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A Novel Type of Liquid/Liquid Extraction for the Preconcentration of Organic Micropollutants from Aqueous Samples: Application to the Analysis of PAH's and OCP's in Water

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1 Introduction

Liquid/liquid extraction is widely used as a cheap and straightforward technique for the analysis of semi-volatile organic micro-pollutants in water. Classical liquid/liquid extraction (LLE) can be performed in various ways. The solvent can be added directly to the water sample in a separatory funnel or a dedicated apparatus can be used where the organic solvent is used repeatedly, *e.g.* continuous LLE. One of the popular solvents in liquid/liquid extraction of water samples is dichloromethane. It is especially due to the relatively large consumption of this and other (chlorinated) organic solvents that classical LLE has lost much of its popularity over recent years. Moreover, prior to injection, the extract often has to be preconcentrated, even if large volume injection is applied. In all cases only a fraction of the extraction liquid will be injected and thus potential sensitivity is lost. These and other factors render classical LLE a rather unattractive technique.

Over the past few years, solid-phase extraction (SPE) has established itself as a versatile and powerful alternative for LLE. SPE is based on the retention of the components of interest from an aqueous sample on a short LC-type column (SPE cartridge) followed by desorption with an organic solvent. Contrary to LLE, SPE is not based on a partitioning equilibrium. It is based on the adsorption of the analytes onto an active surface. A possibly complicating consequence of this is that the breakthrough volume of a certain analyte is affected by the concentration of both the analyte in question and of interfering substances. This is, of course, highly undesirable. When SPE is employed, the consumption of organic solvents is significantly reduced if compared to solvent consumption in LLE, but (low volumes of) organic solvents are still required. Also, with this technique only a fraction of the desorption liquid is injected. Hence, sensitivity is still lost. In conclusion, with SPE the basic disadvantages of LLE are at best partly overcome. There is, however, still significant room for further improvement.

In this article a new approach for LLE is investigated. In the new method, the water is passed through a sorption cartridge containing particles consisting of 100% polydimethylsiloxane (PDMS). The PDMS phase appears to be a solid but its sorptive charac-

teristics are in fact similar to that of a liquid phase. Retention of the analytes will not be based on adsorption of the solutes onto the surface of the PDMS material rather, the solutes will dissolve (partition) into the bulk of this high viscosity liquid phase. Unlike the situation in SPE the solutes will not be desorbed by a solvent but thermal desorption can be used to transfer the analytes onto the GC column. In this way the consumption of organic solvents is minimized and maximum sensitivity is attained since all solutes trapped from the sample are actually introduced in the GC column. Experimentally, the method described here resembles the solid phase extraction/thermal desorption (SPETD) technique described by Vreuls *et al.* [1,2], Mol *et al.* [3] and Müller *et al.* [4]. The underlying principles, however, are different with respect to the mechanism involved in the actual extraction of the analytes. The new method is based on the same principles as open tubular extraction as first described by Kaiser and Rieder [5] and Blomberg and Roeraade [6] and further developed by Mol *et al.* [7,8] and Burger and LeRoux [9]. Now, however, instead of an open tubular trapping column a packed bed is used. Although the sorbent material used in our new 'liquid/liquid' extraction method closely resembles the active part of a solid phase micro extraction (SPME) device, our method is fundamentally different from SPME in that it is not an equilibrium method. In contrast to the situation in SPME extraction in the new method is complete. Hence, the new technique is inherently more sensitive.

2 Experimental

2.1 Packed PDMS Traps

The packed PDMS preconcentration tubes used in all experiments consisted of glass tubes with an inner diameter of 4 mm packed with the sorbent material. This glass tube was filled with PDMS particles prepared by grinding Silastic® silicone laboratory tubing (Dow Corning, Midland, MI, USA) under liquid nitrogen. The dimensions of this high purity 100% polydimethylsiloxane tubing were 0.63 mm o.d. and 0.3 mm i.d. The average particle size of the PDMS particles prepared by grinding is roughly equal to the outside diameter of the starting material (0.63 mm). The density of the PDMS material was determined from the volume and weight of 50 cm of Silastic tubing and was found to be 0.825 g/ml.

The glass tube was filled with 0.325 g of PDMS particles which is equivalent to a volume of 0.394 ml. Since the PDMS bed was 5.8 cm long, the trap void volume (V_0) is 0.334 ml. The phase ratio (β) hence is 0.848. The PDMS bed is kept in place by means of two small plugs of deactivated quartz wool (Chrompack, Middelburg, the Netherlands).

In order to condition the DMS trap, it was first flushed with 50 ml of methanol to remove any high-boiling impurities (mainly grease from manual handling) from the trap. After drying with a vacuum pump for 10 min the PDMS trap was conditioned at 225 °C for 24 hours.

2.2 Experimental Set-Up

The experimental set-up used for all experiments consisted of a Gerstel TDS-2 thermal desorption system (Gerstel GmbH, Müllheim a/d Ruhr, Germany) mounted on top of an HP5890A GC (Hewlett Packard, Avondale, PA, USA). The TDS-2 system basically consists of two PTV injectors in series. The first programmable oven is the TDS-2 Unit which holds the PDMS-packed tubes. Since these tubes are rather large, the maximum heating rate that can be applied is 1 °/s. To refocus the desorption band, a CIS-3 PTV injector is used as a cryotrap. It is kept at -150 °C during thermal desorption and is then ballistically heated to 350 °C at a rate of 12 °/s. Two detectors were used: a flame ionization detector (FID) and a mass selective detector model HP 5970 (Hewlett Packard). The analytical column used was purchased from Chrompack (Middelburg, the Netherlands) and was 13 m long, 200 µm i.d., and coated with a film of 0.33 µm CP Sil 5 CB.

Water samples were pumped through the PDMS sampling tubes off-line. Next, most of the water remaining in the trap is removed by purging with nitrogen (external drying). The final stage of the

drying process was carried out inside the thermal desorption unit (internal drying). In order to prevent water vapor from entering the column during the internal drying process, the column was backflushed. Therefore, a backflush option was added to the system. A schematic overview of the system is shown in **Figure 1**. The standard Graphpack adapter on the bottom of the CIS-3 injector was replaced by a special custom made Graphpack adapter (Gerstel). During the internal drying step inside the TDS-2, the water vapor is discharged via split 1. A gas pressure slightly above the column inlet pressure is now applied at the backflush line. Hence, both the cold trap and the transfer will be backflushed. Also this additional gas stream will exit via split exit 1.

Valves 1 and 2 control the split/splitless state of the system. With the TDS-2 system it is possible to first splitlessly transfer the analytes from the TDS-2 to the cryotrap at a high flow rate. Next, the trapped solutes are transferred from the cryotrap onto the GC column. This again is done in the splitless mode. This implies that all analytes retained by the PDMS cartridge are eventually transferred onto the column which results in an excellent sensitivity. For samples more heavily loaded with analytes, sample splitting at either one or two points can be applied

2.3 Water Sampling

The procedure for water preconcentration is briefly outlined below. The water sample is first filtered through a glass filter to remove any particulate matter. After addition of 3.5% methanol to suppress adsorption of the analytes onto the glass ware and tubing, the water is passed through the PDMS trap by means of a vacuum pump. After the desired volume of water sample is applied, the cartridge is purged with *ca* 10 ml of distilled water in order to remove solubilized salts and other polar materials. The PDMS trap is now dried for 25 min in a nitrogen stream of 300 ml/min to remove most of the water. Next, the cartridge

Figure 1. Experimental set-up for thermal desorption of water-loaded PDMS traps. Carrier = helium, MFC = mass flow controller, BPR = back pressure regulator, P = pressure gauge.

is inserted into the TDS-2 where it is dried at slightly elevated temperatures (50 °C) to total dryness (internal drying). The carrier gas flow rate applied during internal drying is 165 ml/min (helium). During internal drying, the backflush valve is open to prevent water vapor from entering the column and the cold trap. Water vapor is now discharged via split exit 1.

It is important to realize that the flow direction during the sample loading, water purge and the external drying steps is equal. Internal drying and thermal desorption are both carried out in the reverse direction. This means that the analytes that were trapped from the water sample do not have to pass through the entire sorbent bed during desorption. This greatly simplifies desorption, especially of less volatile analytes and is a clear advantage of the instrumental set-up used here over that of Vreuls *et al.* [1,2] and Mol *et al.* [3]. Moreover, performing the water purge and the external drying steps in the same direction as the water loading minimizes the risk of losses of analytes in these steps.

3 Results and Discussion

In a first series of experiments the applicability of the PDMS sorption tubes for the extraction of PAH's from tap water was studied. In these experiments the chromatographic system was equipped with an FID detector. Since this detector provides almost no selectivity, the water sample was spiked at a relatively high level of *ca* 1 ppb (1 µg/l) with 5 PAH's. 100 ml of spiked tap water was passed over the sorption cartridge at a flow rate of 5 ml/min. In **Figure 2** the chromatogram of the PAH analysis is shown. The quantitative data is listed in **Table 1**. The recoveries for the various PAH's were calculated by comparison to a standard. Standards for all components were prepared by injecting 1 µl of a certified solution directly onto the PDMS cartridge. Immediately after spiking, the cartridge was thermally desorbed without any water sampling or drying step.

From the results shown in Table 1 it can be concluded that quantitative extractions can be obtained for anthracene and higher boiling PAH's. Naphthalene and acenaphthene are lost in the sampling and/or drying process. In principle, with this

Figure 2. Chromatogram of the analysis of 100 ml tap water spiked to a level of 1 ppb with 5 PAH's. For recoveries see Table 1.

Table 1. Recoveries of PAH's from a spiked tap water sample.

Component	Recovery (%)
Naphthalene	25
Acenaphthene	50
Anthracene	86
Fluoranthene	104
Pyrene	103

method, it is possible to obtain detection limits in the low ppt range with FID detection. Unfortunately, in real samples too many interfering compounds are present at this level. This implies that for measurements at this level a more selective detector is imminent.

The mass selective detector (MSD) was used in the analysis of organo-chlorine pesticides (OCP's) in water. As an initial experiment, 5 ml of a tap water sample was spiked with 8 OCP's at a level of 0.4 ppb. The MSD was operated in the SIM mode (1 ion/component). Recoveries were again calculated relative to direct thermal desorption of a 1 µl standard. **Figure 3** shows the

Figure 3. Chromatogram of 5 ml of a tap water sample spiked with 0.4 ppb of 8 organo-chlorine pesticides. Peak assignment see Table 2.

Table 2. Analysis of OCP's spiked in tap water.

No	Component	Ion for quantitation	Recovery (%)
1	α -HCH	181	100.0
2	δ -HCH	181	96.5
3	heptachlor	272	89.1
4	heptachlor-epoxide	353	110.9
5	endosulfan I	339	99.3
6	dieldrin	380	92.7
7	endosulfan sulfate	387	100.0
8	methoxychlor	227	73.9

chromatogram of this analysis. The quantitative data are listed in **Table 2**. From the data in this table, it is clear that for most components recoveries close to 100% can be obtained. When using conventional methods, recoveries between 70 and 130% are generally considered acceptable [10].

As a continuation of the work and inspired by the good performance of the system for the determination of OCP's in the spiked samples, it was attempted to determine OCP's in real river water samples. In the analysis of real-world samples, more ions have to be monitored to improve the selectivity of the method. The water samples were analyzed for OCP's in the SIM mode using 4 ions/component. A 100 ml sample of distilled water was spiked with 2 ng of the OCP's. The resulting concentration was 20 ppt. This was used as the reference standard. A 100 ml water sample from the river Dommel in Eindhoven was taken and processed according to the method described before. **Figure 4** shows the chromatogram of this analysis. The quantitative data are listed in **Table 3**. Three OCP's were positively identified. **Table 4** shows a comparison of the spectra of the standard and the river water sample. This example clearly illustrates the potential of the new method for the analysis of organo-chlorine pesticides and other environmentally relevant solutes.

Table 3. Analysis of OCP's in water from the river Dommel.

Component	Concentration (ng/l)
α -HCH	<1.7
δ -HCH	<1.7
Heptachlor	<3.4
Heptachlor-epoxide	1.13
Endosulfan sulfate	8.31
Methoxychlor	3.95

Table 4. Normalized mass spectra of OCP's in standard solution (20 ppt in water) and in the river water sample.

Component	Ion	Standard (%)	Sample (%)
Heptachlor-epoxide	237	13.1	7.96
	263	15.2	11.5
	353	100	100
	388	9.45	14.2
Endosulfan-sulfate	229	54.7	45.7
	272	100	100
	387	85.6	67.6
	422	24.4	9.47
Methoxychlor	212	5.09	7.42
	227	100	100
	274	3.23	5.12
	346	1.63	2.61

Figure 4. Chromatogram of 100 ml of a water sample from the river Dommel, four OCP's were identified. Peak assignment see Table 2.

4 Conclusions

In the present work a new technique for water analysis based on sorption of the analytes into pure PDMS particles followed by thermal desorption is described. The method shows excellent performance for the environmental trace analysis of selected PAH's and OCP's in water samples. Good recoveries were obtained for most components except for naphthalene and acenaphthene which were too volatile.

The detection limits obtained using mass spectrometric detection were in the low ppt range. The most powerful aspect of the system is the possibility to transfer all the analytes from a 100 ml water sample to the GC column resulting in excellent sensitivities. The PDMS extraction cartridges showed no deterioration, not even after 150 extractions. The investigated method has proven to be a powerful alternative for certain LLE and SPE applications. Basic advantages include: superior sensitivity, highly reduced solvent consumption and the possibility to automate the system. Future work will focus on the analysis of more polar pesticides and the use of more sensitive and/or selective detectors.

References

- [1] J.J. Vreuls, U.A.Th. Brinkman, G.J. de Jong, K. Grob, and A. Artho, *J. High. Resol. Chromatogr.* 14 (1991) 455.
- [2] J.J. Vreuls, G.J. de Jong, R.T. Ghijsen, and U.A.Th. Brinkman, *J. Microcol. Sep.* 5(4) (1993) 317.
- [3] H.G.J. Mol, H.-G.M. Janssen, C.A. Cramers, and U.A.Th. Brinkman, *J. High. Resol. Chromatogr.* 16 (1993) 459.
- [4] S. Müller, J. Efer, and W. Engewald, *Chromatographia* 38 (1994) 694.
- [5] R.E. Kaiser and R. Rieder, *J. Chromatogr.* 477 (1989) 49.
- [6] S. Blomberg and J. Roeraade, *J. High Resol. Chromatogr.* 13 (1990) 509.
- [7] H.G.J. Mol, J. Staniewski, H.-G. Janssen, C.A. Cramers, R.T. Ghijsen, and U.A.Th. Brinkman, *J. Chromatogr.* 630 (1993) 201.
- [8] H.G.J. Mol, H.-G. Janssen, and C.A. Cramers, *J. High. Resol. Chromatogr.* 16 (1993) 413.
- [9] B.V. Burger and M. LeRoux, *J. Chromatogr.* 642 (1993) 117.
- [10] R. Soniassy, P. Sandra, and C. Schlett, *Water Analysis*, Hewlett Packard Company, 1994.

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