0)	0.9999
27	chlorfenvinphos	0.196	123	151	7.5	1.4	1.4	0.9995
28	triadimenol	0.474	73	100	8.3	(1.1)	1.3	0.9998
29	vamidothion	0.305	26	12	39	3.3	15	0.9981
30	metamitron	0.817	56	58	9.5	(1.1)	1.3	0.9988
31	oxadixyl	0.826	97	99	11	(1.0)	(1.1)	0.9999
32	hexazinone	0.566	81	119	6.1	(1.0)	(1.2)	0.9999

[a] Recoveries of pesticides obtained after a 1 µl cold splitless injection (0.5-12 µg/ml) and a 60 µl injection of a standard (0.73-17 ng/ml ethyl acetate). [b] Response of pesticides in spiked river water extract relative to standard solution in ethyl acetate (0.73-17 ng/ml); matrix 1 = neutral extract (n = 2), matrix 2 = acidic extract (n = 3): value between brackets, increase not significant (t-test). [c] ng pesticide introduced with the 60 µl injection. [d] RSD values (n = 3) for 60 µl injection of standard solutions. [e] Regression coefficients after multipoint calibration (n = 9) obtained after spiking acidic river water extracts in the ranger 0.10-230 ng/ml. [f] Data not available due to co-elution wilt impurity in ethyl acetate. g) *trans* + *cis*, 0.277ng.

With real sample extracts the matrix can affect the analyte response. For several nitrogen/phosphorus containing pesticides the sample matrix has been found to enhance the response relative to standard solutions in a pure organic solvent [27,28]. The matrix constituents obviously shield active sites in the liner, thereby reducing degradation of the analytes. To study this effect for river water samples, extracts were spiked with the pesticides and analyzed. The response obtained after large volume injection was compared with that of standards of the same concentration in distilled solvent. The response ratio (matrix/distilled solvent) is given in Table 1. Matrices 1 and 2 are extracts in ethyl acetate obtained after solid-phase extraction of neutral and acidified river water, respectively. For the neutral extracts significantly higher responses were observed for eight pesticides. The effect was most pronounced for the polar/labile compounds. The effect was stronger for the acidic extracts (significantly higher response for most compounds) which can be attributed to the presence of larger amounts of matrix constituents (humic acids). The matrix induced liner deactivation is only temporary, i.e. lower ('normal') responses are again observed when analyzing standard solutions. The repeatability for injections of real sample extracts was slightly better than obtained with injection of standards (mean RSD value below 10%). Within each group (standard, neutral, and acidic extracts) the linearity of the response obtained after large volume injection (concentration range in the extract 0.10-230 ng/ml) was excellent (e.g. for acidic extracts see Table 1). This means that for optimum accuracy with some of the polar/labile pesticides, quantification should be done by using calibration curves measured in a matrix similar to that of the sample. The detection limits obtained with the NPD were 2 x 10^{-13} g N/s and 5 x 10^{-14} g P/s for nitrogen-containing pesticides and phos-

Figure 3 shows chromatograms obtained after 60 µl injections of a river water blank and a spiked (0.3-7.2 ng/ml) extract. Sharp peaks are obtained for all pesticides. Noij *et al.* [8] applied large volume injection for the same type of compounds using concurrent solvent evaporation with a loop-type interface. The use of a loop-type interface was preferred over the on-column interface because of its ruggedness. However, with that approach the peaks of pesticides eluting before ethoprophos were severely broadened.

3.2 *PTV-GC -MS: Polycyclic Aromatic Hydrocarbons in River Sediment*

Recently, Rebbert *et al.* [29] reported a procedure for the determination of PAHs in river sediment. The method involves Soxhlet extraction followed by evaporative concentration of the extract to *ca.* 1 ml (Method 1, **Figure 4).** The concentrated extract is applied to a 30 cm x 9 mm i.d. amino column for fractionation of aliphatic hydrocarbons and PAHs. The PAH fraction is evaporatively concentrated to 1 ml and analyzed by injecting 1 µl (on-column) into a GC-MS system.

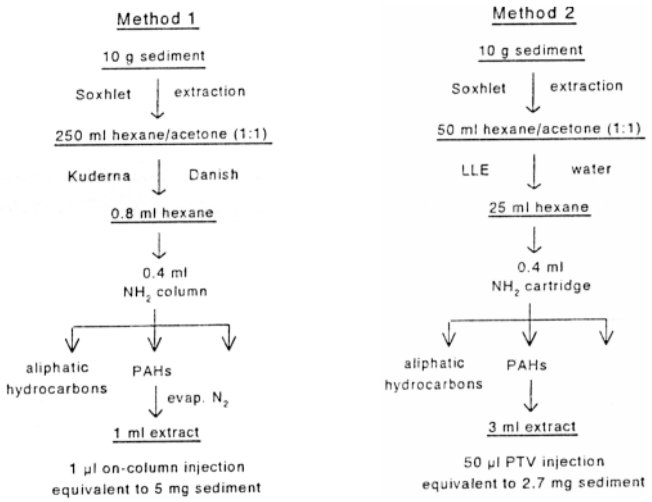

Figure 4. Analytical schemes for the determination of PAHs in river sediment. Method 1 taken from ref. 29; Method 2, this work.

Figure 3. GC-NPD chromatograms obtained after 60 µl injections of a river water blank (lower trace) and a spiked extract (upper trace) (concentration in the extract, 0.3-7.2 ng/ml ethyl acetate). Peak numbers correspond with those in Table 1. PTV: initial temperature 30 °C, after 60 s solvent venting í 8 °/*s* to 300 °C (10 min). Split flow 250 ml/min. GC: 25 m x 0.32 mm. 0.17 µm Ultra-2; Pin 85 kPa; splitless time 1.5 min: temperature program 40 °C (2 min)

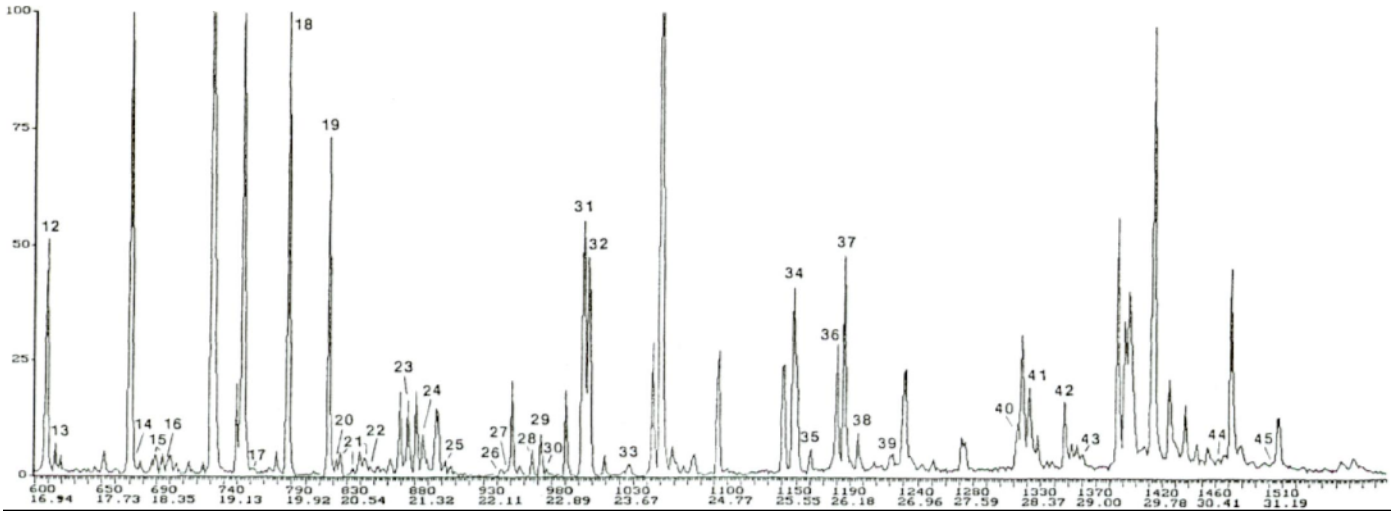

Figure 5. GC-MS (full scan) chromatogram obtained after a 50 µl injection of a river sediment extract obtained by Method 2 (see Figure 4). Split flow 250 ml/min; PTV initial temperature 30 °C, after 45 s solvent venting í 3 °/s to 340 °C (10 min); GC: 25 m x 0.25 mm i.d.. 0.12 µm CP-Sil-5-CB MS, *Pin* 195 kPa; splitless time 4.0 min, temperature program 40 °C (4.5 min) í 10 °/min í 300 °C (10 min). See Table 2 for peak assignment.

This was verified by fractionation of a standard mixture of alkanes and PAHs. The main advantage of the use of the amino cartridge is that the volume of the PAH fraction is only 3 ml and, therefore, no further evaporative concentration is necessary. By injecting a large volume of the eluate into the GC-MS, the overall sensitivity of the method is similar to that of the conventional method. The chromatogram obtained is shown in **Figure 5.** Unambiguous identification of the PAHs by their mass spectra only was not always possible because the spectra of some of the PAHs are very similar. In these cases the retention times (or elution order) are needed for identification. Retention data were obtained by injecting a standard (16 PAHs). In other cases retention data from literature [30] were used. More than 40 PAHs could be provisionally identified **(Table 2).**

3.3 PTV-GC-ECD: Organochlorine Pesticides and PCBs in River Water

The third application concerns the determination of organo-chlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in river water. In routine methods for OCP/PCB determination the analytes are typically extracted from 1 L of river water with 200 ml of petroleum ether. The extract is concentrated to 1 ml by Kudema-Danish evaporation. Then off-line clean-up is performed on an alumina column. The analytes are eluted with 5 ml of petroleum ether which is concentrated to 1 ml. The extract is analyzed by on-column injection of 1.5 µl into the GC-ECD system. Our aim is to (i) replace the Kuderna-Danish evaporative concentration by large volume PTV injection and (ii) evaluate the possibility of on-line clean-up.

OCPs like endrin and *p.p'*-DDT are sensitive to adsorption/thermal degradation in packed liners. This aspect was evaluated by comparing the responses obtained after 2 µl cold splitless injections (10 pg/µl) using an empty liner with a glass frit and the Dexsil packed liner. The empty liner with glass frit was used as a reference because in earlier work little or no degradation was observed with such liners [23,25]. Recoveries with the packed insert were better than 75% for all OCPs which is acceptable regarding the small amount of analyte introduced (20 pg of each pesticide).

With the PTV injector used here 100 µl of petroleum ether could be rapidly injected without flooding the liner. The time needed for evaporation of the solvent was 30 s. **Figures 6A** and **B** show chromatograms obtained after a 1 µl cold splitless injection and a 100 µl injection of a dilute standard, respectively. Apart from some extra peaks (contamination in the sample) the chromatograms are almost identical. No losses of analytes occurred during solvent elimination, not even for the relatively volatile hexachlorobutadiene. Actually, after venting for 45 s recoveries were still quantitative and after 3 min only hexachlorobutadiene was partly lost.

Table 2. PAHs identified from a river sediment sample using PTV-GC-MS after treatment to Method 2.

Peak No.	t_r (min)	Mol.wt.	Name	Concentration in sediment (µg/g)
1	9.73	128	naphthalene	0.023
2	11.39	142	methylnaphthalene	
3	12.89, 13.28	156	dimethylnaphthalene	
4	13.36	152	acenaphthylene	0.003
5	13.76	154	acenaphthene	0.030
6	14.19	168	dibenzofuran	
7	14.44	170	trimethylnaphthalene	
8	14.96	166	fluorene	0.052
9	15.47	182	methyldibenzofuran	
10	16.57	180	9*H*-fluoren-9-one	
11	16.79	184	dibenzothiophene	
12	17.11	178	phenanthrene	0.63
13	17.20	178	anthracene	0.11
14	18.10	198	methyldibenzothiophene	
15	18.32–18.54	192	methylphenanthrenes/methylanthracenes	
16	18.49	190	4*H*-cyclopenta[*d,e,f*]phenanthrene	
17	19.16	212	2.8-dimethyldibenzo[*b,d*]thiophene	
18	19.93	202	fluoranthene	0.85
19	19.39	202	pyrene	0.60
20	19.47	204	1-phenylnaphthalene	
21	19.50, 19.64, 19.78	218	benzo[?]naphtho[?]furans	
22	19.86	220	trimethylphenanthrene	
23	21.05, 21.27	216	benzo[?]fluorenes	
24	21.41	234	retene	
25	21.44, 21.70	216	methylpyrenes	
26	22.33	230	dimethylpyrene	
27	22.44	230	7*H*-benzo[*d,e*]anthracen-7-one	
28	22.69	234	benzo[*b*]naphtho[1,2-d]thiophene	
29	22.78	226	benzo[*g,h,i*]fluoranthene	
30	22.89	234	benzo[?]naphtho[?]thiophene	
31	23.27	228	benzo[*a*]anthracene	0.38
32	23.33	228	chrysene/triphenylene	0.44
33	23.79–24.36	242	methyl-228	
34	25.70	252	benzo[*x*]fluoranthenes (x = *b, j,* and *k*)	0.68
35	25.89	252	benzo[*a*]fluoranthene	
36	26.20	252	benzo[*e*]pyrene	0.27
37	26.32	252	benzo[*a*]pyrene	0.38
38	26.46	252	perylene	
39	26.69–27.09	266	methyl-252	
40	28.23	278	3,4-dihydrobenzo[*g,h,i*]perylene	
41	28.41	276	indeno[1,2,3-*c,d*]pyrene	0.28
42	28.84	276	benzo[*g,h,i*]perylene	0.21
43	29.03	276	antanthrene	
44	30.62	302	naphtho[1,2,3,4-*d,e,f*]chrysene	
45	31.25	300	coronene	

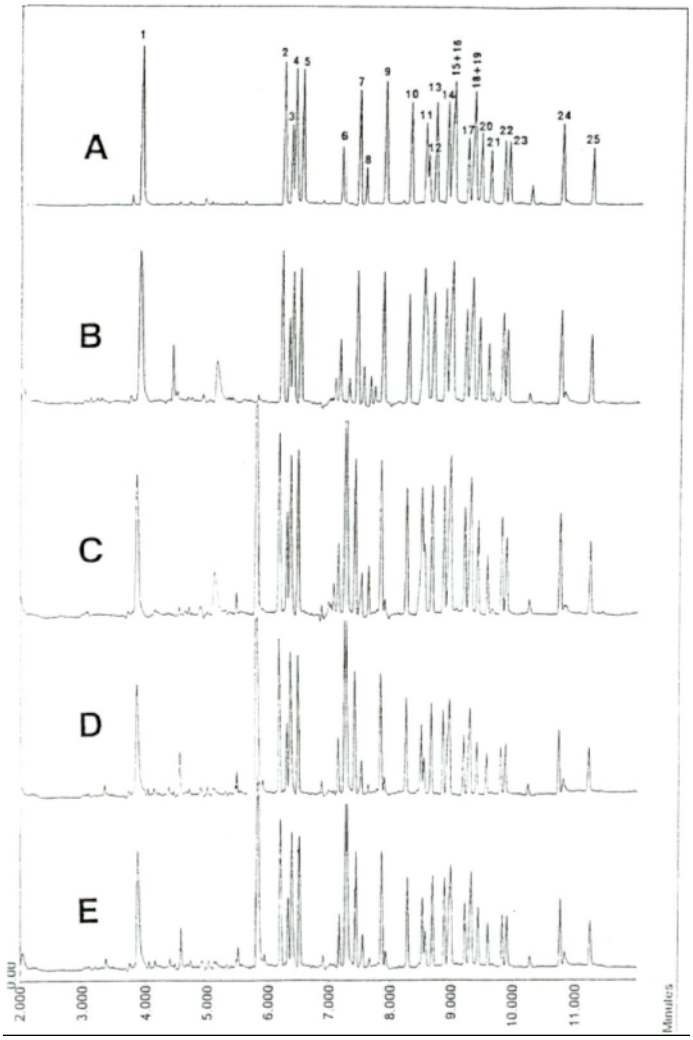

Figure 6. Comparison of different injection modes in large volume PTV injection-GC-ECD. Sample: OCPs and PCBs in petroleum ether (peak numbers correspond with those in Table 3). Injections: (A) cold splitless, 1 µl of 50 ng/ml. (B) 'at-once': 100 µl of 0.5 ng/ml. solvent vent time 30 s. (C) repetitive: 3 x 100 µl of 0.17 ng/ml, solvent vent time 30 s after each injection, (D) speed controlled: 300 µl of *ca.* 0.17 ng/ml at 200 µl/min. splitless transfer is started immediately after completion of sample introduction, (E) Speed controlled: 300 µl of *ca.* 0.17 ng/ml at 300 µl/min, splitless transfer is started 30 s after completion of sample introduction. PTV initial temperature 40 °C. after solvent elimination í12˚/s í 300 °C (till end of run): GC: 25 m x 0.31

On-line Clean-up. The clean-up over alumina applied in the sample pretreatment procedure serves two purposes. First it allows the use of the extraction solvent as obtained from the supplier, *i.e.* distillation before use is not necessary. Secondly it removes many of the coextracted matrix compounds which results in a cleaner chromatogram. It is possible to carry out the clean-up in an on-line fashion by using the set-up schematically depicted in **Figure 7.** First the capacity of the alumina column for retaining contaminants present in the river water extract was examined. For this the pump was filled with extract. The valve was maintained in the load position (shown in Figure 7). After rinsing the alumina column with 200 µl of extract the next 100 µl were rapidly (2 ml/min) introduced into the PTV-GC system for GC analysis. Then 1 ml of extract was pumped through the precolumn and again 100 µl were analyzed. After pumping more than 4 ml of extract through the precolumn the number of contaminants in the GC-ECD chromatogram started to increase due to breakthrough. Next, the volume needed for complete transfer of the organochlorine compounds from the loop *via* the alumina column into the PTV was determined. For this the pump was filled with petroleum ether and the loop with an OCP standard solution. A total of 400 µl (speed 200 µl/min) were needed for quantitative transfer (50 µl void volume + 130 µl sample volume + 220 µl petroleum ether). This means that the alumina column has to be exchanged after some ten runs.

Figure 8 illustrates the performance of the total analytical set-up inclusive of the on-line clean-up, and applied to a spiked river water extract. The chromatogram of Figure 8A was obtained after a 1 µl cold splitless injection of a 5 ng/ml standard. At this level contaminants in

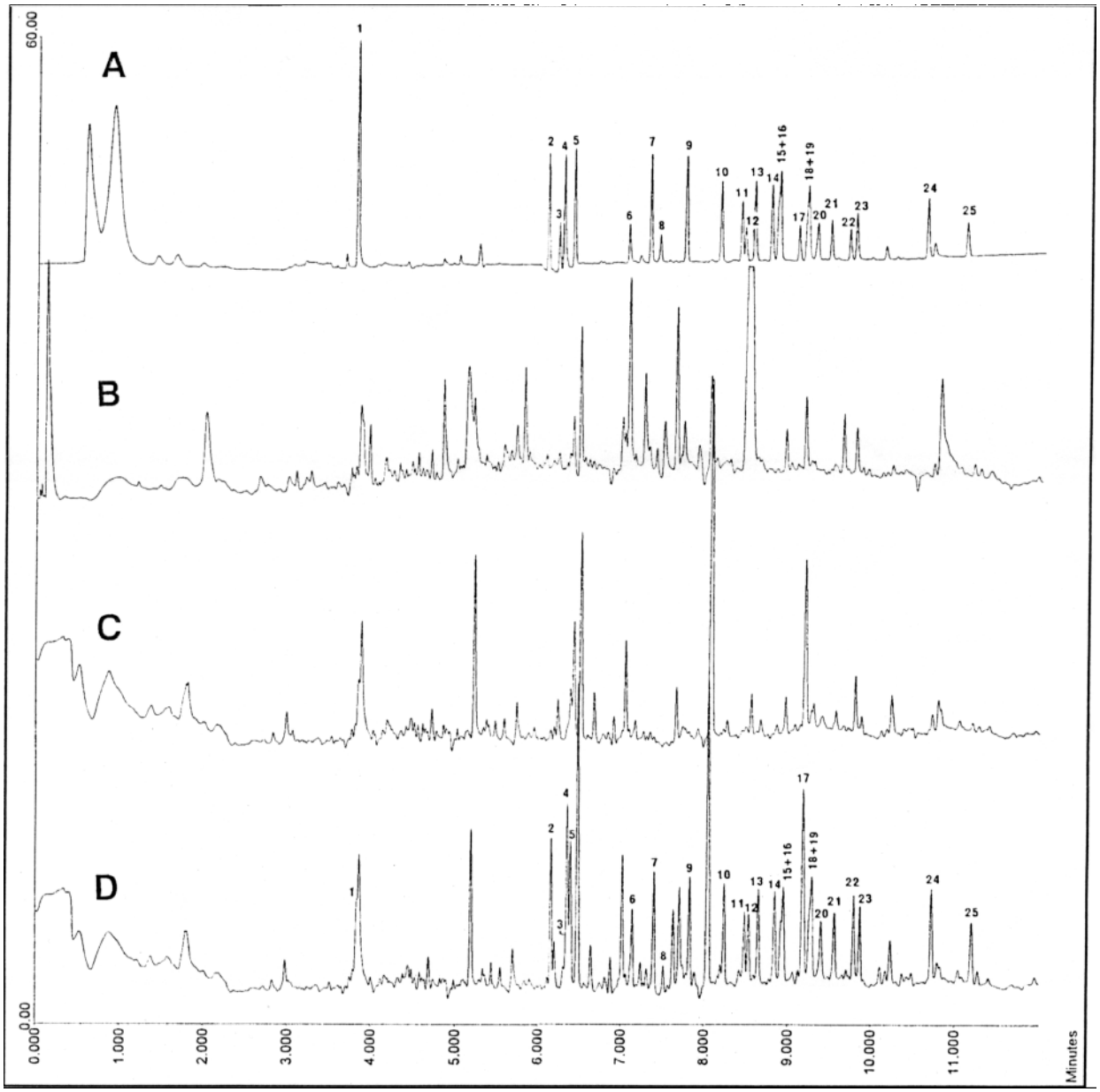

Figure 8. GC-ECD chromatograms obtained after (A) 1µl cold splitless injection of a 5 ng/ml standard. (B) 100 µl injection of a river water extract in petroleum ether before clean-up. (C) on-line clean-up-GC, sample: 130 µl of river water extract, total volume transferred to the PTV is 400 µl at 200 µl/min. (D) as (C) but extract spiked with 50 pg/ml of OCPs and PCBs; for peak identification, see Table 3. Other conditions, see Figure 6.

Table 3. Analytical data on on-line clean-up-PTV-GC analysis of river water extracts (Cf. Figure 8).

No.	Compound	R^{2} [a]		
1	hexachlorobutadiene	–	–	[d]
2	α-hexachlorocyclohexane	0.9977	1.0	5
3	β-hexachlorocyclohexane	0.9840	20	[d]
4	hexachlorobenzene	0.9947	1.5	10
5	γ-hexachlorocyclohexane	0.9986	7.5	5
6	PCB 28	0.9972	1.9	[d]
7	heptachlor	0.9975	2.3	5
8	PCB 52	0.9971	4.2	25
9	aldrin	0.9990	6.6	10
10	heptachlor-epoxide	0.9980	3.1	10
11	*o,p′*-DDE	0.9996	4.6	15
12	PCB 101	0.9968	5.6	[d]
13	α-endosulfan	0.9992	3.2	10
14	*p,p′*-DDE	0.9993	5.3	10
15	dieldrin	[e]	[e]	[e]
16	*o,p′*-DDD	[e]	[e]	[e]
17	endrin	0.9981	5.8	[d]
18	*p,p′*-DDD	[e]	[e]	[e]
19	*o,p′*-DDT	[e]	[e]	[e]
20	PCB 118	–	–	15
21	PCB 153	0.9982	2.9	15
22	*p,p′*-DDT	0.9929	13	[d]
23	PCB 138	0.9999	6.6	10
24	PCB 180	0.9977	7.7	10
25	mirex	0.9998	5.4	15

[a] R^2 = regression coefficient obtained after multipoint calibration (n = 5); concentration in the extract: 50-500pg/ml. [b] RSD = relative standard deviation (n = 3) for 200 pg/ml extracts. [c] Estimated detection limit of OCP or PCB in the extract. [d] data not available due to co-elution with matrix compound. [e] data not available due to co-elution with other OCP or PCB.

the extract interfere with the determination of many of the OCPs and PCBs as can be seen from the chromatogram obtained after a 100 µl injection of the extract before clean-up (Figure 8B). Chromatograms obtained after on-line clean-up-GC of a river water blank and a spiked extract (50 pg/ml) are shown in Figures 8C and 8D, respectively. The clean- up clearly reduces the number of interfering matrix compounds although some five peaks, originating from the petroleum ether, have increased due to the larger volume injected. Despite the clean-up step interfering peaks from the matrix still limit the sensitivity of the method for a number of OCPs and PCBs (e.g. hexachlorobutadiene, β-HCH, PCB 101, endrin). At the low pg/ml level, more selectivity is required for reliable quantification of all organochlorine compounds.

The linearity of the response obtained with the on-line clean-up-PTV-GC system was evaluated by analyzing extracts spiked at a concentration of 50-500 pg/ml. Regression coefficients as well as RSD values are given in Table 3. Taking into account the very low concentration level, the analytical data can be considered to be satisfactory. The detection limits depended on analyte response and matrix interference and typically were in the low pg/ml region.

4 Conclusions

Large volume PTV injection is a simple and rugged technique for large volume sample introduction in capillary gas chromatography. Optimization is straightforward and no special instrumentation is required which enables the implementation of large volume injection in routine laboratories. Maintenance consists of periodical replacement of the septum and the liner. The packed liner can be used for at least 70-100 large volume injections. The technique is also applicable to more polar and volatile analytes and is compatible with several commonly used detectors. However, with some of the polar nitrogen/phosphorus pesticides calibration curves should be measured in a matrix similar to the sample to obtain good accuracy.

Acknowledgment

The authors wish to thank Mrs. M. van der Kooi (KIWA) and Mr. Bijlsma/Mr. Hoofd (WRK) for supplying the river water extracts and for stimulating discussions.

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Ms received: August 25,1995:

Accepted: November 9, 1995