ELSEVIER

Journal of Chromatography A, 805 (1998) 237–247

JOURNAL OF CHROMATOGRAPHY A

Retention model for sorptive extraction–thermal desorption of aqueous samples: application to the automated analysis of pesticides and polyaromatic hydrocarbons in water samples

Erik Baltussen[a,*], Frank David[b], Pat Sandra[a,c], Hans-Gerd Janssen[a], Carel A. Cramers[a]

[a]*Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands*
[b]*Research Institute for Chromatography, Kennedypark 20, B-8500 Kortrijk, Belgium*
[c]*University of Gent, Department of Organic Chemistry, Krijgslaan 281 S4, B-9000 Gent, Belgium*

Received 21 July 1997; received in revised form 3 December 1997; accepted 31 December 1997

Abstract

In this report, an automated method for sorptive enrichment of aqueous samples is presented. It is based on sorption of the analytes of interest into a packed bed containing 100% polydimethylsiloxane (PDMS) particles followed by thermal desorption for complete transfer of the enriched solutes onto the GC column. Compared to other solvent-less sample preparation techniques for water samples, several improvements can be noted of which the most obvious are an enhanced sensitivity and improved blanks. Moreover, degradation products formed from the PDMS material can easily be identified with the use of a mass spectrometric detector. As these products contain silicone, they do not interfere with the target solutes (pesticides, PAHs). In this report a theory model is derived which allows calculation of breakthrough volumes from octanol–water partitioning coefficients ($K_{O/W}$). Alternatively, the $K_{O/W}$ value required for complete retention can be calculated using only the sample volume and trap specific parameters. For a sample volume of 10 ml, theory predicts a required log $K_{O/W}$ of 1.77 for the trap used here which was found to be in good agreement with experimental results. For the most apolar solutes, with a log $K_{O/W}$ in excess of seven, poor recoveries were found. This is most likely due to adsorption of these apolar solutes in the system. With the current set-up, detection limits are in the order of 10 ng/l using mass spectrometric detection in the full scan mode. © 1998 Elsevier Science B.V.

Keywords: Retention models; Sorptive extraction; Thermal desorption; Pesticides; Polynuclear aromatic hydrocarbons; Triazines

1. Introduction

Trace analysis of organic micropollutants in water by gas chromatography–mass spectrometry (GC–MS) is basically hindered by two problems. The first problem is that the water sample is generally too dilute for direct injection, i.e., the water sample has to be concentrated. The second problem is that water is not compatible with most GC stationary phases and therefore its transfer onto the GC column should be prevented. To overcome these problems a number of different methods for phase switching, i.e., transferring the analytes from a large volume of water to a small volume of an organic solvent have been developed.

The most popular methods for phase switching are

*Corresponding author.

0021-9673/98/$19.00
PII S0021-9673(98)00011-9

liquid–liquid extraction (LLE) [1–3] and solid-phase extraction (SPE) [4,5]. Nowadays, LLE is more and more replaced by SPE because the latter technique requires less solvent, is faster, easier to automate and can easily be connected on-line to both GC as well as high-performance liquid chromatography (HPLC) systems [6]. Although SPE has clear advantages over LLE it still suffers from some disadvantages. The most important one being the fact that the retention behavior (breakthrough volume) can depend on both analyte and matrix concentration.

More recently, several solvent-less extraction techniques were proposed in the literature. One of these methods uses SPE with thermal desorption (SPE–TD) instead of liquid desorption [7–9]. The major advantage of this approach is that organic solvents are completely banned. It was, however, found to be difficult to find adsorbents with both favorable adsorption and thermal desorption characteristics. For practical purposes, Tenax appeared to be the best compromise for SPE–TD.

A second approach is to trap the analytes in an open-tubular capillary column coated with cross-linked polydimethylsiloxane (PDMS) as the stationary phase [10,11]. The water sample can be pumped through this column and analytes present in the water sample will partition into the PDMS phase. After a drying step the analytes can be thermally desorbed and are (cryogenically) refocused onto the head of the analytical column. Alternatively, both extraction and GC can be performed in the same column [12]. Advantages of using an open tubular trapping (OTT) column coated with PDMS are the good thermal stability, high degree of inertness and well documented retention properties. However, due to a number of reasons OTT has never gained widespread acceptance. First, as the amount of stationary phase per trap length is low, long traps are necessary. Second, long traps generally require a second GC oven for thermal desorption and allow only low sampling flow-rates. Finally, OTTs were only found to be suitable for very apolar compounds (e.g., polyaromatic hydrocarbons, PAHs), polar solutes are virtually not retained by the thin PDMS layer.

The third approach is called solid-phase microextraction (SPME) which has recently been evaluated for the extraction of a wide variety of pesticides [13,14], PAHs and polychlorinated biphenyls (PCBs) [15] and other solutes from water samples. SPME is based on the sorption (partitioning) of the analytes present in the water sample into a layer of stationary phase coated onto a syringe-like device. The most commonly used stationary phases for SPME are PDMS [13] and polyacrylate [16]. The main advantage of this method is its simplicity; besides the SPME device only standard GC instrumentation is required. The main disadvantage is that since this method is based on a partitioning equilibrium, extraction is in some cases incomplete which renders quantitation difficult. Each analyte should be individually calibrated and the extraction yield should be determined for each solute. Also, sensitivity is moderate in those cases where extraction is incomplete. SPME is especially suited as a rapid screening method, although for certain (e.g., very apolar) solutes long extraction times are necessary, even when stirring is applied.

Recently, a new approach for the analysis of semi-volatiles in aqueous samples called sorptive extraction–thermal desorption (SE–TD) was proposed by Baltussen et al. [17]. Here, an extraction cartridge containing 100% PDMS particles was used as the retaining phase. After applying the water sample, the PDMS-packed cartridge has to be dried. Subsequently, the PDMS trap can be directly thermally desorbed and the analytes released are transferred onto the GC column. The system was shown to be applicable for the analysis of selected PAHs and organochlorine pesticides (OCPs) in tap and river water samples. This approach combines several of the advantages of the three solvent-less preconcentration methods described above. Compared to Tenax which is used in SPE–TD, the PDMS material has the advantage that degradation products from the (ad)sorbent can readily be identified with the use of a mass spectrometric detector as they generate characteristic silicone mass fragments. Therefore, false positives are unlikely to occur. A significant improvement compared to OTT is the fact that an increased amount of stationary phase is present in the trap. Therefore, the sample capacity is significantly increased. Moreover, the packed bed allows the use of higher sampling flow-rates (1–10 ml/min) so that sampling times can be less than 10 min for sample volumes up to 100 ml. A disadvantage compared to OTT is that drying of the trap, which is extremely

fast in the case of an OTT, is rather long in SE–TD. Relative to SPME, increased sensitivity and improved quantitation is attained since all analytes are transferred to the analytical system rather than only a fraction governed by the distribution coefficient.

In this paper, an automated system for SE–TD is described which allows fully automated sample preparation for water samples. A theoretical model is presented which allows prediction of breakthrough volumes from octanol–water partitioning coefficients ($K_{O/W}$). This enables the user to predict the retention of solutes, and thus the suitability of the system for a certain application without any experiments. The new system was used to expand the previous study on the extraction of OCPs and PAHs from water. Compared to the previously reported results, the full range of PAHs and OCPs was included. Additionally, several triazine herbicides were also investigated. Retention characteristics of the PDMS trap for the analytes under investigation were compared with the retention behavior predicted by theory. Agreement and dissimilarities between theory and experiment are discussed in detail.

2. Theory

In recent work, we developed a theoretical model which allows estimation of retention and breakthrough volumes of selected components on polydimethylsiloxane traps from $K_{O/W}$ values [18]. This model was applied to the HPLC–UV and HPLC–MS analysis of several phenylurea herbicides from aqueous samples. The herbicides investigated in that work are relatively polar analytes, and can easily be lost due to insufficient retention of the PDMS trap. In this report a wide range of analytes is studied, ranging from very polar (deisopropylatrazine) to very apolar (indeno[123*cd*]pyrene).

As has been shown previously, the retention volume of an analyte can be calculated by [18]:

$$V_r = V_0\left(1 + \frac{K_{O/W}}{\beta}\right) \quad (1)$$

where V_r is the retention volume, V_0 is the trap void volume, $K_{O/W}$ is the octanol–water partitioning coefficient and β is the phase ratio of the trap. For a given trap, V_0 and β can be determined experimentally [19]. $K_{O/W}$ values can be found in literature for numerous compounds [20,21]. Once the retention volume is known, breakthrough volumes (accepting 5% sample loss) can be calculated according to the equations derived by Lövkvist and Jönsson [22]:

$$V_b = V_r\left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2}\right)^{-1/2} \quad (2)$$

where V_b is the 5% breakthrough volume and N is the plate number of the trap. Plate numbers can be calculated from the Knox equation, as was previously shown in Refs. [18,19]. Therefore, with the equations presented here, breakthrough volumes can be predicted using only literature data and trap specific parameters as input data. Using the equations described above, the required $K_{O/W}$ for quantitative trapping can be expressed as:

$$(K_{O/W})_{req} = \beta\left(\frac{V_S}{V_0\left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2}\right)^{-1/2}} - 1\right) \quad (3)$$

where V_S is the sample volume. From Eqs. (2) and (3) it can be rapidly predicted whether the SE–TD method will give quantitative trapping for a given solute. In this way eliminating the need for trial and error method development.

The equations shown above describe analyte losses due to incomplete trapping from the water sample. In principle, analytes can also be lost during drying of the PDMS phase. Since no losses of the analytes under investigation due to volatility was observed, equations describing this process are not shown here.

3. Experimental

3.1. Test solutes

In this study, three groups of test analytes were selected. An extended list of PAHs and OCPs was included. The full range of US Environmental Protection Agency (EPA) priority PAHs and OCPs was used. The analytes monitored are listed in Table 1. For both classes of analytes, certified standard solutions were obtained from Supelco (Bellefonte,

Table 1
Composition of the test mixture (master standard) containing PAHs, organochlorine pesticides (OCPs) and triazine herbicides (TRIAs) in methanol

No.	Component	Class	Concentration (μg/l)	Quant. ion	Qual. ion	Log $K_{O/W}$	Recovery (%)
1	Naphthalene	PAHs	4	128	101	3.01 [21]	76
2	Acenaphthylene	PAHs	8	153	152	4.07 [21]	128
3	Acenaphthene	PAHs	4	153	152	3.92 [21]	120
4	Fluorene	PAHs	0.4	166	167	4.18 [21]	108
5	Deisopropylatrazine	TRIAs	2	158	145	1.15 [20]	0.0
6	Desethylatrazine	TRIAs	2	172	174	1.51 [20]	1.5
7	α-BHC	OCPs	4	181	183	3.81 [20]	112
8	Simazine	TRIAs	2	186	201	2.06 [20]	75
9	Atrazine	TRIAs	2	200	215	2.40 [20]	76
10	β-BHC	OCPs	4	181	183	3.80 [20]	126
11	Propazine	TRIAs	2	214	229	2.91 [20]	78
12	γ-BHC	OCPs	4	181	183	3.72 [20]	125
13	Terbutylazine	TRIAs	2	173	214	3.06 [20]	127
14	Phenanthrene	PAHs	4	178	176	4.46 [21]	120
15	Anthracene	PAHs	4	178	176	4.45 [21]	116
16	δ-BHC	OCPs	2	181	183	4.14 [20]	120
17	Sebutylazine	TRIAs	2	200	202		76
18	Metribuzin	TRIAs	2	198	182	1.70 [20]	4.6
19	Heptachlor	OCPs	4	272	274	5.27 [20]	114
20	Prometryn	TRIAs	2	184	226	3.34 [20]	80
21	Terbutryn	TRIAs	2	226	185	3.72 [20]	79
22	Aldrin	OCPs	2	263	293	6.50 [20]	128
23	Cyanazine	TRIAs	2	225	227	1.66 [20]	6.5
24	Fluoranthene	PAHs	0.8	202	200	5.53 [21]	108
25	Heptachlor-epoxide	OCPs	4	351	388	5.40 [20]	129
26	Pyrene	PAHs	0.4	202	200	5.32 [21]	111
27	Endosulfan I	OCPs	4	241	277		128
28	*p,p′*-DDE	OCPs	4	246	248	5.69 [20]	103
29	Dieldrin	OCPs	4	263	277	4.54 [20]	108
30	Endrin	OCPs	4	263	281	4.56 [20]	107
31	Endosulfan II	OCPs	4	159	195		112
32	*p,p′*-DDD	OCPs	4	235	237	4.28 [21]	101
33	Endrin-aldehyde	OCPs	4	345	347		78
34	Endosulfan-sulfate	OCPs	4	272	387		117
35	*p,p′*-DDT	OCPs	4	235	237	6.38 [20]	121
36	Endrin-ketone	OCPs	4	317	281		101
37	Benz[*a*]anthracene	PAHs	4	228	226	5.61 [21]	106
38	Chrysene	PAHs	4	228	226	5.61 [21]	105
39	Methoxychlor	OCPs	4	274	212	3.31 [20]	77
40	Benz[*b*]fluoranthene	PAHs	0.8	252	250	6.57 [21]	108
41	Benz[*k*]fluoranthene	PAHs	0.4	252	250	6.84 [21]	108
42	Benz[*a*]pyrene	PAHs	0.4	252	250	6.04 [21]	101
43	Indeno[123*cd*]pyrene	PAHs	0.4	276	274	7.66 [21]	25
44	Dibenz[*ah*]anthracene	PAHs	0.8	278	276	7.97 [21]	20
45	Benz[*ghi*]perylene	PAHs	0.8	276	274	7.23 [21]	23

Concentrations are those in the spiked water sample (Fig. 5) and recoveries are at this level.

PA, USA). These were diluted with methanol. Additionally, a test mixture containing 11 triazine herbicides (TRIAs) was prepared in methanol at a concentration of 1000 ppm. The three mixtures were combined into one mixture (master standard) which was used for all experiments. The exact composition

of this mixture is listed in Table 1. Spiked tap water sample was prepared by adding 10 μl of the master standard to 95 ml of tap water (to which 4.99 ml of methanol was added). The resulting concentrations are listed in Table 1.

3.2. PDMS cartridges

The PDMS particles were prepared from Silastic® silicone laboratory tubing (Dow Corning, Midland, MI, USA) according to the procedure described by Baltussen et al. [19]. The particles were sieved into the range 240–400 μm (average $d_p = 320$ μm). In the present work, a novel trap design was used. The starting dimensions of the PDMS extraction cartridges are: 177.8 mm×4 mm I.D.×6 mm O.D. Since this cartridge can only be partially filled, a relatively large empty volume remains. This caused problems during the drying step. To facilitate drying of the packed PDMS bed, the extraction tube was narrowed on the end were no PDMS is present. The inner diameter in this section of the tube was reduced to 0.8 mm. An illustration of the new trap design is shown in Fig. 2.

The glass tube was filled with 339 mg of the PDMS phase. This results in a bed length of 71 mm. The phase ratio of the trap is 0.85 and V_0 is 0.41 ml. To keep the PDMS bed in place two plugs of knitted Silastic® tubing were pushed onto the bed. Thus, a packed PDMS extraction cartridge is obtained which contains no active sites since neither glasswool nor an active adsorbent or support material is present. In fact, the extraction cartridge consists only of the retaining silicone phase and the glass wall, hence degradation of the analytes is minimized.

3.3. Instrumental set-up

The instrumental set-up described previously [17], was modified to allow automated operation. It consisted of a Gerstel TDS-2 thermodesorption system (Gerstel, Mülheim a/d Ruhr, Germany) mounted on an HP 6890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA). A CIS-4 PTV injector (Gerstel) was used for cryogenic focusing of the thermally released analytes. For full automation of the total procedure, a TDS on-line rack (Gerstel) was used. This is a modification of the existing TDS-autosampler (Gerstel) that enables automated SE–TD of water samples. In Fig. 1 a schematic representation of the thermodesorption system and the TDS on-line rack is shown. In Fig. 2 the system used for loading the samples onto the cartridge and for the external drying step is shown. The combined set-up shown in Figs. 1 and 2 is controlled by the Gerstel controller. One of the most important modifications necessary for reliable operation is the backflush adapter installed directly at the bottom of the CIS-4 cryotrap. During the internal drying step, when water vapor is exiting the PDMS cartridge, this water vapor is prevented from entering the GC column by applying a gas pressure at the backflush line that exceeds the pressure of the carrier gas. In this way, both the cryotrap and the transfer line are backflushed. The combined carrier gas flow and backflush gas flow exit via split exit 1.

For all experiments an HP-5MS column of 30 m×0.25 mm I.D., film thickness 0.25 μm was used. The GC program started at 40°C with a 3 min hold. The temperature was then programmed at a rate of 10°C/min to 325°C. An HP5972 mass selective detection (MSD) system was used in the full scan mode scanning from 40–400 u at a speed of 2.2 scans/s.

3.4. Sampling program

Here, the sampling program used for automatic sorptive enrichment/thermal desorption of water samples is described. Details of the precise procedure for loading the water sample, drying and transfer of the components to the GC column are listed in Table 2. At the start of the sampling program, the TDS-2 unit contains an empty glass tube. At this time, the TDS on-line rack contains a PDMS filled tube. First, the PDMS cartridge is conditioned with 10 ml of HPLC grade water. Then, the water sample is loaded at a flow-rate between 1 and 10 ml/min. Next, the cartridge is washed with HPLC grade water to remove interfering substances. Now, the PDMS cartridge has to be dried. It is very important that the cartridge is dried to full dryness. Failure to do so can result in distorted analyses. The first part of the drying step is carried out outside the TDS thermal desorption oven while the cartridge is still in the TDS on-line rack (external drying).

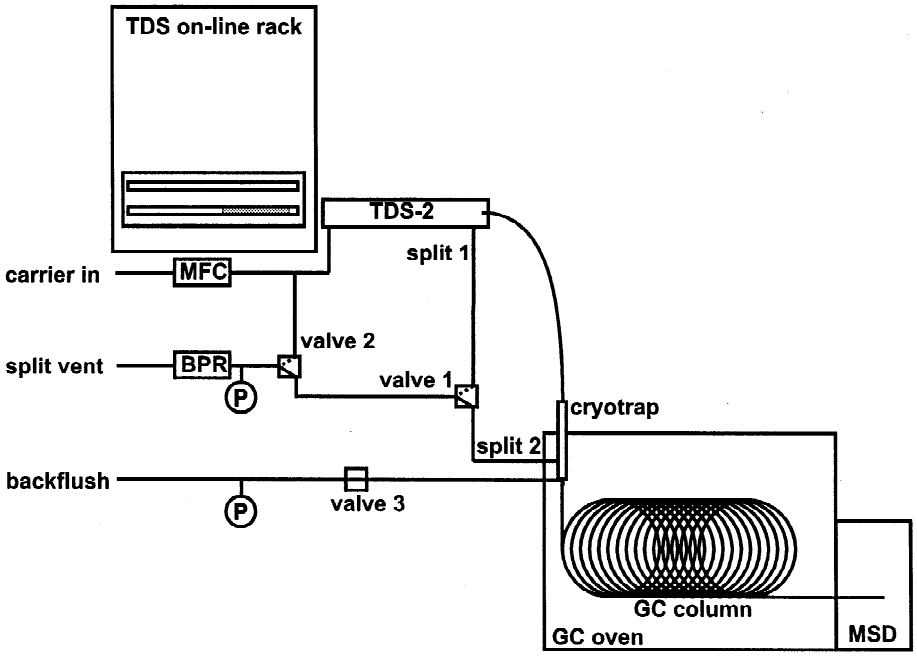

Fig. 1. Schematic overview of the Gerstel TDS-2 thermodesorption system and TDS on-line rack. MFC = Mass flow controller, BPR = back pressure regulator.

During this step, the cartridge is purged in backflush with nitrogen at ambient temperature to remove most of the water. After 12.5 min external drying, when water can no longer be visually observed in the cartridge, the cartridge is automatically transferred to the TDS-2. Inside the TDS-2, the cartridge is dried to total dryness (internal drying) under a flow of helium at a slightly elevated temperature. During the internal drying step, the CIS-4 and the transfer line are backflushed to prevent water from entering the analytical column. When internal drying is complete, the CIS-4 is cooled down to the initial temperature (−100°C) and the thermal desorption program is started. Upon completion of the thermal desorption program, the PDMS tube inside the TDS-2 is exchanged for the empty tube and the GC and MSD programs are started.

4. Results and discussions

Freshly prepared PDMS traps were conditioned by pumping 50 ml of methanol through the trap. The trap was subsequently dried and processed as indicated in Table 2, omitting steps 1 through 3. If, after completion of this procedure, non-siloxane components are found in the blank chromatogram, the cartridge is also thermally conditioned at 250°C for 2 h. A conditioned cartridge can in principle be stored in the autosampler. If a cartridge is to be stored outside of the autosampler, metal end-caps are used which are commonly used to prevent the trapping of contaminants from air onto the sorbent.

The first experiments concerned the blank chromatograms generated by the PDMS sorbent. After thorough conditioning, 10 ml of HPLC grade water was passed through the PDMS cartridge. The chromatogram obtained from this analysis is shown in Fig. 3. Although this chromatogram contains several distinct peaks, these do not interfere in the analysis of target solutes, because from their mass spectrum they are all readily identified as siloxane breakdown products. This is one of the most powerful aspects of the PDMS material: the risk of inadvertently identifying a sorbent degradation peak as an actually sampled analyte is minimal.

In Fig. 4 the chromatogram obtained after preconcentration of 10 ml of the spiked water sample

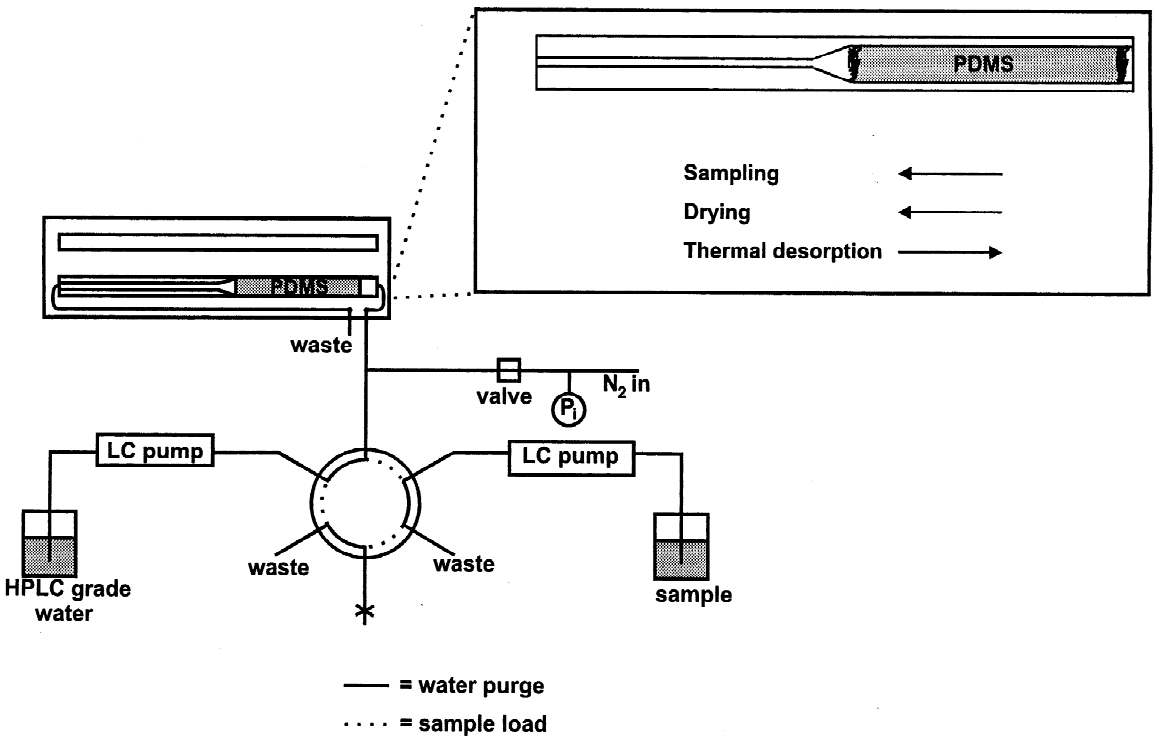

Fig. 2. Schematic representation of the system used for loading the aqueous samples. Insert shows the new design of the PDMS extraction cartridge. Diameter of the tube is 4 mm where PDMS is present and 0.8 mm at the narrow end. Arrows indicate flow directions during sampling, drying and thermal desorption.

Table 2
Sample preparation program of the automated sorptive extraction–thermal desorption procedure

No.	Step	Action	Time (min)
1	Condition cartridge	Flush cartridge with 10 ml HPLC grade water (5 ml/min)	2
2	Load sample	Load the water sample, 10 ml, 1 ml/min	12
3	Wash cartridge	Flush cartridge with 10 ml HPLC grade water (5 ml/min)	14
4	External drying	Purge cartridge with N_2, 800 ml/min, 12.5 min	26.5
5	Insert cartridge	Insert cartridge into TDS-2, backflush valve is switched on	27
6	Internal drying	Purge cartridge with He, 250 ml/min, 5 min, 50°C	32
7	Cryotrap cooldown	CIS-4 is cooled to the initial temperature (−100°C). Backflush valve is switched off	33
8	Thermal desorption	TDS-2 thermal desorption program is started:	
		50°C – 1°C/s – 225°C (5 min)	41
9	Thermal desorption end	TDS-2 is cooled to 50°C, PDMS cartridge is removed	42
10	Sample injection	CIS-4 is ramped from −100°C to 300°C at 10°C/s	
		GC and MSD are started	42
11	GC program	Initial 40°C (3 min) then at 10°C/min to 325°C	82

Steps 1–4 (26.5 min) can are carried out outside the thermal desorption system during the GC run, steps 5–9 (15.5 min) are carried out inside the thermal desorption system prior to the next GC run (40 min).

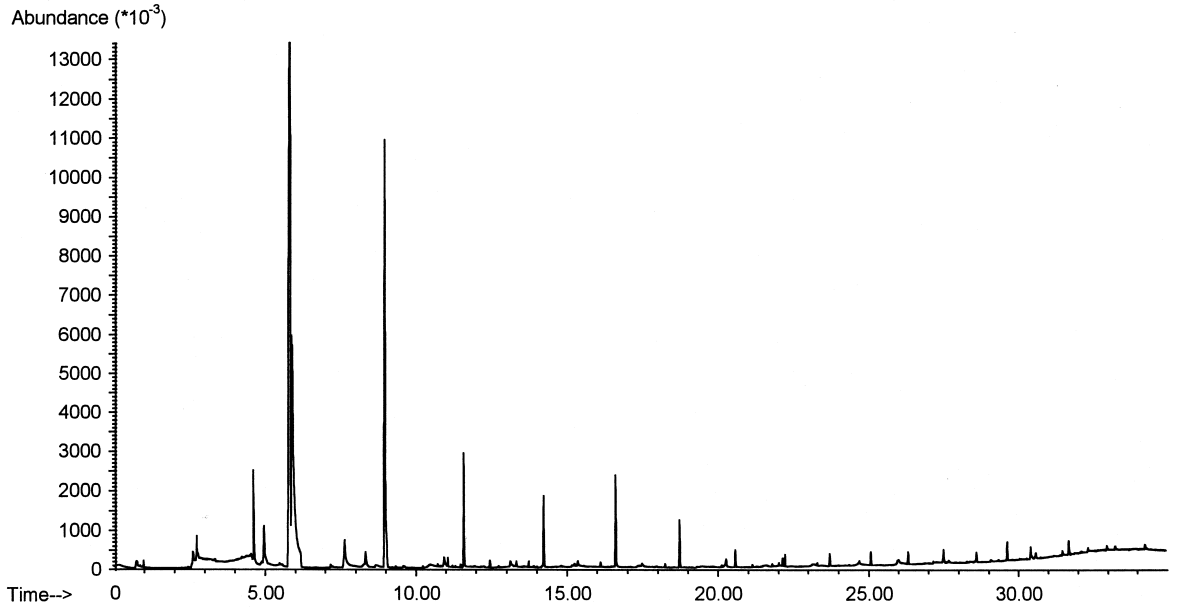

Fig. 3. Chromatogram of 10-ml HPLC grade water. Conditions as in Table 2. All peaks present in the blank are siloxane degradation products. Major peaks are a series of cyclic siloxane breakdown products.

(concentrations see Table 1) is shown. Recoveries determined versus a 1 ml cold splitless injection are also listed in Table 1. During initial experiments concentration levels of 10- and 100-times those listed in Table 1 were also used. For these, more concentrated samples, identical recoveries were found as those listed in Table 1, only solutes 43, 44 and 45 were found in considerably higher recovery. For most components a recovery between 70 and 130% is observed, which is adequate for quantitation purposes. However, for seven solutes poor recoveries ranging from 0 to 25% were observed. The solutes lost are three PAHs (indeno[123*cd*]pyrene, dibenz-[*ah*]anthracene and benz[*ghi*]perylene) and four triazines (desethylatrazine, deisopropylatrazine, metribuzin and cyanazine). Losses of solutes are probably not due to volatility, as the most volatile solute (naphthalene) is quantitatively retained. The two groups of (partially) lost solutes however, have very different characteristics concerning polarity. The three PAHs are the most apolar solutes present in the test mixture. Since the PDMS phase is also apolar, affinity of the PAHs for this phase is expected to be very high. Losses of these solutes are therefore unlikely to occur due to incomplete trapping by the PDMS material. Most probably, the PAHs are lost due to adsorption in tubing, valves, HPLC pumps etc. which is supported by the fact that at higher concentrations higher recoveries were found for these solutes. This despite the fact that 5% methanol was added to suppress adsorption. Unfortunately however, it was found that increasing the methanol concentration to values in excess of 5% result in additional losses of the polars, therefore it was decided not to change the amount of methanol modifier.

The other group of lost analytes are the most polar triazines. These solutes are very polar and are therefore expected to exhibit only a very moderate affinity for the apolar PDMS phase. The poor recoveries observed for these solutes are hence most likely caused by incomplete trapping of the solutes by the PDMS material rather than by adsorption somewhere in the system. This loss on the ''polar end'' can be explained using the theory described in Section 2. For the PDMS trap used here, the estimated plate number is 5.1 [18,19]. The sample volume, V_S, is 20 ml (10 ml sample and 10 ml wash). Substitution of these values and the PDMS trap parameters in Eq. (3) result in a $(K_{O/W})_{req}$ of 60 and

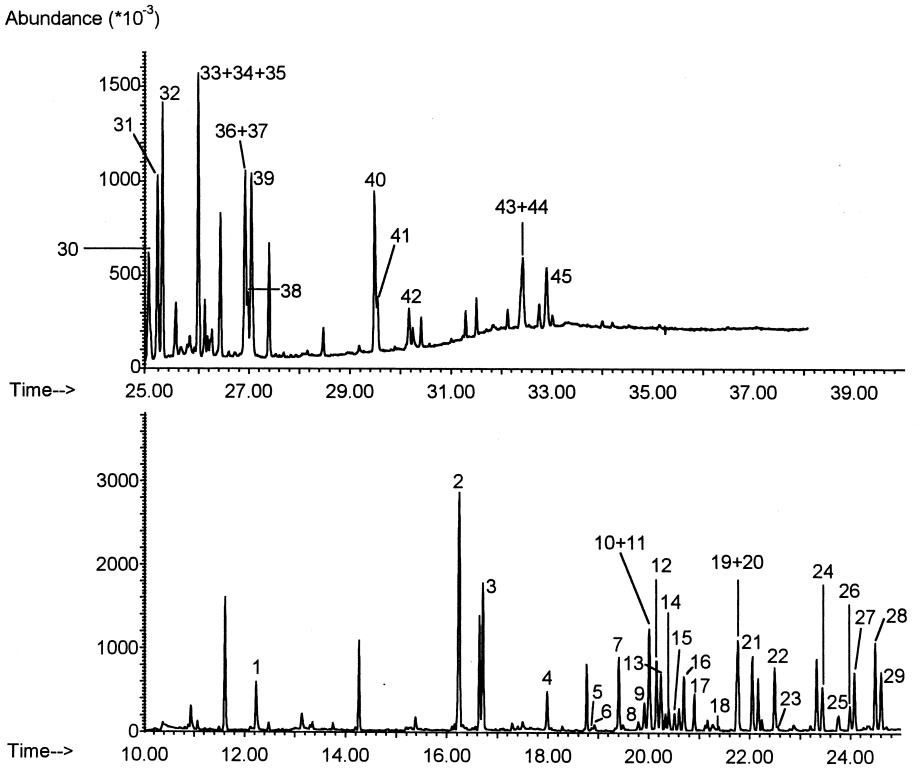

Fig. 4. Chromatogram of the 45 analytes in tap water at a level of 0.4–8 ppb (10 000-fold dilution of sample listed in Table 1). Other conditions as in Table 2.

a log $(K_{O/W})_{req}$ of 1.77. Solutes with a $K_{O/W}$ in excess of 1.77 should be quantitatively retained. In Fig. 5 recoveries of the test solutes are plotted versus their octanol–water partitioning coefficient to show the losses of solutes at both ends of the scale. A vertical line is drawn at $K_{O/W}$ 1.77. From Fig. 5 it is clear that all solutes with a $K_{O/W}$ in excess of 1.77 are quantitatively retained (except the three most apolar PAHs). On the polar end (low $K_{O/W}$) four solutes are lost. The most polar solute that is quantitatively retained is simazine which has a $K_{O/W}$ of 2.06. This indicates that there is a very good agreement between the theoretically calculated required $K_{O/W}$ and the actual $K_{O/W}$ value above which quantitative retention is realized. For solutes with log $K_{O/W}$ above 7, problems might occur due to system adsorption effects. For practical purposes an application range of 2–7 in log $K_{O/W}$ can be used. Repeated experiments showed that the PDMS extraction cartridge could be re-used for up to at least 150 experiments. Relative standard deviations ($n=3$) were between 10–25% for all solutes under investigation.

Extension of the polarity range to values below a log $K_{O/W}$ of 2 is desired since there are also interesting solutes in this range. With the PDMS material this is, in principle, only possible by reducing the sample volume (or water wash steps) which of course has clear drawbacks such as a reduced sensitivity and a higher change of cartridge and system pollution. A better approach is to investigate more polar phases which will have a higher affinity for polar analytes.

5. Conclusions

The results presented in this report indicate that packed PDMS extraction cartridges are excellent enrichment devices for the preconcentration of a

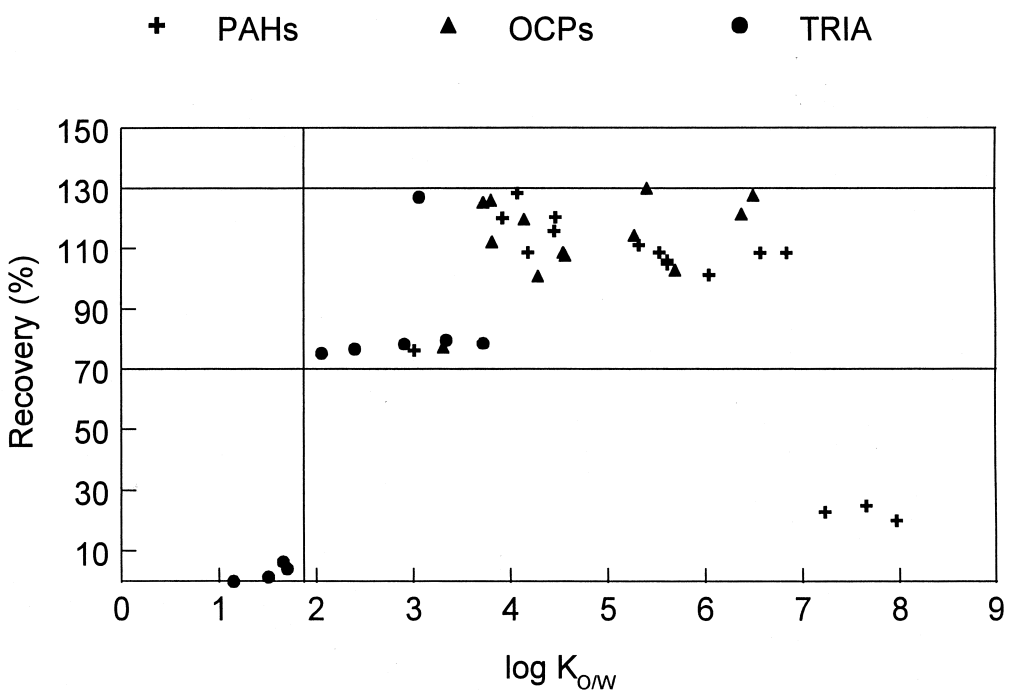

Fig. 5. Recovery of the 45 analytes used versus their octanol–water partitioning coefficient. Line at $K_{O/W} = 1.77$ is the theoretical limit above which all solutes should be quantitatively retained. The three most apolar PAHs are lost due to adsorption in the water sampling system.

large number of pesticides and PAHs from aqueous samples. The procedure described here closely resembles SPE–TD however with some very important differences. Retention on the PDMS sorbent is based on sorption (partitioning) while all SPE methods employ adsorbents which adsorb molecules onto their surface. Advantages of sorption were addressed in the text, the most important ones being: improved inertness, well known retention properties (e.g., from GC and SPME) and good blanks.

Degradation peaks of the PDMS sorbent can be readily identified as siloxane breakdown products by the use of the mass spectrometric detection. A fully automated set-up allowing automatic sample loading, drying, thermal desorption and GC–MS analysis was described. For most solutes investigated, quantitative recoveries were found, only some of the highly polar triazines and the most apolar PAHs were (partially) lost. Losses of apolar solutes is most likely due to adsorption in the system which can only be prevented by adding an organic modifier, e.g., methanol, to the water sample. Here, methanol is used as the modifier at a fixed concentration of 5%.

A theoretical model was derived which allows calculation of breakthrough volumes and recoveries from octanol–water partitioning coefficients ($K_{O/W}$). Alternatively, the $K_{O/W}$ value required for quantitative trapping can be calculated from the sample volume. The application range roughly ranging from log $K_{O/W}$ 2 to log $K_{O/W}$ 7 where the high end is restricted by system adsorption effects. With the set-up used here, using mass spectrometric detection in the scan mode, detection limits are in the order of 10 ng/l.

References

[1] M. Biziuk, A. Przyjazny, J. Czerwinski, M. Wiergowski, J. Chromatogr. A 754 (1996) 103.
[2] J.J. Vreuls, U.A.Th. Brinkman, G.J. de Jong, K. Grob, A. Artho, J. High Resolut. Chromatogr. 14 (1991) 455.
[3] E.C. Goossens, D. de Jong, G.J. de Jong, F.D. Rinkema, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 18 (1995) 38.
[4] J.S. Salau, R. Alonso, G. Batiló, D. Barceló, Anal. Chim. Acta 293 (1994) 109.

[5] A.J.H. Louter, J.v. Doormalen, J.J. Vreuls, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 19 (1996) 679.
[6] M. Biziuk, A. Przyjazny, J. Chromatogr. A 733 (1996) 417.
[7] J.J. Vreuls, U.A.Th. Brinkman, G.J. de Jong, K. Grob, A. Artho, J. High Resolut. Chromatogr. 14 (1991) 455.
[8] J.J. Vreuls, G.J. de Jong, R.T. Ghijsen, U.A.Th. Brinkman, J. Microcol. Sep. 5 (1993) 317.
[9] H.G.J. Mol, H.-G. Janssen, C.A. Cramers, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 16 (1993) 459.
[10] B.V. Burger, M. LeRoux, J. Chromatogr. 642 (1993) 117.
[11] H.G.J. Mol, H.-G. Janssen, C.A. Cramers, J. High Resolut. Chromatogr. 16 (1993) 413.
[12] R.E. Kaiser, R. Rieder, J. Chromatogr. 477 (1989) 49.
[13] S. Magdic, J.B. Pawliszyn, J. Chromatogr. A 723 (1996) 111.
[14] T.K. Choudhury, K.O. Gerhardt, T.P. Mawhinney, Environ. Sci. Technol. 30 (1996) 3259.
[15] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[16] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[17] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 395.
[18] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, J. Chromatogr. A 802 (1998) 285.
[19] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 385.
[20] A. Noble, J. Chromatogr. 642 (1993) 3.
[21] K. Verschueren, Handbook of Environmental Data on Organic Compounds, van Nostrad Reinhold, New York, 1996.
[22] P. Lövkvist, J.Å. Jönsson, Anal. Chem. 59 (1987) 818.