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Development of a prototype system for quasi-continuous analysis of organic contaminants in surface or sewage water based on in-line coupling of solid-phase microextraction to gas chromatography

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Abstract

A prototype of an analytical system allowing the quasi-continuous monitoring of organic contaminants in surface water which should be also applicable to the analysis of sewage water was developed. It consists of a flow-through cell and an automated solid-phase microextraction (SPME) unit, coupled in-line to a gas chromatograph. This system combines the advantages of SPME as a simple, fast, sensitive, and solvent-free sample introduction technique, with the advantages of on-line processing of aqueous samples as a less time-consuming, efficient, and continuous technique. Organochlorine pesticides and triazine herbicides were selected as test analytes for the system evaluation. The flow-through cell was shown to provide a successful way for automated on-line SPME coupled in-line to gas chromatography with a repeatability of ca. 10% R.S.D. for the investigated triazines.

Keywords: Water analysis; Sample handling; Environmental anlaysis; Extraction methods; Pesticides; Organochlorine compounds; Triazines

1. Introduction

The solid-phase microextraction (SPME) was developed and introduced by Pawliszyn and co-workers [1–5]. The SPME method is based on an equilibration of the analytes between the aqueous and an immobilised liquid phase coated onto a silica fiber as a stationary phase, i.e., polydimethylsiloxane or polyacrylate polymers. It is used for the direct extraction of organic trace compounds from water by simply dipping the fiber into the aqueous sample. After absorption, the fiber is transferred into the heated injector of the gas chromatograph and exposed for a given period of time, where the organic compounds are thermally desorbed from the polymeric phase. The amounts absorbed by the polymer on the fiber can be described by Nernst's partitioning law [2]. The transport of the analyte into the absorbing polymer can be enhanced by vigorous agitation methods [6]. The entire system is easily automated using a modified gas chromatography (GC) autosampler [4,7]. This method represents a further important advance in the development of efficient extraction methods for organic pollutants from aqueous samples at trace levels [5,8]. So far, SPME has been applied to the extraction of organic compounds from different matrices including air [5], water [8] and soil [9].

In this study a fully automated quasi-continuous sampling system was developed for on-line analysis. The sample is pumped continuously through the flow-through cell mounted on a commercial GC

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autosampler. The fiber is dipped in regular intervals into the flowing sample. In this first laboratory prototype the sample placed in a brown-glass bottle was pumped through the cell using a peristaltic pump. In the future a bypass of a river or a sewage effluent will be pumped through the cell thus allowing the direct and quasi-continuous monitoring of organic compounds at trace levels in surface waters. The triazines which can be effectively absorbed by SPME [8,10,11] were selected as model compounds in order to characterise and evaluate this new on-line system.

2. Experimental

2.1. Materials

All pesticide standards used in this study were purchased from Riedel-de Haën (Seelze-Hannover, Germany). They were of purity ≥98% and used as received. Methanol (Pestanal quality) was also from Riedel-de Haën. Water was obtained from a Milli-Q water-purification system (Millipore/Extrel, Pittsburgh, PA, USA).

2.2. The analytical system

2.2.1. The gas chromatograph

The GC investigations were carried out using a Varian (Walnut Creek, CA, USA) type 3400 gas chromatograph equipped with an electron-capture (ECD) and flame-ionisation detection (FID). The detector temperature was 300°C. A PTE-5 column (30 m×0.32 mm I.D., 0.25 μm film thickness) from Supelco (Bellefonte, PA, USA) was used for all GC separations. The septum programmable injector (SPI) was equipped with a special SPME insert from Varian and 11 mm O.D. pre-drilled LB-2 septa from Supelco. The following temperature program was used: 90°C for 5 min, 90–180°C at 30 C° min^{-1}, 180–290°C at 10 C° min^{-1}, 290°C for 1 min (total run time 20 min). All injections with the SPME unit were performed automatically with the Varian autosampler 8200 unit controlled by the Varian Star version 4.0 software.

2.2.2. Solid-phase microextraction

A solid-phase microextraction (SPME) fiber holder for autosampler use with a 85 μm polyacrylate fiber from Supelco was used for all SPME experiments. The fiber was thermally conditioned prior to its first absorption at elevated temperatures. In general, the 85 μm polyacrylate fiber was conditioned at 300°C under helium for several h (4 h or more) to reduce bleeding. This can be achieved by simply exposing the fiber to an split/splitless injector while the purge is open.

2.2.3. Flow-through cell and on-line equipment

A flow-through cell made of glass was constructed by us for the on-line solid-phase microextraction. This cell was mounted onto the commercial autosampler modified to take up the cell as shown schematically in Fig. 2. For this arrangement nine positions for autosampler vials had to be removed. The glass flow-through cell forms a half-circle with the absorption position in the middle. At this position which is arranged exactly at the site of one of the original autosampler vials the cell is sealed by a septum. The fiber fixed to the SPME-autosampler dips directly through the seal into the cell. This allows the use of the normal software procedure to control both the entire absorption and desorption steps for this flowing sample arrangement. The sample was pumped through the cell with a peristaltic pump (type: IKA PA-20, IKA Labortechnik, Staufen i.Br., Germany). Silicone tubings of 6 mm internal diameter and 1.5 mm film thickness were used for the connection of the cell, the pump, and the reservoir. The aqueous sample was pumped in a loop (see Fig. 1) at a flow-rate of ca. 300 ml min^{-1}. A detailed list of the experimental parameters is shown in Table 1.

2.3. Sampling and desorption conditions

The procedure for SPME is very simple because there are no further sample preparation steps. First, the fiber is exposed to the sample which is pumped at a constant flow through the cell for a given period. Second, the fiber is withdrawn from the sample and introduced automatically into the GC-injector, where thermal desorption occurs. An absorption time of 10 min was used in this study. This time does not

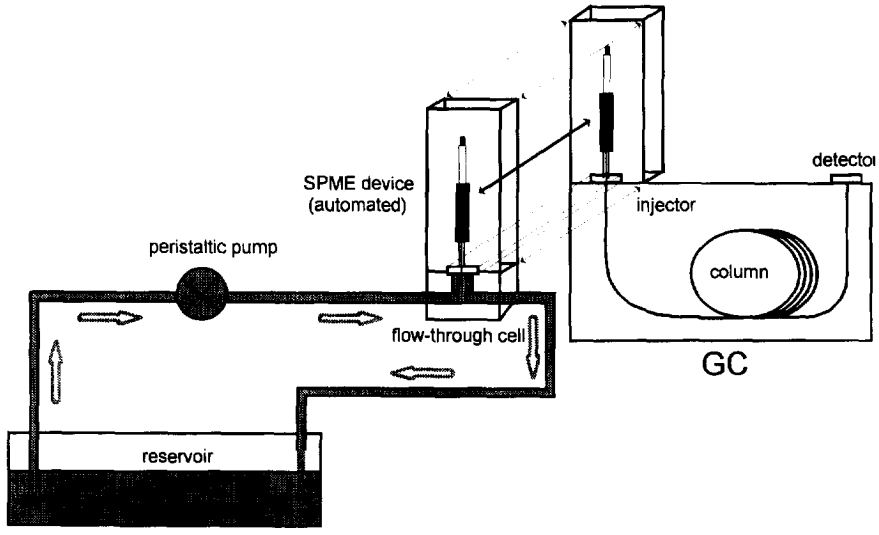

Fig. 1. Schematic illustration of an automated analytical system for on-line SPME enrichment GC.

necessarily represent the equilibration time or an optimised absorption time, which in general would be longer. However, it represents a good compromise to achieve a high reproducibility at an acceptable time.

After thermal desorption the fiber is withdrawn from the injector and again automatically dipped into the flowing sample. While the next sample is absorbed by the fiber the preceding sample is chromatographed by the GC. This overlapping of absorption and chromatography reduces the average time for an overall analysis of each sample. Thermal desorption of the pesticides in the hot GC injector (vide infra) was carried out for 5 min. During this time the oven temperature of the GC was held at 90°C while the GC-injector temperature was kept at 300°C for desorption. Under these conditions the peaks of all compounds do not show any tailing. All SPME and GC parameters are although summarised in Table 1.

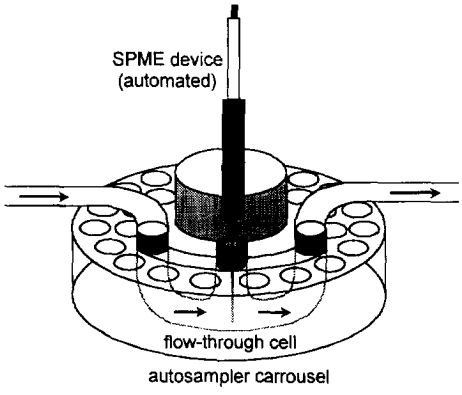

Fig. 2. Detailed view of the flow-through cell mounted on an autosampler carousel.

The aqueous samples were stored in 1 l brown-glass bottles during the on-line SPME analysis. The 1 l sample contains 0.4% (v/v) methanol which originates from the methanolic standard solution spiked into the sample. However, this amount of methanol has no significant effect on the extraction as shown by us in the past [8]. All experiments were carried out with Milli-Q water. For reproducibility studies concentrations of 600 ng ml^{-1} of each pesticide were used.

2.4. Calibration

The calibration for the SPME analysis is achieved by standards containing the target compounds in methanol which are spiked into water at different amounts. Calibration performed in this way includes both the extraction and instrumental determination. If environmental samples are to be analysed, where matrix effects are often not reproducible, internal

Table 1
Parameters of the on-line SPME-GC system

SPME parameters	
SPME fiber	85 μm polyacrylate
Sample flow	~300 ml min^{-1}
Extraction temperature	room temperature (21°C)
Extraction time	10 min
Desorption temperature	300°C
Desorption time	5 min
Detector temperature	300°C
Detection method	ECD or FID
GC conditions	
Injector	SPI
Liner	SPME liner
Column	PTE-5 (30 m×0.32 mm I.D., 0.25 μm film thickness)
Oven program	90°C hold for 5 min; 90–180°C with 30 C° min^{-1}; 180°C hold for 0 min; 180–290°C with 10 C° min^{-1}; 290°C hold for 1 min

standards should be used preferentially. As SPME depends strongly on some basic parameters such as pH or concentration of salts (which influences the ionic strength of the sample) [8,12], equal extraction conditions can be obtained only when these parameters are standardised for the SPME method. The calibration using external standards is linear over at least three orders of magnitude. The coefficients of correlation for the calibration are usually better than 0.99. For optimum calibration of the continuous flow-through system two methods may be used: first, standard solutions positioned in the autosampler carousel are measured under static conditions. After determining the ratio of standard solutions measured under static and dynamic conditions future calibrations can be carried out with standard solutions positioned in the autosampler carrousel under static conditions. Second, the standards are spiked directly into the flowing sample. If varying matrix effects, e.g., pH values or salt concentrations, are observed, their influence on the calibration can be taken into account by monitoring these parameters, e.g., pH value, in parallel.

3. Results and discussion

In this first prototype of an automatic system for quasi-continuous analysis of contaminated water the flowing surface or sewage water was simulated by a spiked aqueous sample stored in a reservoir and pumped through the cell continuously. The in-line SPME-GC system works fully automatically using the normal software control of the autosampler and gas chromatograph. The system was tested using four organochlorine pesticides and ECD and four triazine herbicides using FID. Unfortunately a more selective detection method (nitrogen-phosphorus detection) was not available for the latter compound class which made it necessary to use rather high amounts of these compounds. Extensive testing of the developed system showed a good performance in particular with respect to reproducibility and ruggedness.

When a flowing water system is simulated by a sample stored in a reservoir and pumped continuously through the cell as in this study, depletion of the concentration is observed as a result of the continuous extraction steps (in contrast to the real surface or waste water case). To compensate for this decreasing concentration in a long term experiment described below the original sample in the reservoir was replaced by a fresh sample after 10 extraction steps.

Using this approach 150 extractions were performed with a single fiber showing neither a significant deterioration of its performance nor any mechanical damage, illustrating that the analytical system discussed here is characterised by satisfactory ruggedness. This ruggedness is of particular importance for an on-site operation of the system, e.g., at an effluent outflow of a waste water plant. In this case the automatic system may be run without

Table 2
Repeatability of peak areas with in-line SPME–GC–FID of four triazine herbicides[a]

Run	Peak area			
	Atrazine	Propazine	Terbuthylazine	Sebuthylazine
1st	500 767	1 045 973	1 667 698	1 125 493
2nd	554 167	1 054 627	1 580 270	1 148 395
3rd	552 131	1 044 474	1 510 415	1 152 403
4th	539 924	995 386	1 393 018	1 078 797
5th	519 148	952 905	1 289 028	1 058 975
6th	565 444	1 016 453	1 335 792	1 103 219
7th	554 972	983 582	1 267 297	1 085 216
8th	503 771	888 062	1 138 265	974 806
9th	571 455	975 021	1 205 939	1 069 309
10th	558 406	943 433	1 144 294	1 015 502
Mean[b]	542 019	989 992	1 353 202	1 081 212
S.D.	24 070	50 207	173 233	53 221
R.S.D. (%)	4.4	5.1	12.8	4.9

[a] At a sample flow of 260 ml min^{-1}.
[b] From ten repetitive injections of a 1 l sample ($n=10$). The concentration was 600 $\mu g\ l^{-1}$ for each pesticide.

intervention of an operator. Remote control is possible, e.g., by transmitting the data via modem to a laboratory. Furthermore, the daily performance of the system can be controlled by adding continuously a marker compound as an internal standard, which gives information on the overall performance of the entire system. Such a marker also allows quality control of the system.

The repeatability of this automatic enrichment and analysis system was first tested using ten successive extractions. The results are summarised in Table 2 which demonstrates a reproducibility of 4–13% R.S.D. The high standard deviation of terbuthylazine a compound with a high affinity to the polyacrylate phase is probable a result of above described depletion of concentration.

In addition the reproducibility was tested for a series of 50 successive extractions carried out in five cycles as described above. From these 50 extractions every 5th run was selected and is shown in Table 3.

Table 3
Repeatability of peak areas of every 10th run[a] in a long term experiment with 50 injections with in-line SPME–GC–FID, of four triazine herbicides[b]

Run	Peak area			
	Atrazine	Propazine	Terbuthylazine	Sebuthylazine
5th	544 208	927 805	1 178 289	1 072 502
15th	491 576	822 464	1 110 718	903 635
25th	519 148	952 905	1 289 028	1 058 975
35th	571 172	1 005 546	1 310 385	1 085 924
45th	517 306	979 582	1 354 360	1 064 325
Mean[c]	528 682	937 660	1 248 556	1 037 072
S.D.	26 995	63 191	90 102	67 335
R.S.D. (%)	5.1	6.7	7.2	6.5

[a] Beginning with run 5.
[b] At a sample flow of 260 ml min^{-1}.
[c] From five injections (every 10th run) in a 50 injection cycle ($n=5$). Each 1 l sample was extracted 10 times. The concentration was 600 $\mu g\ l^{-1}$ for each pesticide.

Also for this long term experiment a good repeatability, <8% R.S.D., was observed. The concentration of the target compounds can be monitored using the parameters in Table 1 at a time resolution of two data points per hour, i.e., 48 concentration data per day. A gas chromatogram of four triazines by in-line SPME-GC-FID using the described quasi-continuous analysis system is shown in Fig. 3. Fig. 3a displays the chromatogram after the first absorption/desorption cycle, Fig. 3b that after the 50th cycle.

An example of the high sensitivity which may be obtained with this new technique is shown in Fig. 4. Four organochlorine pesticides at a concentration of 0.06 $\mu g\,l^{-1}$ could be identified with SPME–GC–ECD without difficulty. As shown previously even more selective detection methods may be applied to the SPME analysis, such as atomic emission detection [13], and mass spectrometry (MS) [14]. These techniques will be coupled to the on-line

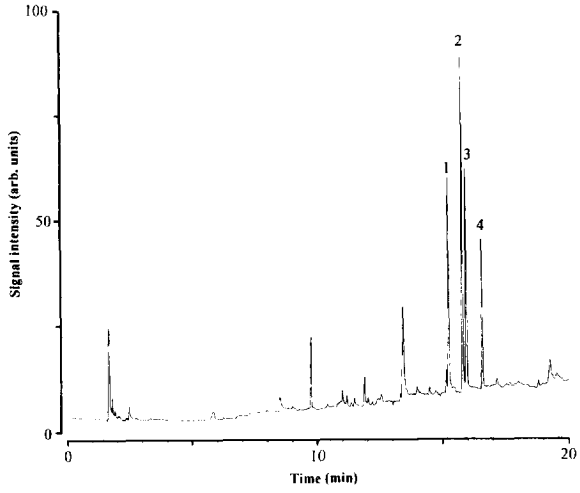

Fig. 4. Gas chromatogram of four organochlorine pesticides with on-line solid-phase microextraction and GC–ECD. Concentration of each compound was 0.06 $\mu g\,l^{-1}$. Peak assignment: 1=2,4′-DDE; 2=4,4′-DDE; 3=dieldrin; 4=4,4′-DDD.

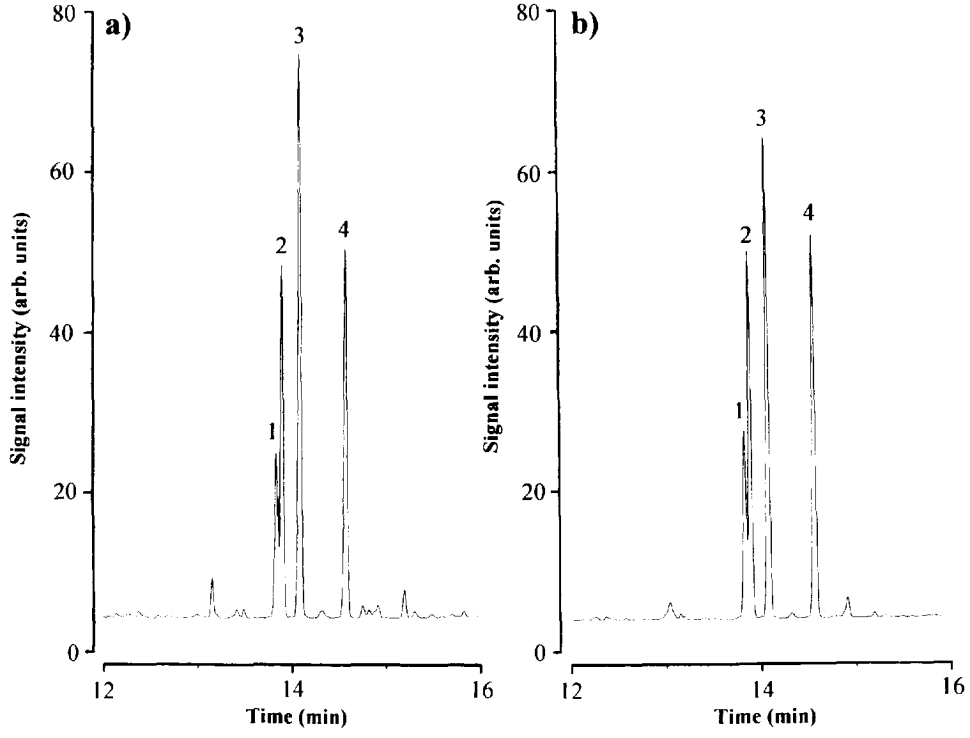

Fig. 3. Part of a gas chromatogram of four triazine herbicides with on-line solid-phase microextraction and GC–FID: (a) the first run and (b) the final run in a series of 50 injections (identical scale of the axis). Concentration of each compound was 600 $\mu g\,l^{-1}$. Peak assignment: 1=atrazine; 2=propazine; 3=terbuthylazine; 4=sebuthylazine.

system described in this study in the future if environmental samples with complex matrices are to be monitored. Off-line monitoring of surface and sewage water has been carried out by us in the past [8,14].

4. Conclusions

Within this study the performance of a first prototype of an automatic system for analysing organic contaminants in flowing water samples is reported. The system is characterised by a good reproducibility and long term stability (ruggedness). Furthermore, the system has the following major advantages: (a) the extraction is achieved without the use of solvents; (b) the method is very simple, fast and automated; (c) the method is very sensitive if coupled in-line to GC and will be more selective if coupled to hyphenated techniques in GC, e.g., GC–MS; (d) The fibers can be used repeatedly for more than 150 absorption/desorption cycles with a good precision.

Although this system has not been applied to flowing environmental samples it is expected to have great potential for on-site monitoring. The described analytical system will be used in the future for on-site and quasi-continuous monitoring of organics in aqueous systems, e.g., river or effluent outflows of wastewater plants.

Acknowledgments

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