Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 988 (2003) 41–51
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Trace analysis of technical nonylphenol, bisphenol A and 17α-ethinylestradiol in wastewater using solid-phase microextraction and gas chromatography–mass spectrometry

P. Braun[a,*], M. Moeder[a], St. Schrader[a], P. Popp[a], P. Kuschk[a,b], W. Engewald[c]

[a]*Department of Analytical Chemistry, UFZ Centre for Environmental Research Leipzig-Halle, Permoserstrasse 15, D-04318 Leipzig, Germany*

[b]*Department of Remediation Research, UFZ Centre for Environmental Research Leipzig-Halle, Permoserstrasse 15, D-04318 Leipzig, Germany*

[c]*Institute of Analytical Chemistry, University of Leipzig, Linnéstr. 3, D-04103 Leipzig, Germany*

Received 19 July 2002; received in revised form 1 November 2002; accepted 9 December 2002

Abstract

To enable high sample throughput, an automated solid-phase microextraction (SPME) method coupled with GC–MS for the trace analysis of technical nonylphenol, bisphenol A and 17α-ethinylestradiol was developed. The extraction performance of different SPME fibre coatings was examined, with polyacrylate proving most suitable. Although study of the extraction time showed that the analytes have not reached equilibrium after 3 h, as a compromise an extraction time of 1 h was applied in all the experiments with detection limits between 0.04 and 1 μg l^{-1} for wastewater effluent. The mean reproducibility of the technique is 8% RSD. Carry-over effects are negligible. The linearity of calibration curves ranges over three orders of magnitude. The method was tested for determining the analytes in influents and effluents of constructed wetland plants and in model wastewater used in laboratory experiments.

Keywords: Endocrine disruptors; Solid-phase microextraction; Water analysis; Nonylphenol; Bisphenol A; 17α-Ethinylestradiol

1. Introduction

In the early 1990s British scientists showed that male rainbow trout produce the yolk precursor protein vitellogenin when they are exposed to sewage effluents or contaminated surface waters [1]. Normally only female rainbow trouts produce vitellogenin. Such reproductive abnormalities in various wildlife species are caused by estrogenic active substances (denominated as endocrine disruptors or EDs). EDs include both naturally occurring hormones and anthropogenic chemicals such as synthetic hormones and industrial products like alkylphenols.

The target analytes of our investigations were technical nonylphenol (t-NP), bisphenol A (BPA) and 17α-ethinylestradiol (EE) (Fig. 1). Technical nonylphenol is a degradation product of nonylphenol

*Corresponding author. Tel.: +49-341-235-2657; fax: +49-341-235-2625.
E-mail address: wild@ana.ufz.de (P. Braun).

0021-9673/02/$ – see front matter
doi:10.1016/S0021-9673(02)02052-6

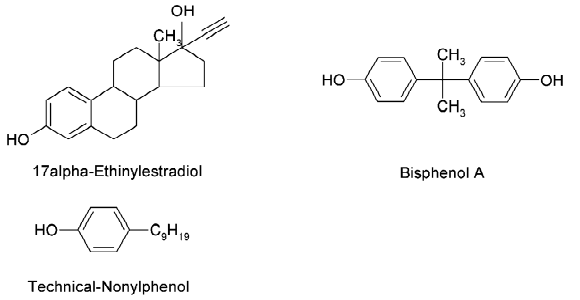

Fig. 1. Chemical structures of the target analytes.

polyethoxylates (NPEOs) which are used as non-ionic surfactants in detergents, paints, herbicides, pesticides and plastics [2]. Bisphenol A is one of the most commonly produced industrial chemicals in the world and is a component of polycarbonate plastics and epoxy resins, the uses of which include lining food cans [2,3]. The alkylphenoles mainly enter municipal wastewater treatment plants via industrial effluents. Due to their polarity, persistence and water solubility alkylphenols can pass through wastewater treatment plants and enter the aquatic environment [1,4]. 17α-ethinylestradiol is a synthetic estrogen which is used as contraceptive. It occurs mainly in domestic sewage. The ethinyl group in position 17 inhibits the metabolism of EE and is thus detectable in surface water [5].

Reliable methods are required for the trace detection of chemicals with endocrine disrupting potential. The snag about the analytical procedures currently used for the determination of EDs—liquid–liquid-extraction (LLE) [6–8] and solid-phase extraction (SPE) [5,9–11]—is that they are lengthy and substance-consuming as LLE involves the high consumption of organic solvents and additional further clean up steps. And although SPE needs lower amounts of organic solvents, the manual version, needed for concentrations of large sample volumes, still takes 8 to 10 h. Furthermore, the target analytes have to be derivatized if GC–MS is used for analysis. Although some applications of SPME in connection with on-line silylation and GC–MS have been published [12,13], they appear unsuitable for routine analysis.

In this work the capability and suitability of solvent-free solid-phase microextraction [9,14–17] was investigated for the enrichment of EDs. The method was examined in terms of its practicability for the determination of the three components in the sewage influents and effluents of wetland plants.

In addition, the applicability of the SPME–GC–MS method to model wastewater was examined with a view to usage as a screening method for estimating ED elimination behaviour in plant model systems [18–20].

2. Experimental

2.1. Chemicals and materials

Technical nonylphenol (Pestanal, purity grade≥ 94%) was obtained from Riedel de Haen (Seelze, Germany), bisphenol A (purity grade≥97%) and 17α-ethinylestradiol (purity grade≥85%) were purchased from Fluka (Zwijndrecht, Netherlands), and sodium chloride and methanol (SupraSolv) from Merck (Darmstadt, Germany). 4n-nonylphenol (4n-NP) was obtained from Dr. Ehrenstorfer (Augsburg, Germany) and β-estradioldiacetate from ICN Biomedicals (Aurora, Ohio, USA). Additionally, 2-bromo-2,3-dihydro-1H-indene-1-ol (short form: bromindanol) and deuterium labelled [$^{2}H_{14}$] bisphenol A (BPA d14) were synthesized at the University of Leipzig (Germany) and used as internal standards.

For method development pure water from the Modulab® Analytical purification system produced by Christ (Stuttgart, Germany) was used.

All samples, real wastewater samples and standards, were extracted automatically with the Multipurpose Autosampler (MPS 2) from Gerstel (Mühlheim, Germany). All fibres studied for SPME method development were supplied by Supelco (Bellefonte, PA, USA). Before first use each fibre was conditioned in the split/splitless injector of the GC as described in the Supelco's conditioning instructions followed by blank analysis to determine the condition quality.

Crimp capped vials (10 ml) sealed with a PTFE-lined silicon septum were obtained from Gerstel (Mühlheim, Germany). Stock standard solutions of technical nonylphenol and ethinylestradiol (1000 μg ml^{-1}) were prepared in methanol and bisphenol A (1000 μg ml^{-1}) in isopropanol, respectively. Stan-

dard mixtures in methanol were prepared weekly. All solutions were stored in the dark at 4 °C until use.

2.2. Sampling collection

Influent wastewater samples from a pilot scale wetland plant in Langenreichenbach (Germany) were collected over 24 h and effluent samples were taken once a day. The samples were collected in 1 l amber glass bottles with glass plugs and cooled at 4 °C. Analyses were performed within 2 days after sampling.

Model wastewater composition in accordance with DIN 38412 T24 was stored at 4 °C in the dark and investigations were performed within 5 days after production.

Stock solutions of the internal standards bromindanol (10 mg ml^{-1}), 4n-nonylphenol and β-estradioldiacetate (1000 μg ml^{-1} each) in methanol and deuterium-labelled [$^{2}H_{14}$] bisphenol A (1000 μg ml^{-1}) in isopropanol, respectively were diluted with methanol.

The detection limits of the analytes in the various water samples were determined and compared with those obtained using SPE.

2.3. SPME method development

SPME method development includes selecting the optimum fibre coating, i.e. choosing a coating material which provides high sensitivity and selectivity. An 85 μm polyacrylate (PA), 100 μm polydimethylsiloxane (PDMS) and 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) were examined as fibre types. A 9.5 ml amount of water containing 105 mg ml^{-1} NaCl was acidified with 2% H_2SO_4 to pH 2. Furthermore 19 ng bromindanol and an aliquot of methanolic ED-solution were added. Each fibre was completely immersed for 1 h in the aqueous standard solution, which was agitated at 500 r.p.m.

Optimization of the extraction yields of the analytes depending on time was performed in the range of 20–180 min.

The optimum pH and salt level were examined as parameters influencing the extraction efficiency. In this context 10 ml pure water was spiked with the EDs and extracted at pH 2, 4 and 8. In addition spiked water samples containing 105, 210, 263 and 333 mg ml^{-1} NaCl at pH 2 were enriched. In both cases extraction was performed with an 85 μm PA fibre for 30 min.

Furthermore the desorption time was varied between 2 and 4 min and the desorption temperatures chosen were 280 °C and 310 °C.

In all the optimization experiments a concentration level of 4–5 μg l^{-1} of each ED was used and the extraction temperature was always about 30 °C.

The linearity of the method was determined using two methanolic standard solutions at concentration levels of 10–13 and 100–130 μg ml^{-1}, respectively. The stock mixtures were diluted into a series of 13 standard solutions for calibration. All calibration points were arithmetic means of duplicate measurements.

Precision was ensured by a 5-fold SPME procedure for spiked pure water samples.

2.4. SPE procedure

Solid-phase extraction (SPE) for the determination of EDs in wastewater samples was performed in accordance with Stumpf et al. [5] with minor modifications. Briefly, a 1 l water sample was filtered (glass fibre filter GF52 from Schleicher and Schüll, Dassel, Germany), acidified to pH 2 and spiked with 100 μl of internal standard (1,2,3,4-tetrachloronaphthaline, BPA d14, 4n-NP and estradioldiacetate; final concentration 0.1 μg l^{-1} each). Glass cartridges were filled with 100 mg LiChrolut® EN and 250 mg LiChrolut® RP-18 from Merck (Darmstadt, Germany), conditioned with *n*-hexane and acetone as well as pure water of pH 2. After sample addition at a flow rate of 3 ml min^{-1}, the cartridges were dried for 90 min with inert gas (argon). The analytes were eluted with 8×1 ml acetone and the extracts were concentrated to about 200 μl by a gentle stream of argon. The samples were cleaned up on a 1 g silica gel column (deactivated with 1.5% water) preconditioned with an *n*-hexane/acetone mixture (65/35; v/v). After loading the sample, the analytes were eluted with 10 ml *n*-hexane/acetone (65/35; v/v). For off-line derivatization the eluate was evaporated to dryness. Then the analytes were silylated for 1 h at 60 °C with 100 μl Sylon BTZ (Supelco, Belle-

fonte, PA, USA). Excessive reagent was hydrolyzed with 200 μl pure water of pH 2 and the analytes were extracted with 500 μl *n*-hexane. Then the organic phase was concentrated to a final volume of 200 μl, dried over sodium sulphate and transferred to a 100 μl insert.

2.5. Instrumental parameters

A GC–MS system of Agilent Technologies (6890 GC with 5973 MSD, San José, USA) was used for analysis. The capillary column was a fused-silica HP-5 MS (30 m×0.25 mm I.D., 0.25 μm film thickness; Agilent Technologies, San José, USA). The deactivated glass liner had an internal diameter of 2 mm.

The fibre was desorbed at 280 °C for 3 min in splitless mode. The penetration depth of the fibre was about 5.4 cm. The GC oven temperature was as follows: 50 °C held for 4 min, 20 K/min to 140 °C, maintained for 1 min, then heated at 10 K/min to 280 °C and held for 8 min. Helium was used as carrier gas at a pressure of 55 kPa.

The transfer line was held at 280 °C and the ion source at 250 °C. The MS worked in selected-ion-monitoring (SIM) mode and the electron impact energy was set to 70 eV.

The following ions were chosen: *m/z* 107/135 for t-NP, *m/z* 213/228 for BPA, *m/z* 213/296 for EE, whereas the first one mentioned was used for quantification. For quantitation of t-NP the sum of areas of all isomers was chosen. For 4n-NP *m/z* 107/220, BPA d14 *m/z* 222/239, β-estradioldiacetate *m/z* 314/356 and bromindanol *m/z* 133/115 were selected. For quantification ions at *m/z* 107, 222, 314 and 133 were used.

Concerning the SPE procedure, about 1 μl sample was injected at 280 °C into the split/splitless-injector of the GC–MS system described above, the pulsed splitless mode being selected. The temperature of the oven was initially set at 40 °C for 3 min. It was increased to 280 °C at a rate of 10 K min^{-1} and held for 8 min. For quantitation (qualification) the corresponding characteristic ions of the derivatives were used: *m/z* 207 (221) for t-NP, *m/z* 357 (372) for BPA and *m/z* 285 (300, 425, 440) for EE. The following fragment ions were selected for the internal standards: *m/z* 179/292 for 4n-NP, *m/z* 366/383 for BPA d14, *m/z* 314/356 for estradioldiacetate and *m/z* 266/264 for 1,2,3,4-tetrachloronaphthaline. The first-mentioned fragment ion was used for quantification.

3. Results and discussion

3.1. Selection of the optimum SPME-fibre coating

The SPME coatings tested for the extraction efficiency of the selected EDs differ in their polarity and sorptive properties. For example PA and PDMS/DVB are mostly used for the extraction of polar compounds like phenols, whereas PDMS fibres are useful for the enrichment of more non-polar compounds [14,21]. Moreover while polyacrylate and polydimethylsiloxane belong to the absorptively working coatings they show linearity over a wide concentration range. Fibre coatings containing divinylbenzene and carbowax, respectively, possess adsorptive properties and hence linearity over a smaller concentration range [22]. As the target analytes under study belong to a more polar class, the maximum extraction yields would be expected to be obtainable using PA or PDMS/DVB [21]. Fig. 2 shows the extraction yields obtained for each coating material. Technical nonylphenol with the highest log K_{OW} of all the analytes in this study exhibits good enrichment behaviour on each fibre type. Maximum sensitivity was obtained on 100 μm PDMS. PDMS/DVB seems best suited for the extraction of BPA. Unfortunately, blank analysis indicates partially high noise values for BPA, caused by BPA contained in the epoxy resin connecting the fibre needle to the fibre holder. Some fibre charges release high amounts of BPA and avoid the detection of BPA in the lower μg l^{-1} range. The ageing of fibres by multiple use decreases the BPA noise, but this process is accompanied by lower extraction efficiency.

As shown in Fig. 2 all EDs can be extracted in acceptable amounts with a PA fibre; this approach was used in the following experiments. The lower extraction yield for the internal standard bromindanol is tolerable, especially bearing in mind that real wastewater samples are analyzed using 4n-NP, BPA d14 and β-estradioldiacetate as internal standards.

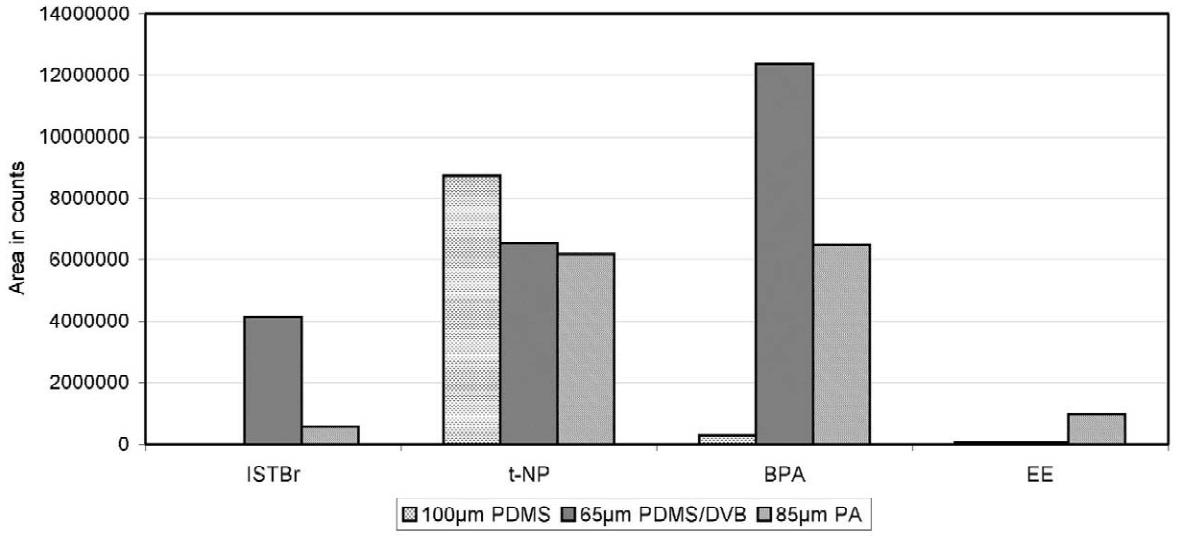

Fig. 2. Selection of the optimum fibre coating. Examined fibre types, 100 μm PDMS, 65 μm PDMS/DVB, 85 μm PA. 9.5 ml pure water containing 2 μg l^{-1} bromindanol (ISTBr), 4.08 μg l^{-1} t-NP, 5.2 μg l^{-1} BPA and 4.64 μg l^{-1} EE, 1 g NaCl at pH 2; extraction time, 60 min; extraction temperature, 30 °C; agitation speed, 500 r.p.m.; desorption temperature, 280 °C; desorption time, 3 min.

Nevertheless, during development work bromindanol was added to pure water samples in order to control reproducibility during the extraction and the desorption step. Blank analysis of every fibre type in pure water was performed and the chromatograms also indicated noise values for t-NP. In the case of t-NP contamination was probably caused by water preparation. Experiments with only deionized, bidistilled and commercially available water of HPLC grade indicated different amounts of t-NP. The lowest contamination was found in multiple distilled water.

The background concentration of BPA in PA-fibres was estimated and found to be in the range of 0.07–0.5 μg l^{-1}. The blank level of t-NP in pure water—approximately 0.1 μg l^{-1}—complicates sample quantitation by necessitating standard addition.

3.2. Extraction time

The extraction time was investigated from 20 to 180 min. Fig. 3 shows the extraction yield depending on time. The equilibrium time is reached when a further increase in the extraction time does not result in a significant increase in the detector response. The adjustment of equilibrium is a long-term process for all analytes; no compound reaches equilibrium after 180 min. However, t-NP and BPA show good response during the whole extraction time profile, whereas the sensitivity for EE is lower. As a compromise an extraction time of 60 min was applied in all the experiments for all the analytes. In this case extraction was stopped before the analytes had reached equilibrium. Compared to manual SPME, the automated SPME procedure enables the strict observance of exact extraction times, enabling better reproducibility and a decrease in relative standard deviation values.

3.3. pH and salt level

The influence of pH on extraction efficiency was studied at pH 2, 4 and 8. The higher the pH, the lower the response and so a pH value of 2 was used in all the experiments.

The result of salt addition is shown in Fig. 4; for t-NP the response decreases significantly as the salt concentration increases. BPA and EE show a slight increase in extraction yield at a NaCl concentration of 105 mg ml^{-1}, which is hardly lowered up to the saturated condition. The higher the salt concentration, the higher the response of the internal standard bromindanol. To analyse the selected compounds,

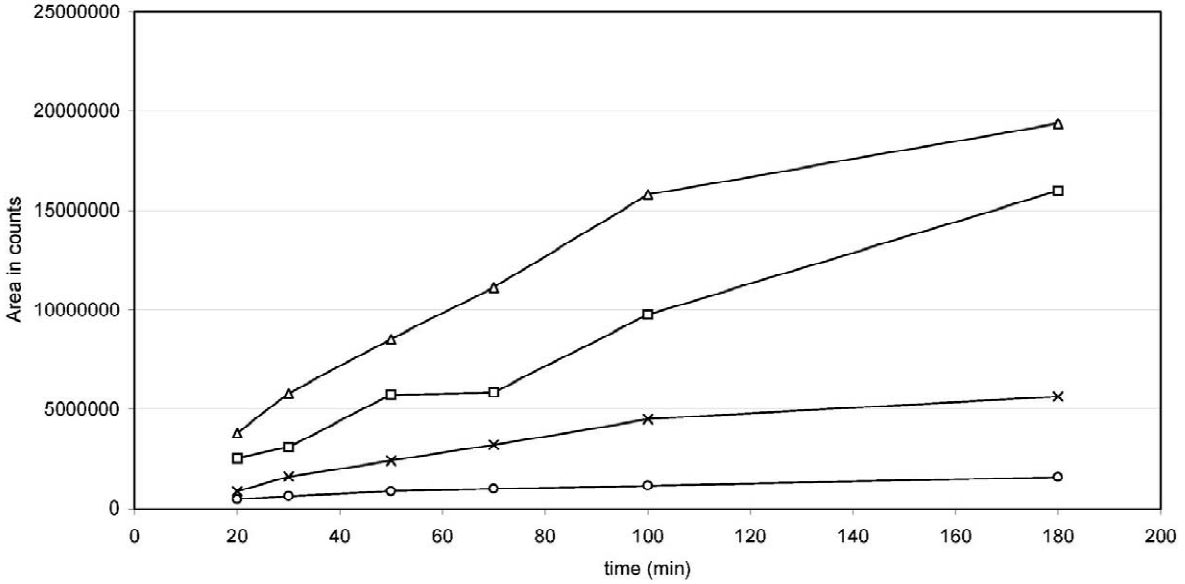

Fig. 3. Extraction time profile for 85 μm PA fibre. Extraction conditions as in Fig. 2. ○, bromindanol; □, t-NP; △, BPA; ×, EE.

the addition of salt is not necessary. However, with regard to the multicomponent analysis of environmentally relevant compounds, in particular alkyl- and chlorophenols [23] as well as pharmaceuticals [9], where salt saturation leads to higher extraction yields, a salt level of 105 mg ml^{-1} sodium chloride was used as a compromise in the following experiments.

3.4. Optimization of desorption conditions

Two different desorption temperatures (280 and

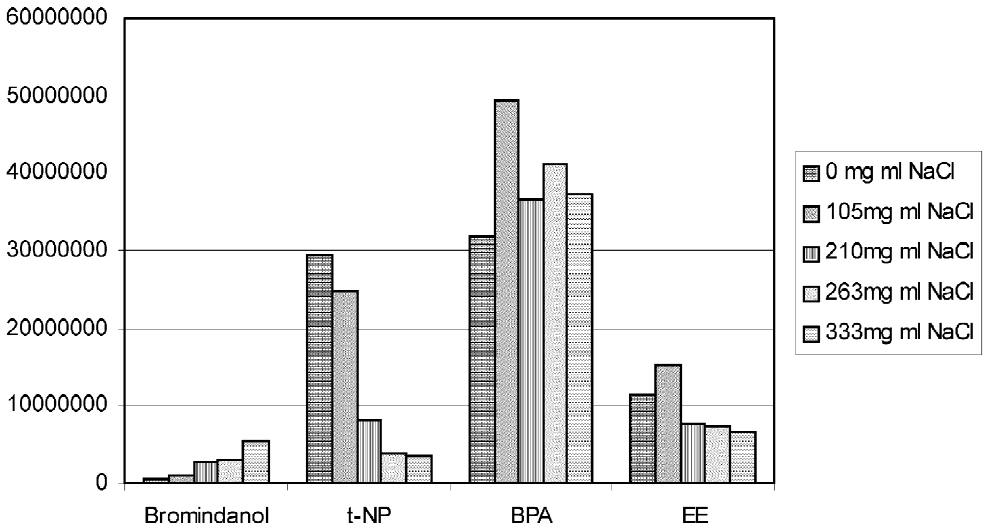

Fig. 4. Effect of salt addition, for 0, 105, 210, 263 and 333 mg ml^{-1} sodium chloride, respectively, added to 10 ml pure water containing 5 μg l^{-1} I.S. TBr, 4.08 μg l^{-1} t-NP, 5.2 μg l^{-1} BPA and 4.64 μg l^{-1} EE. Extraction conditions: 85 μm PA fibre; extraction time, 30 min.

Table 1
Linear range, detection and quantitation limits as well as precision (LODs, LOQs for SPE–GC–MS method are listed in brackets)

Compound	Linear range studied ($\mu g\ l^{-1}$)	Corr. Coef. (r^2)	LOD ($\mu g\ l^{-1}$) [a]				LOQ ($\mu g\ l^{-1}$)[b]				Precision[c] (% RSD)
			pure[d]	model[e]	effluent[f]	(SPE)[g]	pure	model	effluent	(SPE)	
t-NP	0.27–153	0.9919	0.2	0.4	0.8	(0.06)	0.6	1.2	2.4	(0.18)	6
BPA	0.34–195	0.9972	0.3	1	1	(0.02)	0.9	3	3	(0.06)	10
EE	0.03–174	0.9977	0.02	0.03	0.04	(0.01)	0.06	0.09	0.12	(0.03)	9

[a] The limit of detection (LOD) corresponds to a signal-to-noise ratio of about 3:1.
[b] The limit of quantitation (LOQ) is defined as three times the LOD.
[c] $n=5$.
[d] Pure water.
[e] Model wastewater composition in accordance to DIN 38412 T24.
[f] Effluent of the pilot scale wetland plant of Langenreichenbach (Germany).
[g] Limit of detection in effluent by use of SPE.

310 °C) within the recommended 85 μm fibre operating range were evaluated for a desorption time of 3 min. Due to the fairly high blind values of BPA illustrated in Section 3.1 which increased with the desorption temperature, 280 °C was chosen.

Desorption time was studied at 2, 3 and 4 min. The results showed that desorption was complete after 3 min at the selected concentration level.

In short, the optimum sampling of EDs from water works with an 85 μm PA fibre for 1 h in 9.5 ml water of pH 2 and 105 mg ml^{-1} NaCl, agitated at a fixed value of 500 r.p.m. and the analytes were desorbed at 280 °C for 3 min.

3.5. Linearity, precision and detection limits

The linearity of the SPME procedure was examined between 0.027 and 195 μg l^{-1}. All analytes showed good linearity with correlation coefficients of $r^2 \geq 0.99$ (Table 1).

Precision was measured by a 5-fold SPME procedure at a concentration level of 4 μg l^{-1} for each analyte. The RSD values were about 6% for t-NP, 10% for BPA and 9% for EE. Under the optimized desorption conditions, carry-over of these samples was negligible, 0% for t-NP and BPA and 2% for EE, and was completely prevented by keeping the fibre in the PTV-injector (split mode) for 5 min.

The LODs determined in pure water and wastewater samples (effluent and model wastewater), respectively, correspond to a signal-to-noise ratio of about 3:1. The LODs of the EDs in pure water were appointed with blank values and lower calibration levels used for the determination of the linear range and were found to range from 0.03 μg l^{-1} for EE to 0.4–1 μg l^{-1} for BPA. The limit of quantitation (LOQ) defined as three times the LOD were also calculated and listed in Table 1.

3.6. Analysis of water samples

Prior to real sample analysis, pure water was spiked with different amounts of 4n-NP, BPA d14 and estradioldiacetate in order to find the optimum internal standard concentration with finally 0.2 μg l^{-1} 4n-NP, 0.4 μg l^{-1} BPA d14 and 0.04 μg l^{-1} estradioldiacetate being chosen. First of all, wastewater influent samples were examined at this internal standard level. Extraction was carried out using the conditions described in the experimental section.

Compared with a pure water sample spiked at the same concentration level as the influent sample, the chromatogram (Fig. 5) indicates a decrease in sensitivity for each internal standard by a factor of 7 for 4n-NP and 2 for BPA d14. There is no signal visible for estradioldiacetate in the total-ion-chromatogram (TIC) of the influent sample; only the extracted ion of m/z 314 shows a small signal for estradioldiacate, which emphasizes a clear analyte-supressing effect.

With regard to the significant matrix influence on the response, all the following measurements with wastewater effluents and model wastewater samples were examined at a higher internal standard level.

To determine detection limits in defined effluent samples (constructed wetland in Langenreichenbach) and in model wastewater from laboratory reactor, standard addition was used. The samples were multiply extracted: one sample only with internal standard and the other ones with both internal standard and aliquots of an ED-standard mixture. The samples were compared with references (pure water) of the same concentration levels. Whereas 4n-NP and t-NP are suppressed 13- and 4-fold, respectively, for BPA, BPA d14 and EE no decrease in response was observed. In Fig. 6 selected chromatograms of effluent, model wastewater and a reference of spiked pure water are overlaid in order to show the matrix influence.

Comparing the chromatograms of the model wastewater and the reference, no matrix influence is observable for BPA, BPA d14 or EE. The sensitivity of t-NP and estradioldiacetate is reduced by a factor of 2 and for 4n-NP by 6. The LODs and LOQs of effluent and model wastewater are listed in Table 1. Due to the high noise values for BPA, detection limits below 1 μg l^{-1} are not achievable, i.e. the relatively high detection limits of BPA are not caused by the matrix (Section 3.1).

As Table 1 shows, the LODs of the EDs obtained using SPME are much higher than those of SPE [5,10,11]. Concerning only LODs, SPME seems not to be the method of choice for trace analysis of the target analytes. However, the method's performance characterized by high precision, reproducibility, good linearity and last but not least fast, simple and

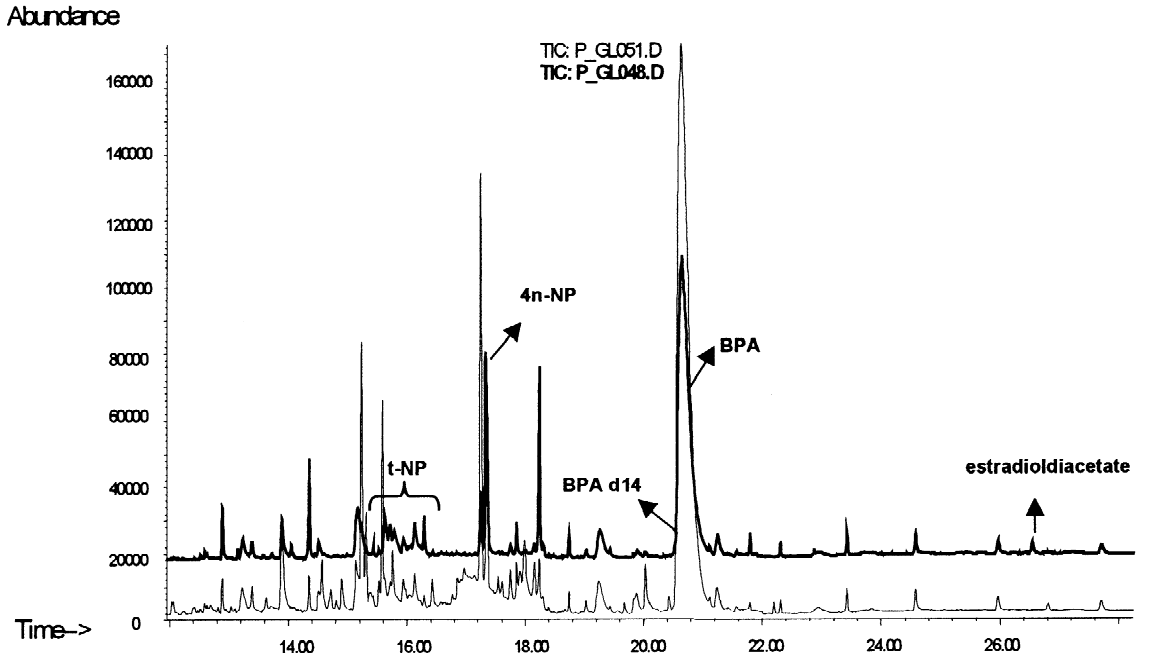

Fig. 5. The SPME–GC–MS-chromatogram with the narrow plotted line corresponds to an influent sample from the pilot-scale wetland plant in Langenreichenbach spiked with internal standard only; as reference pure water spiked with 4n-NP, BPA d14 and estradioldiacetate at the same concentration level was used (bold line).

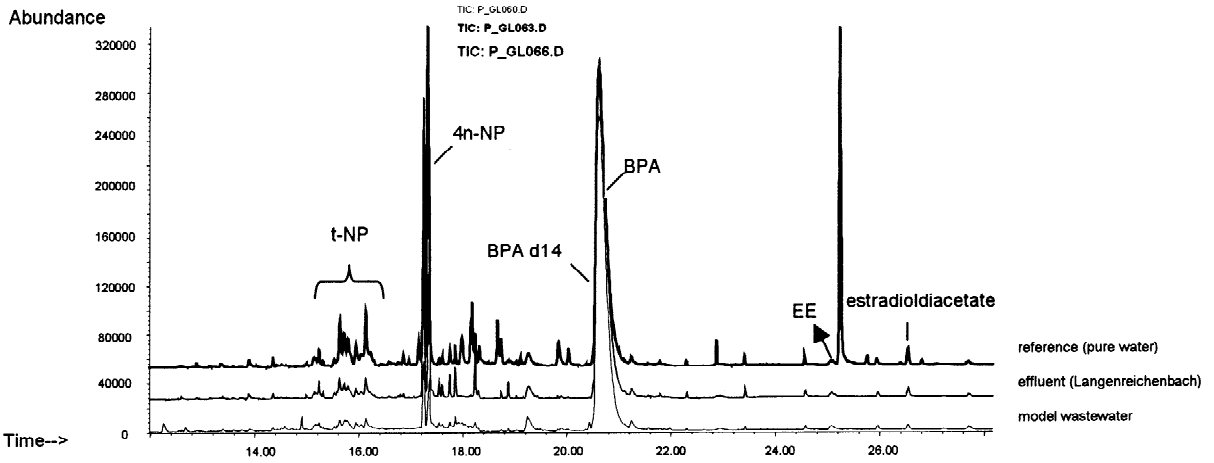

Fig. 6. GC–MS-chromatogram of SPME-enriched analytes for an effluent from the pilot-scale wetland plant in Langenreichenbach, model wastewater and pure water. All samples were spiked with internal standards and ED standard mixture at the same concentration level (0.8 $\mu g l^{-1}$ for 4n-NP and t-NP, 0.16 $\mu g l^{-1}$ for BPA d14 and 2 $\mu g l^{-1}$ for BPA, 0.16 $\mu g l^{-1}$ for estradioldiacetate and EE).

solvent free operation qualifies this method for analysis at the lower μg l^{-1} level.

4. Conclusions

This work was mainly focused on the development of a time- and substance-saving extraction technique automatically coupled to GC–MS. It was in this context that solvent-free SPME was examined. Polyacrylate was found to be the most effective coating material in connection with the optimized extraction conditions comprising 1 g sodium chloride per 9.5 ml water sample, pH 2 and an extraction time of 1 h at 30 °C using the fixed agitation speed of 500 r.p.m. (Multipurpose Autosampler MPS 2).

The linearity of the method was found for over three orders of magnitude. The optimized method showed good precision with RSD values between 6 and 10%. Carry-over was negligible. Detection limits were in the lower μg l^{-1} range. Thus the SPME–GC–MS procedure can only be useful for determining a higher ED concentration with a minimum of time, effort and avoidance of any solvent use. Matrix influence was found to be a sensitive parameter in method development. It is recommended that for matrix changing a method adjustment is needed. In the case of highly matrix loaded waters standard addition is preferred using an isotope-labelled internal standard.

Attention has to be paid to the sometimes fairly high noise values of BPA and t-NP caused by SPME fibre production which use materials contaminated by BPA (epoxy resin) as well as t-NP. BPA sample data always has to be corrected by fibre blanks. The blind value of t-NP is lower than BPA, but can hardly be avoided because of the ubiquity of this substance.

Although the SPE procedure is very time-consuming and labour-intensive, it eliminates matrix compounds, features high enrichment capacity and allows detection limits in the ng l^{-1} range. Hence SPE coupled to GC–MS analysis is the method of choice for the trace analysis of EDs in wastewater samples. Alongside SPE, which has been established as the standard protocol for determination of analyte traces ($\leq$ ng l^{-1}), SPME–GC–MS has been proved to be an additional method for the fast, simple screening and monitoring of the target analytes at the μg l^{-1} scale. The automation of the procedure combines high sample throughput with high reliability, making it useful for monitoring industrial processes and laboratory experiments.

Acknowledgements

The authors would like to thank the BMBF (German Ministry of Education and Research) for the financial support kindly provided (02WA9982/1).

References

[1] K. Fent, Ecotoxicology, Thieme Verlag, Stuttgart, New York, 1998.
[2] M. Regitz, J. Falbe, Römpp Lexikon der Chemie, Thieme Verlag, Stuttgart, New York, 1999.
[3] The Bisphenol A Global Industry Group, Bisphenol A, 1 and 2, Washington D.C., 1999 and 2000.
[4] R.E. Hester, R.M. Harrison, in: Endocrine Disrupting Chemicals, Issues in Environmental Science and Technology, Vol. 12, The Royal Society of Chemistry, Cambridge, 1999.
[5] M. Stumpf, T.A. Ternes, K. Haberer, W. Baumann, Vom Wasser 87 (1996) 251.
[6] N. Theobald, C. Meyer, Forschungsbericht FKZ 29922281, Bundesamt für Seeschifffahrt und Hydrographie, Hamburg, 2001.
[7] S. Cathum, H. Sabik, Chromatographia 53 (2001) 400.
[8] S. Cathum, H. Sabik, Chromatographia 53 (2001) 394.
[9] M. Moeder, S. Schrader, M. Winkler, P. Popp, J. Chromatogr. A 873 (2000) 95.
[10] R. Holtey-Weber, H. Färber, H.F. Schöler, Vom Wasser 92 (1999) 1.
[11] P. Spengler, W. Körner, J.W. Metzger, Vom Wasser 93 (1999) 141.
[12] M.I.H. Helaleh, S. Fujii, T. Korenaga, Talanta 54 (2001) 1039.
[13] Y. Takao, H.C. Lee, K. Arizono, Bunseki Kagaku 48 (1999) 589.
[14] J. Pawliszyn, Solid Phase Microextraction—Theory and Practice, Wiley–VCH, New York, Weinheim, 1997.
[15] H. Kataoka, M. Ise, S. Narimatsu, J. Sep. Sci. 25 (2002) 77.
[16] J. Salafranca, R. Batlle, C. Nerin, J. Chromatogr. A 864 (1999) 137.
[17] Y. Takao, H.C. Lee, Y. Ishibashi, S. Kohra, N. Tominaga, K. Arizono, Jpn. J. Toxicol. Environ. Health 45 (1999) 39.

[18] U. Kappelmeyer, A. Wiessner, P. Kuschk, M. Kaestner, Chemie Ingenieur Technik 73 (11) (2001) 1472.
[19] U. Kappelmeyer, A. Wiessner, P. Kuschk, M. Kaestner, Chem. Eng. Technol., in press.
[20] U. Kappelmeyer, A. Wiessner, P. Kuschk, M. Kaestner;, in: A. Leeson (Ed.), Proceedings of the International In Situ and On-Site Bioremediation Symposium, 6th, San Diego, CA, United States, June 4–7, 2001, Vol. 5, Battelle Press, Columbus, Ohio, 2001, p. 337.
[21] A. Peòalver, E. Pocurull, F. Borrull, R.M. Mareé, Trends Anal. Chem. 18 (1999) 8.
[22] J. Pawliszyn, Applications of Solid Phase Microextraction, The Royal Society of Chemistry Chromatography Monographs, Cambridge, 1999.
[23] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.