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Analysis of 35 priority semivolatile compounds in water by stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry
I. Method optimisation

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Abstract

A multiresidue method for the determination of 35 organic micropollutants (pesticides and polycyclic aromatic hydrocarbons) in water has been optimised using stir bar sorptive extraction (SBSE) and thermal desorption coupled to capillary gas chromatography–mass spectrometry (GC–MS). In the present work, the different parameters affecting the extraction of the analytes from the water samples to the PDMS-coated stir bars and optimisation of conditions affecting thermal desorption are investigated. The optimised conditions consist of a 100-ml water sample with 20% NaCl addition extracted with 20 mm length×0.5 mm film thickness stir bars at 900 rpm during 14 h at ambient temperature. Desorption is carried out at 280 °C during 6 min under a helium flow of 75 ml/min in the splitless mode while maintaining a cryofocusing temperature of 20 °C in the programmed-temperature vaporisation (PTV) injector of the GC–MS system. Finally, the PTV injector is ramped to a temperature of 280 °C and the analytes are separated in the GC and detected by MS using full scan mode (m/z 60–400). Under the described conditions, the good repeatability, high analyte recoveries and robustness, make SBSE a powerful tool for routine quality control analysis of the selected semivolatile compounds in water samples.

Keywords: Stir bar sorptive extraction; Extraction methods; Thermal desorption; Optimization; Water analysis; Pesticides; Organochlorine compounds; Organophosphorus compounds; Triazines; Polynuclear aromatic hydrocarbons

1. Introduction

In recent years, there has been an increasing interest in developing new analytical techniques in the environmental field, especially for the monitoring of organic pollutants in water, because a large number of new organic compounds are being introduced into the environment every year. This increasing problem obliges the governmental authorities to adapt their legislation in order to protect human health and the environment. For example, the recent European Directive 98/83/CE related to water consumption [1] incorporated new organic pollutants to be monitored. The tendency in routine analytical laboratories is to obtain results for a large number of samples on the day of sampling. Since chromatographic methodologies are generally time-consuming due to sample pre-treatment and clean-up steps, the trend is to develop accurate, easy-to-automate and

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sensitive methods, which reduce sample handling. Generally, more than two different methodologies based on liquid–liquid extraction (LLE) or solid-phase extraction (SPE) coupled to GC or HPLC are used to detect the organic micropollutants below 0.1 μg/l to assure the potability of the water samples according to European legislation.

A novel sample preparation method, stir bar sorptive extraction (SBSE), was introduced by Baltussen et al. [2,3], which is based on the same mechanisms as SPME [4]. In SBSE, a magnetic stirring bar coated with polydimethylsiloxane (PDMS) is added to water samples of 10–200 ml to promote the transport of analytes into the coating polymer [1]. After a predetermined extraction period, the analytes are thermally desorbed in the GC injector or solvent extracted for HPLC analysis. The main advantage of SBSE is that 25–100 μl PDMS polymer is used instead of 0.5 μl as in SPME. The applications developed with SBSE have shown low detection limits (sub-ng/l to ng/l levels) and good repeatability, confirming the great potential of this technique [2,5,6]. Applications have been developed for the analysis of polycyclic aromatic hydrocarbons (PAHs) in water samples by SBSE coupled to GC–MS [2,6,7] and solvent extraction and HPLC–fluorescence detection [8]. Selected dicarboximide fungicides in wine have been analysed by SBSE [9], organochlorine pesticides and chlorobenzenes in strawberries [5], polychlorinated biphenyls, PAHs and chlorophenols in water and organotin compounds in several environmental matrices [10].

In the present work, the optimisation of a stir bar sorptive extraction and thermal desorption coupled to capillary gas chromatography–mass spectrometry (SBSE–TD–GC–MS) for the determination of semivolatile organic micropollutants in water destined for human consumption is described. The parameters affecting the extraction of the analytes from water into PDMS-coated stir bars and optimisation of the conditions affecting thermal desorption are investigated for 35 semivolatile compounds, including 17 chlorinated pesticides, four organophosphorus pesticides, eight triazines, and six PAHs covering a wide range of physico-chemical properties and permitting the evaluation of the potential of SBSE–TD–GC–MS for multiresidue analysis.

2. Experimental

2.1. Standards

A standard containing 17 organochlorine pesticides [α-hexachlorocyclohexane (α-HCH), β-HCH, δ-HCH, lindane, heptachlor, heptachlor epoxide, metoxichlor, aldrin, endrin, dieldrin, endrin ketone, endosulfan I, endosulfan II, endosulfan sulphate, *p,p′*-DDD, *p,p′*-DDE and *p,p′*-DDT] at a concentration of 2000 mg/l in methanol was purchased from Supelco (Oakville, Canada). Triazines (simazine, atrazine, propazine, terbutylazine, trietazine, ametryn, prometryn and terbutryn) and organophosphorus pesticides (diazinon, parathion, methyl parathion and ethion) were purchased from Dr Ehrenstorfer (Augsburg, Germany) and Riedel-de Häen (Seelze, Germany), respectively. PAHs (fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) were purchased from Dr Ehrenstorfer and from Fluka (Buchs, Swizerland). The purity of all the standards was always higher than 97%. A working solution containing all compounds studied at a concentration of 500 μg/l in methanol was prepared.

2.2. Materials and sample description

The extractions were carried out with 10 mm×0.5 mm (length×film thickness) and 20 mm×0.5 mm PDMS commercial stir bars, supplied by Gerstel (Mülheim a/d Ruhr, Germany) using either 20 ml headspace vials or 100-ml Erlenmeyer flasks. Prior to use, the stir bars were conditioned in an empty thermal desorption tube at 300 °C for 4 h with a helium flow of 50 ml/min. Agitation was carried out using a 15 position magnetic stirrer (Gerstel, Mülheim a/d Ruhr, Germany). Sodium chloride and HPLC-grade methanol (Merck, Darmstadt, Germany) were used for matrix modification experiments.

Samples were prepared daily using Milli-Q water (Millipore, Milford, MA, USA) by adding the corresponding working solution containing all target compounds in methanol at 500 μg/l.

2.3. Apparatus

The coated stir bars were thermally desorbed using a commercial thermal desorption unit TDS-2 (Gerstel) connected to a programmed-temperature vaporisation (PTV) injector CIS-4 (Gerstel) by a heated transfer line. The PTV injector was installed in an Agilent 6890 GC-5973 MS system (Agilent Technologies, Palo Alto, CA, USA). The TDS-2 unit was equipped with a TDSA autosampler (Gerstel) able to handle the program for 20 coated stir bars (Twisters, commercial name). After the extraction, the stir bar was removed from the water sample, gently dried with a paper tissue and finally introduced into a glass desorption tube. All glass tubes containing a Twister were placed in a magazine which was assembled in the TDSA autosampler, and were successively introduced into the thermal desorption module by the autosampler. Then, the temperature was programmed to the final desorption temperature under helium flow and the desorbed analytes cryofocused in the PTV system with liquid nitrogen. Finally, the PTV system was ramped to the final temperature for analysis by GC–MS. The analyses were carried out using a HP-5 MS column (30 m×0.25 mm I.D. 0.25 μm film thickness, 5% phenyl–95% polydimethylsiloxane). The column was kept at 70 °C for 2 min, ramped at 30 °C/min to 200 °C and held for 1 min and increased at 3 °C/min to 280 °C and held for 2 min. Detection was carried out using electron impact ionisation (EI+) in the full scan mode, in the m/z range 50–400 and a characteristic ion for each compound was used to obtain the peak areas presented in all the graphs (Fig. 1).

2.4. Optimisation procedure

2.4.1. Factors affecting desorption

Desorption temperature, desorption time and desorption flow (helium flow) and cryofocusing temperature in the PTV injector were evaluated to achieve the best global analyte transfer from the stir bars to the column by comparing the peak areas obtained under the same conditions: 20 ml Milli-Q water and 20% NaCl, fortified at 0.1 μg/l level for all compounds studied extracting with 10 mm×0.5 mm PDMS stir bars during 4 h at 1400 rpm.

2.4.2. Factors affecting extraction

The factors affecting the analyte extraction (salting out effect, addition of methanol, volume of samples, use of two different commercial stir bars, equilibrium–time profile and stability of the analytes in the stir bars after extraction) were evaluated to achieve the best global analytical conditions, mainly focusing on the more polar analytes where the extraction to the apolar PDMS is less effective.

3. Results and discussion

3.1. Factors affecting desorption

3.1.1. TDS desorption temperature and desorption time

3.1.1.1. Desorption temperature

Desorption temperatures of 280 and 300 °C were compared at a fixed desorption time of 10 min and a cryofocusing temperature of −100 °C in the PTV injector. The same peak areas were obtained with no carryover effect at either temperature, even for the high-molecular mass PAHs. Siloxane bleeding from the PDMS coating was significantly lower at 280 °C, which was selected for the rest of the experiments.

3.1.1.2. Desorption time

Desorption times from 4 to 8 min (at a desorption flow of 50 ml/min recommended by the stir bars supplier) were tested. After 6 min, desorption was complete for all the investigated compounds (Fig. 2). For the more volatile compounds, such as α-HCH or lindane and even for simazine and atrazine, 4 min desorption time is long enough for complete desorption. To ensure that complete desorption was achieved, carryover was investigated by a second thermal desorption of the stir bars. In the case of 6 min desorption time, carryover for the less volatile compounds, such as indenopyrene and benzo[*ghi*]perylene was around 0.05%. A desorption time of 6 min was selected for the rest of the experiments.

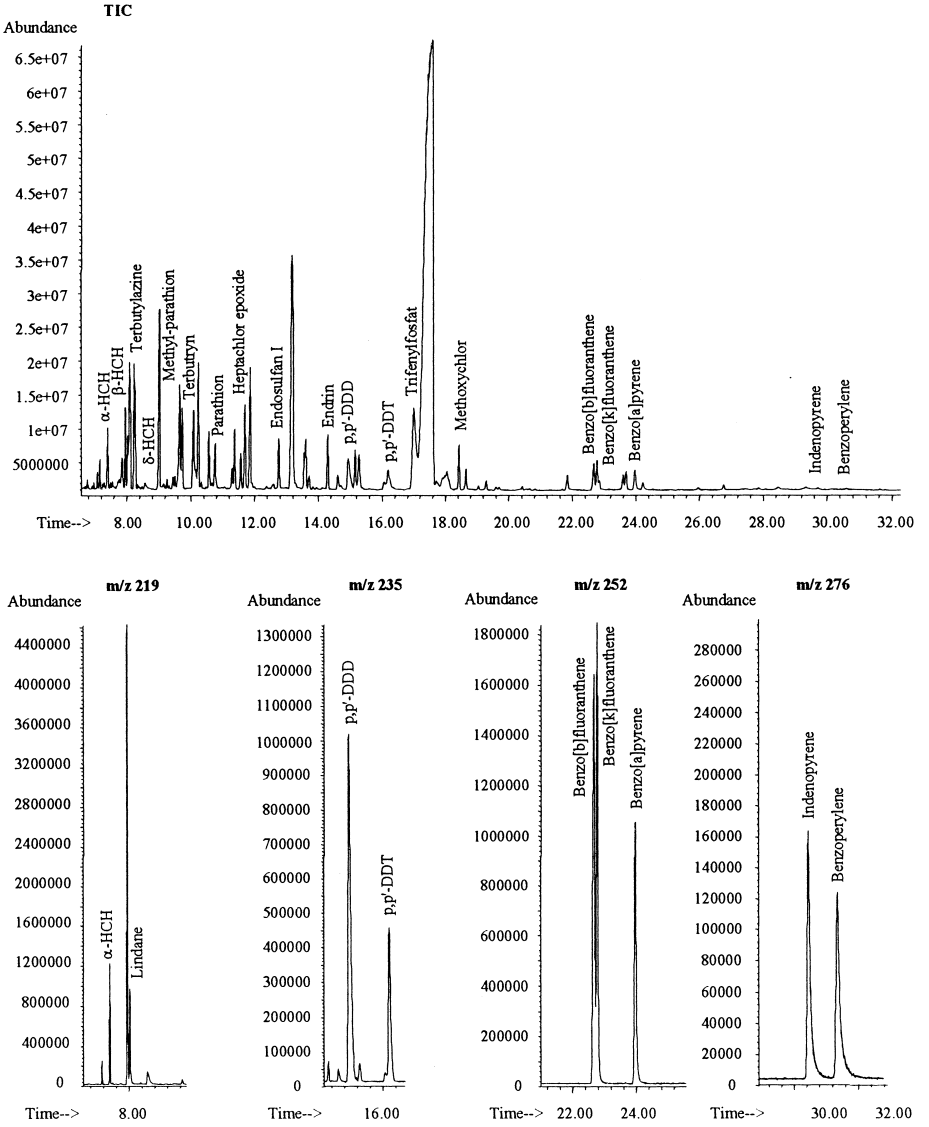

Fig. 1. GC–MS chromatogram of a tap water sample fortified with the 35 target compounds at the 50 ng/l level. The total ion current (TIC) is shown at the top and some selected fragment ion chromatograms below.

3.1.2. Desorption flow and cryofocusing temperature

3.1.2.1. Desorption flow

Helium flow-rates of 20, 50, 75 and 100 ml/min were compared while the PTV temperature was maintained at −100 °C. In general, there is an increase in the signal when the helium flow increases. A 20 ml/min helium flow is clearly insufficient for adequate transfer to the PTV cooled injector, especially for the less volatile compounds such as methoxychlor, indenopyrene or benzo[*k*]-fluoranthene. Carryover with stir bars desorbed at 20 ml/min was 31% for indenopyrene and 9% for benzo[*k*]fluoranthene. In general, a 100 ml/min flow gave the highest signals. For the more volatile

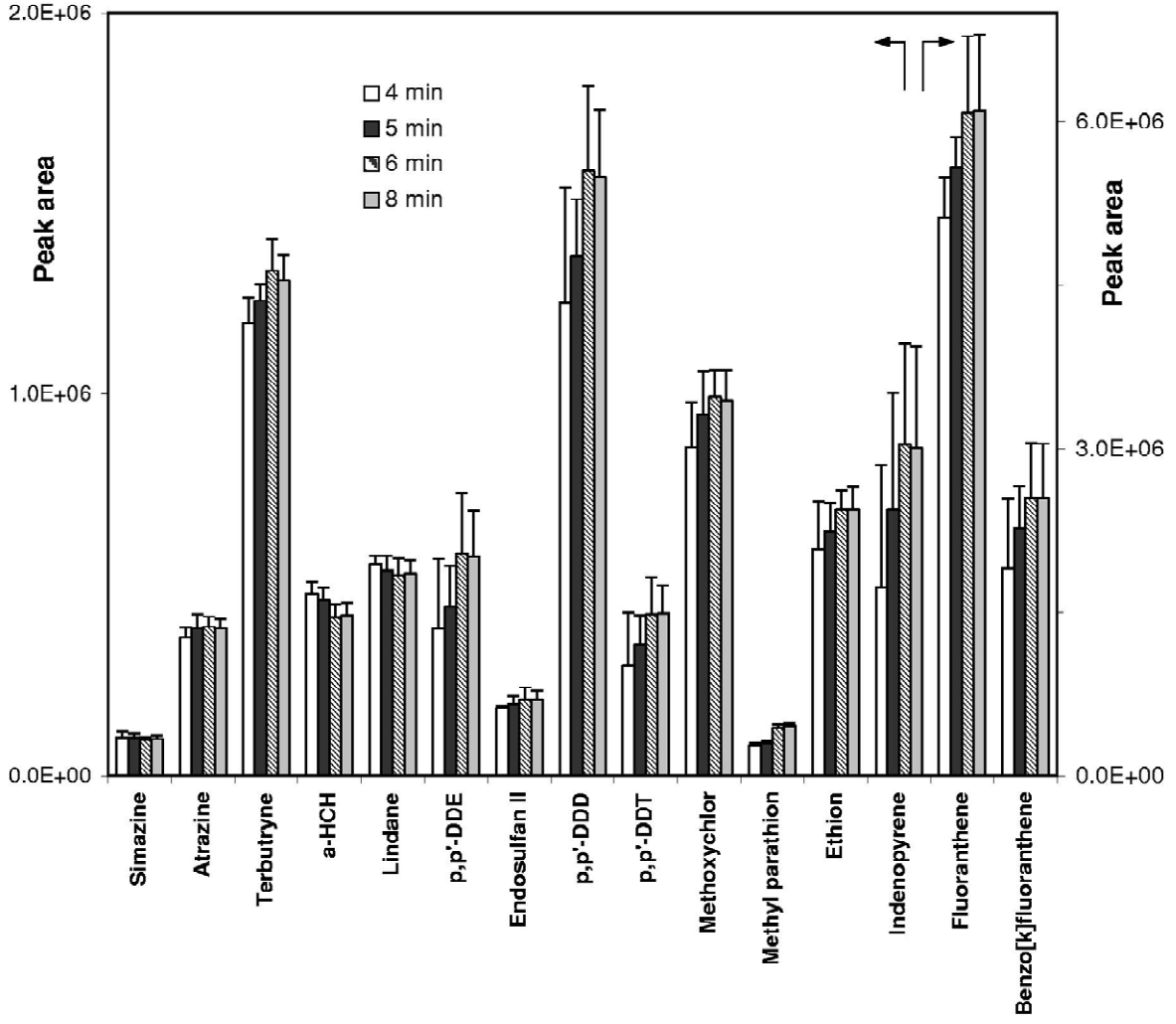

Fig. 2. Effect of desorption time on the peak area for selected compounds. Desorption flow: 50 ml/min. Desorption temperature: 280 °C. Cryofocusing temperature: −100 °C. Five replicates.

compounds such as α-HCH, lindane, simazine and atrazine, the signal decreased at 100 ml/min flow due, probably, to inadequate trapping in the cooled PTV injector. Therefore, a flow of 75 ml/min was finally selected.

3.1.2.2. Cryofocusing temperature

To study trapping efficiency, temperatures of −100, −30, 0, +20, +40 and +60 °C were compared. The most volatile compounds such as hexachlorocyclohexanes (HCHs) are poorly trapped at 60 °C (Fig. 3). No significant differences were encountered in the trapping efficiencies when working at 40 or 20 °C compared with the lowest −100 °C for these compounds. For the rest of the compounds, temperatures below 0 °C in the PTV injector gave, in general, unexpectedly smaller peak areas compared with those obtained at 20 or 40 °C. Perhaps transfer of the trapped analytes from the PTV injector to the column is less effective below 0 °C, due to water condensation and frosting in the injection port or other phenomena. A 20 °C

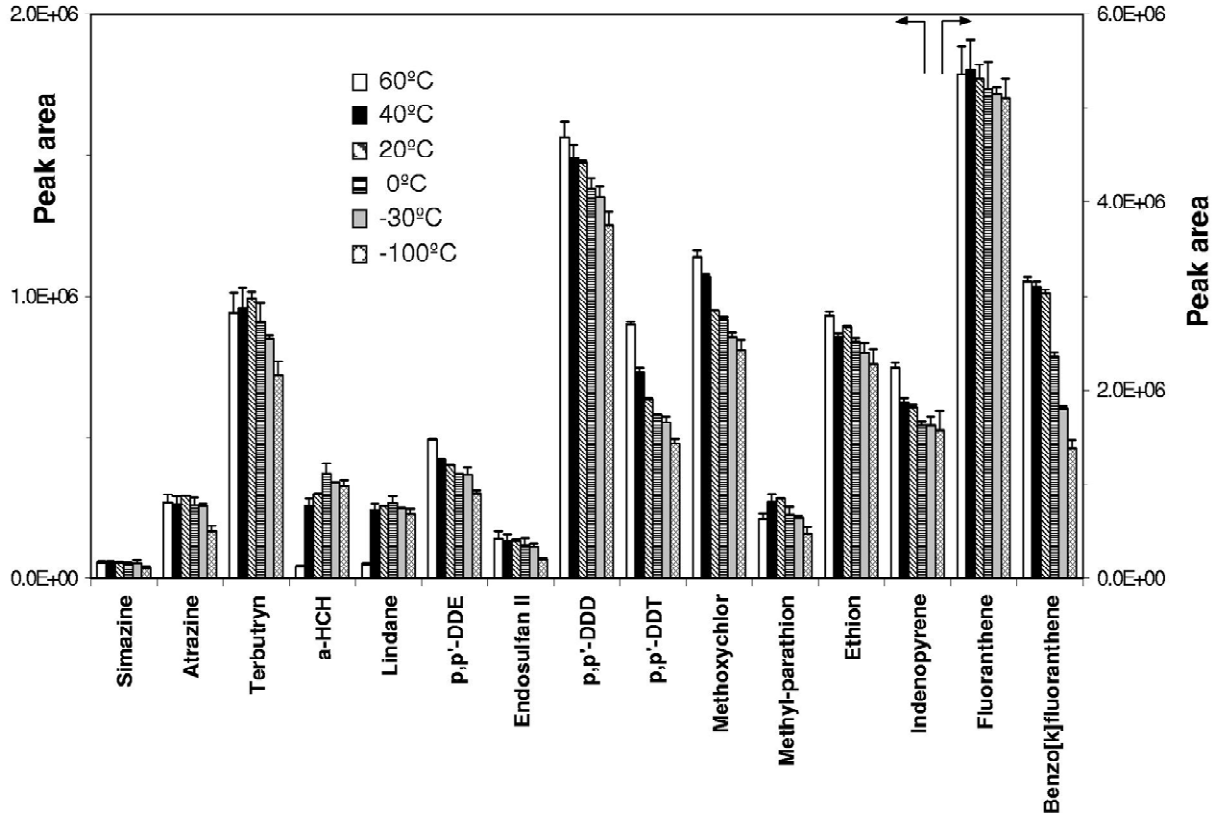

Fig. 3. Effect of cryofocusing temperature on the peak area for selected compounds. Desorption time: 6 min. Desorption temperature: 280 °C. Desorption flow: 75 ml/min. Five replicates.

cryofocusing temperature was selected for the rest of the experiments.

3.2. Factors affecting extraction

According to Ref. [2], only two parameters, the octanol–water partition coefficient (K_{ow}) of the analyte and the phase ratio, affect the recovery of an analyte at equilibrium. Nevertheless, matrix modifications such as salting out or methanol addition can modify the extraction efficiency and were investigated. After this, selection of the phase ratio for best sensitivity was studied by testing two different commercial stir bars with different sample volumes. Finally, the equilibrium–time profile under the selected conditions and the stability of the extracted stir bars were studied.

3.2.1. Salting-out effect

For the compounds investigated, K_{ow} ranged from 100 ($\log K_{ow}=2$) for the polar simazine to 4.6×10^{7} ($\log K_{ow}=7.66$) for the apolar indeno[1,2,3-*cd*]pyrene. Extraction efficiency of polar compounds will be lower than those of the more apolar ones [2]. To enhance the extraction efficiency particularly for simazine and atrazine (with $\log K_{ow}$ of 2 and 2.31, respectively) by salting out, NaCl addition was investigated as recommended [12–14]. Table 1 shows the analyte response at NaCl concentrations from 0 to 30%. Increased ionic strength favours the recovery of triazines, with an increase in the peak area of 40, 90, 130 and 200% (expressed as global increase for the group of triazines) for 5, 10, 20 and 30% of NaCl, respectively. This increase is particularly significant for simazine and atrazine, the

Table 1
Effects of NaCl addition on the peak area for all compounds studied

Compound	Response (area counts $\times 10^5$)				
	0% NaCl	5% NaCl	10% NaCl	20% NaCl	30% NaCl
α-HCH	5.77±0.17	5.66±0.08	5.77±0.37	5.75±0.70	4.80±0.37
Simazine	0.27±0.03	0.40±0.05	0.64±0.06	1.23±0.11	2.35±0.08
Atrazine	1.00±0.08	2.31±0.26	3.27±0.16	5.29±0.19	7.90±0.18
Propazine	2.17±0.11	3.77±0.21	5.47±0.24	8.11±0.16	9.81±0.25
β-HCH	1.71±0.15	2.20±0.04	2.55±0.16	2.78±0.13	3.61±0.25
Lindane	5.15±0.12	5.10±0.15	5.13±0.24	5.13±0.06	4.97±0.10
Terbutylazine	2.83±0.20	3.98±0.26	4.94±0.09	5.87±0.11	6.49±0.06
Trietazine	9.32±0.27	12.51±0.36	13.71±0.07	14.69±0.23	14.61±0.18
Diazinon	2.64±0.04	2.70±0.02	2.70±0.12	2.58±0.05	2.36±0.12
δ-HCH	2.71±0.16	3.98±0.09	4.34±0.05	4.57±0.19	4.86±0.02
Methyl-parathion	2.33±0.33	3.10±0.28	3.41±0.27	3.52±0.23	3.79±0.08
Heptachlor	3.12±0.25	2.82±0.05	2.51±0.28	1.45±0.28	0.89±0.09
Ametryn	3.09±0.41	5.43±0.72	7.23±0.59	9.86±0.22	11.27±0.21
Prometryn	5.68±0.64	7.64±0.66	9.31±0.29	10.39±0.29	10.84±0.20
Terbutryn	7.60±0.55	9.08±0.25	9.66±0.35	10.04±0.39	10.36±0.23
Aldrin	3.68±0.08	3.42±0.06	2.98±0.13	1.64±0.11	0.87±0.09
Parathion	3.14±0.15	3.55±0.22	3.60±0.13	3.55±0.12	3.38±0.03
Heptachlor epoxide	5.76±0.08	5.99±0.08	5.87±0.06	5.64±0.14	4.70±0.15
Fluoranthene	71.83±0.68	72.71±0.48	71.97±0.53	67.48±3.04	55.98±0.63
Endosulfan I	1.64±0.02	1.55±0.09	1.53±0.03	1.41±0.02	1.36±0.05
p,p′-DDE	9.00±0.19	8.32±0.43	6.60±0.42	3.47±0.55	1.95±0.30
Dieldrin	2.37±0.05	2.35±0.02	2.31±0.01	2.14±0.13	1.54±0.08
Endrin	1.91±0.23	2.12±0.09	2.17±0.06	2.00±0.04	1.61±0.07
Endosulfan II	1.66±0.05	1.69±0.05	1.64±0.02	1.57±0.13	1.28±0.09
p,p′-DDD	23.14±0.18	22.81±0.57	20.32±0.49	13.07±1.36	6.11±0.70
Ethion	9.84±0.29	10.09±0.31	9.50±0.39	7.10±0.16	3.32±0.51
Endosulfan sulphate	2.93±0.16	3.12±0.07	2.99±0.07	2.97±0.10	2.76±0.06
p,p′-DDT	6.09±0.62	5.94±0.37	5.25±0.95	2.56±0.30	1.39±0.12
Endrin ketone	2.97±0.07	3.14±0.12	3.19±0.02	3.15±0.11	2.99±0.02
Metoxiclor	9.22±1.47	10.97±0.37	11.75±1.91	9.69±0.30	4.95±0.23
Benzo[*b*]fluoranthene	42.03±1.28	40.75±1.38	34.09±1.30	20.98±1.79	11.16±1.84
Benzo[*k*]fluoranthene	50.77±1.06	49.36±1.99	43.69±2.08	27.05±3.53	14.95±1.90
Benzo[*a*]pyrene	37.76±0.87	38.96±1.29	32.21±1.65	19.70±1.70	10.32±1.60
Indenopyrene	22.89±2.64	22.20±2.42	15.76±1.91	8.30±1.09	5.31±0.73
Perylene	24.28±2.12	22.98±2.12	16.72±1.88	8.94±1.42	5.24±0.84

Agitation speed: 1400 rpm; extraction period: 4 h; five replicates.

most polar triazines, for which response improved by 800% at 30% of NaCl. Unfortunately, addition of NaCl reduces the extraction of apolar compounds, as reported for PDMS [15] and polyacrylate [16] with SPME. With 30% NaCl added, a 75% global reduction for the group heptachlor, aldrin, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, ethion and PAHs was observed. No significant effect was observed for the rest of the compounds. A 20% NaCl addition was finally selected as a compromise.

3.2.2. The effect of methanol addition and silanization on adsorption onto glass walls

Limited recoveries for very apolar compounds such as PAHs, mainly five- and six-ring PAHs, and polychlorinated biphenyls were observed when working with SPME and SBSE [2,6,17–19] due to adsorption on glass walls and the use of methanol was proposed to keep these compounds in solution. Adsorption for five-ring PAHs (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene),

six-ring PAHs (indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene), *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT and, to a lesser extent, aldrin, ethion and methoxychlor was observed among the 35 target compounds. Adsorption depends on the state of the glass surface: vials or Erlenmeyer flasks whose surfaces were damaged by abrasive cleaning materials or strong acids adsorb more strongly. The walls of old glass vials adsorbed 60–70% of the total amount of six-ring PAHs spiked in the water sample. Adsorption was evaluated by rinsing the walls of the vials or Erlenmeyer flasks with methanol after the SBSE process and analysing the methanol extract. New vials and Erlenmeyer flasks adsorbed 20% of six-ring PAH, 15% of *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT and five-ring PAHs and around 10% of aldrin, ethion and methoxychlor spiked in the sample. Nevertheless, the repeatability of the amount of analyte extracted in the stir bars using different vials or Erlenmeyer flasks was good for these compounds. A relative standard deviation (RSD) of around 10–15% was obtained for six-ring PAHs for five replicates, indicating that adsorption of the analyte on the walls of different vials or Erlenmeyer flasks (of the same supplier) is constant.

Addition of 5 and 10% methanol reduced the adsorption of five- and six-ring PAHs by 30–100% (Table 2). Extraction of the more polar compounds, mainly simazine and atrazine, decreased by around 30 to 70% at 5 and 10% methanol, respectively because the distribution constant $K_{\mathrm{PDMS/water}}$ for polar compounds decreases when the methanol content increases and the desired limit of detection for simazine could not be reached. Due to the multiresidue purpose of the present application, methanol addition was discarded.

Finally, the effect of silanization suggested in Refs. [5,15] was investigated. Vials and Erlenmeyer flasks were washed with methanol and acetone, dried at 180 °C for 2 h, immersed in dimethyldichlorosilane–toluene (10:90, v/v) for 1 h, washed again using methanol and acetone and dried for 30 min at 180 °C. The extent of analyte adsorption onto the silanized vials was compared with that obtained without silanization. Surprisingly, no difference was observed (data not shown) for the apolar compounds. Therefore, commercially available silanized Erlenmeyer flasks were purchased from Teknokroma (Barcelona, Spain) and tested. Again, no reduction in the extent of adsorption was observed. Further investigation to explain these results should be carried out because specific interactions between these apolar analytes and the glass walls were not eliminated by silanization.

3.2.3. Sample volume and PDMS volume

According to Ref. [2], the total amount extracted also depends on the phase ratio, which is the quotient of the volume of the water sample and the volume of the PDMS sorbent. Therefore two commercially available stir bars: 10 mm×0.5 mm (25 μl of PDMS) and 20 mm×0.5 mm (50 μl of PDMS) with different sample volumes were tested. Headspace sample vials were used for the 20-ml sample volume experiment and 100-ml Erlenmeyer flasks for the rest of the experiments (fixed extraction period of 4 h). Under non-equilibrium conditions, extraction time must be controlled precisely in order to have good repeatability. As shown in Fig. 4, four different phase ratios were compared using the maximum stirring rate that gave a stable rotation of the stir bar. Repeatability for the four conditions is acceptable (below 15% expressed as RSD). As expected, the amounts extracted with 20 mm×0.5 mm stir bars are higher than those with 10 mm×0.5 mm stir bars. For apolar compounds with high K_{ow} values, such as fluoranthene, α-HCH, lindane or terbutryn (log $K_{\mathrm{ow}}>3.5$), increased sample volume increases the amount of analyte extracted. For the more polar compounds, mainly simazine and, to a lesser extent atrazine, increased sample volume has little effect on the amount extracted. For more apolar compounds, such as indenopyrene or benzo[*k*]fluoranthene, the amount extracted barely increased from 50 to 100 ml, because for the less volatile compounds, equilibrium will take much longer periods than 4 h for 100-ml samples. It is also important to consider the geometry of the sample container depending on the sample volume and stir bar length. For instance, the use of the 100-ml Erlenmeyer flask for the 50-ml sample and 10 mm×0.5 mm stir bar is not the best situation, because agitation is not effective and the required equilibration time is much longer than in the other three experiments. Due to the high signal difference and good repeatability, 100-ml sample volumes and 20 mm×0.5 stir bars were selected.

Table 2
Effect of methanol addition on the peaks for all compounds studied

Compound	Response (area counts $\times 10^5$)		
	0% Methanol	5% Methanol	10% Methanol
α-HCH	3.94±0.10	4.76±0.17	4.67±0.17
Simazine	1.07±0.11	0.56±0.02	0.30±0.05
Atrazine	5.19±0.18	3.34±0.38	2.58±0.20
Propazine	7.16±0.54	6.14±0.23	3.91±0.24
β-HCH	2.54±0.21	2.46±0.09	1.71±0.09
Lindane	4.22±0.08	4.67±0.07	4.53±0.04
Terbutylazine	5.19±0.26	5.07±0.08	3.64±0.04
Trietazine	13.00±0.39	13.49±0.13	11.13±0.21
Diazinon	2.47±0.16	2.84±0.03	2.75±0.13
δ-HCH	3.56±0.30	3.60±0.12	3.02±0.16
Methyl-parathion	3.33±0.11	3.54±0.14	2.87±0.21
Heptachlor	0.43±0.05	0.74±0.08	1.01±0.13
Ametryn	9.35±0.25	8.11±0.11	6.75±1.00
Prometryn	8.86±0.92	10.22±0.45	8.42±0.31
Terbutryn	9.37±0.69	10.80±0.11	8.66±0.50
Aldrin	0.75±0.10	1.08±0.04	1.67±0.32
Parathion	3.30±0.17	3.98±0.08	3.53±0.13
Heptachlor epoxide	4.56±0.04	5.33±0.05	5.64±0.28
Fluoranthene	49.19±1.10	61.99±1.07	67.52±2.17
Endosulfan I	1.04±0.08	1.39±0.06	1.47±0.14
p,p′-DDE	1.47±0.34	1.56±0.12	3.21±0.24
Dieldrin	1.63±0.05	1.82±0.12	2.07±0.10
Endrin	1.74±0.03	1.93±0.07	2.03±0.08
Endosulfan II	1.17±0.04	1.45±0.07	1.49±0.08
p,p′-DDD	6.24±0.63	7.30±0.69	11.41±0.79
Ethion	4.53±0.23	4.97±0.40	6.50±0.54
Endosulfan sulphate	2.58±0.08	2.93±0.04	2.82±0.03
p,p′-DDT	0.87±0.27	0.99±0.11	2.22±0.25
Endrin ketone	2.70±0.09	3.03±0.03	3.02±0.11
Metoxiclor	5.05±0.23	6.28±0.57	9.05±0.53
Benzo[*b*]fluoranthene	9.33±1.32	12.00±0.92	24.39±2.60
Benzo[*k*]fluoranthene	9.90±1.46	12.40±1.11	24.67±1.97
Benzo[*a*]pyrene	7.18±1.05	9.47±0.44	20.08±2.08
Indenopyrene	3.36±0.62	2.95±0.26	7.50±0.47
Perylene	3.27±0.70	3.51±0.29	8.96±0.73

Agitation speed: 1400 rpm; extraction period: 4 h. Analysis performed at the optimised thermal desorption conditions. Five replicates.

3.2.4. Extraction–time profile

The extraction–time profile for a given compound is dependent on the stirring rate and temperature. The extraction–time profile was studied at the selected optimised conditions; a 100-ml sample volume, 20 mm×0.5 mm stir bars, 900 rpm and ambient temperature (21 °C). Equilibrium is reached for the more volatile compounds (HCHs, simazine, or fluoranthene) in 4–6 h (Fig. 5), 14 h is needed for atrazine, terbutryn, ethion and methyl-parathion, while 24 h is needed for the least volatile compounds such as methoxychlor and the rest of the PAHs. An extraction period of 14 h was selected as a good compromise between sensitivity and practicality.

3.2.5. Stability of the extracted sample

Under optimised conditions, the whole analytical process takes 58 min for each stir bar. Thus, for 20 samples in the Gerstel commercial autosampler, the samples should be stable. To study this, stir bars were thermally desorbed for analysis after different periods from the end of the extraction process. In general, the decrease in response was statistically insignificant (for a Student *t*-test = 95%) for all the

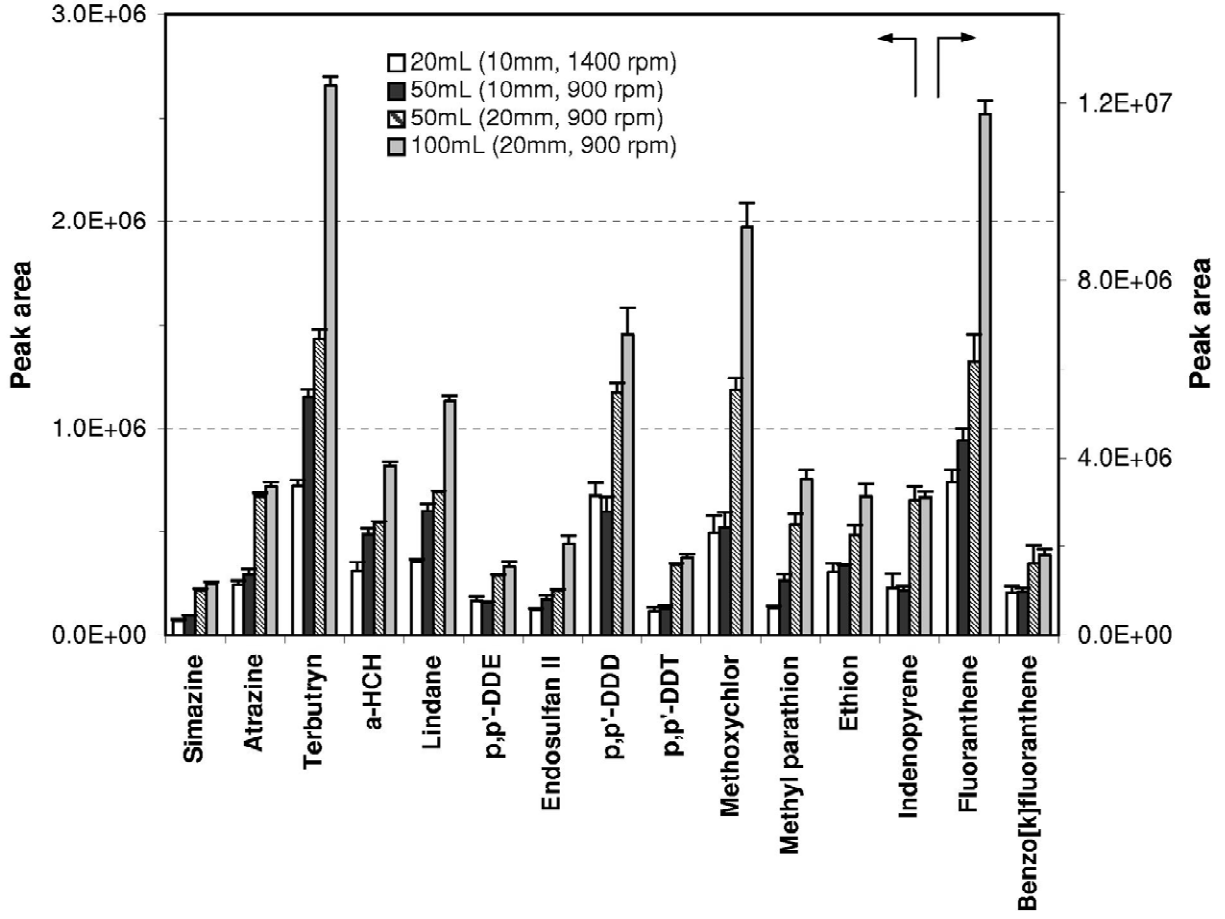

Fig. 4. Effect of phase ratio on the peak area for selected compounds: 10 mm: 25 μl PDMS; 20 mm: 50 μl PDMS. Extraction period: 4 h. Analysis performed at the optimised thermal desorption conditions. Five replicates.

compounds, up to 30 h. At 40 and 63 h, analyte recovery for some PAHs (indenopyrene and benzo[*ghi*]perylene), *p,p′*-DDE, and *p,p′*-DDT decreased by 10–25%. We have no explanation for these results because losses of α-HCH, lindane or fluoranthene due to volatilization were expected.

4. Conclusions

The optimised conditions found for the analysis of 35 priority pollutants in water using SBSE–TD–GC–MS include extraction of 100-ml water samples fortified with 20% NaCl using 20 mm×0.5 mm stir bars agitated at 900 rpm for 14 h at ambient temperature. After this, the stir bars are thermally desorbed in the splitless mode at 280 °C for 6 min and the analytes are transferred with a helium flow-rate of 75 ml/min to the PTV injector which remains at 20 °C. Finally, the PTV is ramped to 280 °C to transfer the analytes to the GC–MS column.

Under these conditions, the good repeatability, high analyte recoveries, robustness, simplicity and automation make SBSE a powerful tool for the routine quality control analysis of selected semivolatile compounds in water samples. The method will be validated, including application for the

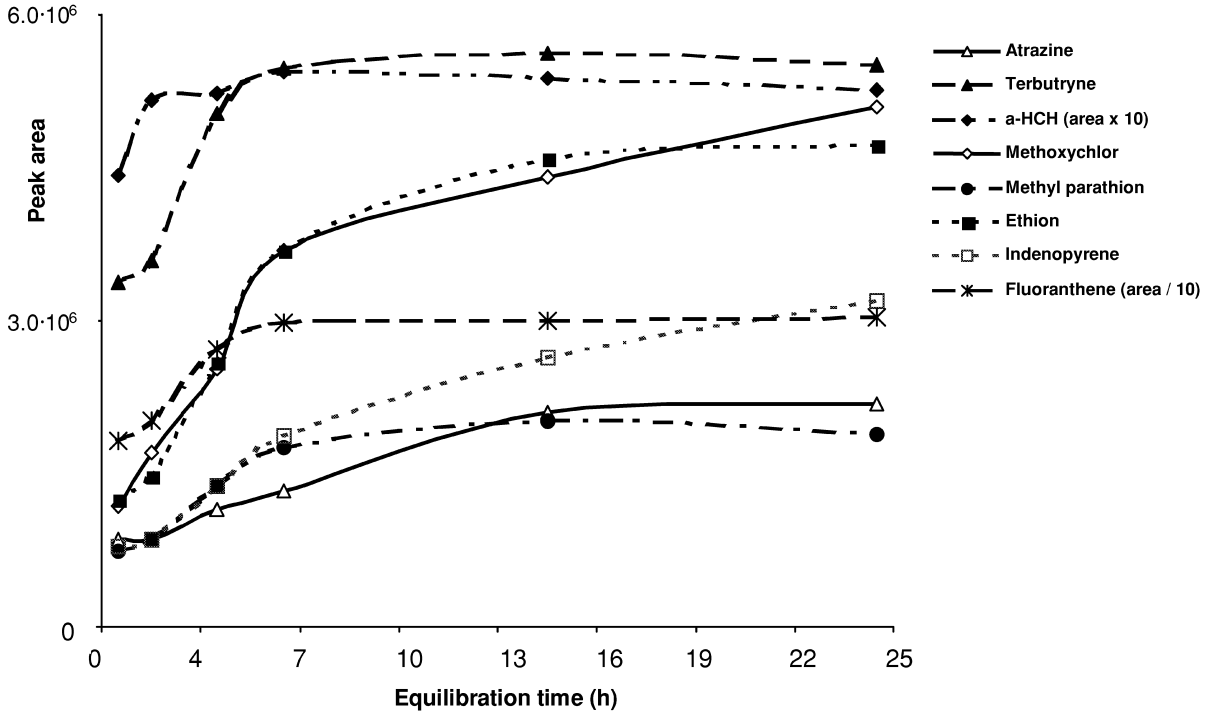

Fig. 5. Extraction–time profiles for selected compounds. Conditions: 100-ml sample, 50 μl PDMS and 20% NaCl, 900 rpm. Analysis performed at the optimised thermal desorption conditions. Three replicates.

analysis of real samples, according to Ref. [11], and will be published in Part II of this study.

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