Talanta 87 (2011) 152–160

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Development of a screening method for the analysis of organic pollutants in water using dual stir bar sorptive extraction-thermal desorption-gas chromatography–mass spectrometry

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ARTICLE INFO

Article history:
Received 5 April 2011
Received in revised form
22 September 2011
Accepted 27 September 2011
Available online 1 October 2011

Keywords:
Dual stir bar sorptive extraction (dual SBSE)
Thermal desorption
Capillary GC–MS
Organic pollutants
Water analysis

ABSTRACT

The development of a method for screening of organic compounds with a wide range of physico-chemical properties in water, based on dual stir bar sorptive extraction coupled with thermal desorption and gas chromatography–mass spectrometry (dual SBSE-TD-GC–MS) is described. The investigated water sample is divided into two aliquots and extracted with stir bar sorptive extraction at two different conditions: using addition of methanol or sodium chloride, respectively. Following extraction, the two stir bars are inserted into the same glass thermal desorption liner and are simultaneously desorbed and analysed by GC–MS. The method optimisation was performed using 45 environmentally harmful substances with different volatilities (boiling point from 193 to 495 °C), polarity (log K_{ow} from 2.17 to 8.54) and acido-basic properties. The majority of model compounds was selected from the EU list of priority substances in the field of water policy and from the US EPA method 625, respectively. Optimisation was performed for extraction parameters (sample volume, extraction time, stirring rate, addition of modifiers) as well as for the thermal desorption conditions (desorption flow, desorption time, cryofocusing temperature). Performance characteristics (recovery, repeatability, carryover, linearity, limits of detection and quantification) were determined for the optimised method. An example of analysis of a contaminated groundwater sample is presented.

1. Introduction

Current and proposed environmental regulations in the field of water policy require analysis of different organic pollutants exhibiting a wide range of physico-chemical properties. Among the variety of techniques intended for preconcentration and isolation of organic compounds from water matrix, stir bar sorptive extraction (SBSE) has become a popular solventless sample preparation method [1–5]. The method, introduced in 1999 by Baltussen et al. [6], is based on sorptive extraction, whereby the solutes are extracted into a polymer coating (mostly polydimethylsiloxane – PDMS) on a magnetic stir bar during sample stirring. The extraction step is followed by thermal or liquid desorption of the extracted analytes before their chromatographic or electrophoretic separation and appropriate detection. The advantages and good performance characteristics of SBSE are reflected in the fact that the number of published papers dealing with the use of SBSE has linearly increased in the past 10 years, reaching more than 350 peer reviewed articles in 2010 [7].

To enhance solute recovery from the aqueous matrix (and the sensitivity of determination) the SBSE conditions have to be optimised, which is a key task in the case of multiresidual analysis. Several parameters affect the SBSE procedure, from which the most important are addition of modifiers (NaCl, MeOH, pH adjustment), extraction time, stirring rate, sample and PDMS stir bar coating volumes. An overview of SBSE parameters, which have been applied in the analysis of environmentally important pollutants, is presented in Table 1 [8–17]. Listed parameters were applied in the single-shot mode, when SBSE procedure and the subsequent instrumental analysis were accomplished with a single sorptive stir bar.

Analysis of a suite of compounds with a broad range of physico-chemical properties requires different extraction conditions for optimum extraction of different compounds. In such case the dual, multi-shot or sequential mode of SBSE procedure can be employed. The dual SBSE mode was employed by Ochiai et al. [18] in a multiresidue screening method for the determination of 82 pesticides (OCPs, OPPs, carbamate, pyrethroid and others) in aqueous samples. In this method two SBSE extractions are performed simultaneously on a 20-mL sample containing 30% NaCl and a 20-mL sample without modifier (100% sample solution), respectively. The extraction with NaCl addition targets more hydrophilic pesticides (log K_{ow} < 3.5) and the other extraction with unmodified sample

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doi:10.1016/j.talanta.2011.09.055

Table 1
SBSE parameters and analytes determined in water matrix in some published studies.

Sample volume (mL)	Modifiers			PDMS phase dimension	Extraction time (h)	Stirring rate (rpm)	Analytes	Ref.
	NaCl (%)	MeOH (%)	Others					
100	20	0	–	20 mm × 0.5 mm	14	900	35 priority semivolatiles	[8]
10	1	0	–	10 mm × 1.0 mm	1	1200	endocrine disrupters (pesticides)	[9]
30	0	5	–	20 mm × 0.5 mm	1	750	PAHs, PCBs, OCPs, OPPs,PEs, APs, herbicides and others	[10]
10	23	0	–	10 mm × 0.5 mm	1	1000	64 pesticides	[11]
100	0	20	–	20 mm × 0.5 mm	25	900	PBDEs	[12]
20	20	20	–	10 mm × 0.5 mm	12	1000	PAHs, PCBs, PBDEs, PBBs, PEs, NPs and NPEOs	[13]
15	25	0	HCl (pH 2)	10 mm × 0.5 mm	4	500	phenols, acid herbicides and pharmaceuticals	[14]
10	9	0	–	10 mm × 0.5 mm	14	900	PAHs, PCBs, OCPs, OPPs and triazines	
100	9	0	–	20 mm × 0.5 mm	14	900		[15]
20	0	10	HCl (pH 2)	10 mm × 0.5 mm	3	1000	9 UV filters	[16]
100	3.4[a]	9	–	20 mm × 1.0 mm	24	900	PAHs, PCBs, PBDEs, OCPs, NPs	[17]

PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; OCPs, organochlorine pesticides; OPPs, organophosphorous pesticides; PEs, phthalate esters; APs, alkylphenols; PBDEs, polybrominated diphenyl ethers; PBBs, polybrominated biphenyls; NPs, nonylphenols; NPEOs, nonylphenol ethoxylates.
[a] Synthetic seawater.

solution targets the more hydrophobic solutes ($\log K_{ow} > 3.5$). After extraction, the two stir bars are placed in the same glass desorption liner and are simultaneously desorbed and analysed by low thermal mass GC–MS. The dual-shot approach was applied by Giordano et al. [19] in the SBSE-LC–MS/MS method for the determination of 16 pesticides in surface waters. This method requires two 50-mL aliquots of a water sample. To one sample aliquot 30% of NaCl is added and the sample is stirred at 900 rpm during 1 h for extraction of five pesticides with $\log K_{ow} < 3.0$. The other aliquot is extracted without modifier addition following the same procedure for the rest of the pesticides with $\log K_{ow} > 3.0$. After extraction, analytes from each stir bar are desorbed in 1 mL of methanol using sonication. Each extract is analysed separately. As most of the pesticides are extracted by both methods, the different recoveries obtained with salt and without salt addition can be used as an additional confirmation tool for establishing the presence of pesticide residues in the water sample.

A multi-shot SBSE mode was employed for screening endocrine-disrupting chemicals (EDCs) and pharmaceuticals in aqueous samples [20]. Four 10 mL aliquots of water were taken for SBSE and were treated under different conditions to determine a wide range of EDCs (phenolic EDCs, amine-based and acid-based EDCs, organotin compound and highly non-polar compounds). After SBSE, the four stir bars, were placed in the single thermal desorption (TD) tube together with a plug of glass wool with *bis*(trimethylsilyl)trifluoroacetamide to derivatize hydroxyl functionalities and were simultaneously analysed by TD-GC–MS.

In the sequential SBSE, only one sample aliquot is taken for the analysis and during sample treatment procedure the extraction conditions are sequentially modified. For SBSE one or more stir bars can be used. The sequential approach to SBSE was applied by Ochiai et al. [21] in a multiresidue method for the analysis of 80 model pesticides. SBSE was performed sequentially on a 5-mL sample without modifier using one stir bar (for 1 h), then on the same sample after addition of 30% NaCl using a second stir bar (1 h). The first extraction with an unmodified sample was mainly targeting hydrophobic solutes ($\log K_{ow} > 4.0$); the second extraction with a modified sample with salt addition was targeting solutes with low and medium K_{ow} ($\log K_{ow} < 4.0$). After extraction the two stir bars were placed in a single TD tube and were simultaneously desorbed and analysed by TD-GC–MS. Sampedro et al. [22] applied the sequential SBSE for the quantification of 37 pesticides with $\log K_{ow}$ ranging between 1.5 and 5.9. The extraction procedure was carried out by SBSE performed sequentially on a 10 mL salt-free sample using one stir bar (first extraction), and then other stir bar on the same sample after addition of 2 g of sodium sulphate anhydrous (second extraction). The first extraction targeted mainly solutes with high K_{ow}, while the second extraction with sodium sulphate addition targeted solutes with medium and low K_{ow}. After SBSE, both stir bars were placed in a single stainless steel desorption tube and were analysed by automated TD-GC–MS.

The aim of the present study was the development of a dual SBSE-TD-GC–MS method for the screening analysis of organic compounds with a wide range of physico-chemical properties in water. Priority pollutants for water quality monitoring and other environmentally harmful substances were chosen as model compounds.

2. Experimental

2.1. Standards and reagents

Neat standards of isophorone, 1,2,4-trichlorobenzene and hexachlorobenzene were obtained from Sigma–Aldrich (St. Louis, MO, USA); *N*,*N*-dimethylaniline and hexachloro-1,3-butadiene were from Avocado (Heysham, UK); 2,4-dinitrotoluene and diethyltoluamide were from Merck (Darmstadt, Germany); endosulfan II was from PolyScience (Niles, IL, USA); acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, *p*,*p*′-DDE and 3,3′-dichlorobenzidine were purchased from Supelco (Bellefonte, PA, USA); 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-*tert*-octylphenol, 4-*n*-nonylphenol, trifluralin, simazine, atrazine, lindane, chlorpyrifos, chlorpyrifos-methyl, heptachlor, alachlor, aldrin, isodrin, dieldrin, endrin, endosulfan I, *p*,*p*′-DDT, di-*n*-octylphthalate and isotope labelled anthracene-d10 were obtained from Dr. Ehrenstorfer (Augsburg, Germany). The purity of these standards ranged from 95 to 99.8%. PCB-Mix 3 containing PCB congeners 28, 52, 101, 118, 138, 153 and 180 diluted in cyclohexane at a concentration of 10 ng μl^{-1} was purchased also from Dr. Ehrenstorfer.

HPLC gradient grade methanol from J.T.Baker (Deventer, The Netherlands) and sodium chloride ReagentPlus (Sigma–Aldrich, St. Louis, MO, USA) baked for 4 h at 420 °C were used for SBSE conditions modification.

Stock standard solutions (0.5–50 mg mL^{-1}) of individual analytes were prepared by dissolution in acetone. Working solutions of a mixture of analytes at concentrations of 1 and 10 $\mu g\,mL^{-1}$, respectively, were obtained by dilution of the stock standard

solutions with acetone. Anthracene-d10 was diluted in methanol and was used as an internal standard at concentration of 1 μg mL^{-1}. Aliquots of working solutions were added to tap water (pH around 7.6) or Danube river water to give the test samples and calibration solutions. Tap water and river water was preferred over distilled or ultrapure water to determine method performance parameters in an environmentally relevant matrix.

2.2. Instrumentation

Analyses were carried out on an Agilent Technologies (Palo Alto, CA, USA) 6890N GC system coupled to a 5973 mass selective detector (MSD). The GC was equipped with a Twister desorption unit (TDU) assembled to a cooled injection system (CIS4 PTV) (both Gerstel, Mülheim a/d Ruhr, Germany). A Gerstel multipurpose sampler MPS2L equipped with a Twister tray allowing automated desorption of 98 Twister stir bars was installed on top of the GC. The analytes were separated on an HP-5MS capillary column (30 m × 0.25 mm I.D., film thickness 0.25 μm) from Agilent Technologies using helium as the carrier gas.

Stir bars coated with 10 mm × 0.5 mm PDMS layer, commercially available as Gerstel Twisters, were used for the preconcentration of the analytes from water solutions. The agitation was carried out with IKA Big Squid magnetic stirrers (Staufen, Germany).

TD was performed by ramping the TDU from 40 °C (0.5 min) to 280 °C (6 min) at a rate of 720 °C min^{-1} in the splitless mode under helium flow of 75 mL min^{-1} (vent pressure 48 kPa), while the CIS was programmed in the solvent venting mode. Following TD analytes were cryofocused on a glass wool packed liner of the CIS4 PTV at −30 °C using liquid CO_2. After desorption, the analytes were transferred to the analytical column (splitless period 2 min) by heating CIS4 PTV to 280 °C (10 min) at a rate of 12 °C s^{-1}. Simultaneously, temperature programming was started for a GC oven. The oven was programmed from 70 °C (2 min) to 150 °C at a rate of 25 °C min^{-1}, then to 200 °C at a rate of 3 °C min^{-1} and finally to 300 °C (3 min) at a rate of 8 °C min^{-1}. This is the temperature program required for use of the retention time locking (RTL) pesticide database from Agilent Technologies [23]. The head pressure of the carrier gas was adjusted to elute chlorpyrifos-methyl at a constant retention time of 16.60 min.

The MSD was operated in the scan mode using electron impact ionization (70 eV). Transfer line, quadrupole and ion source temperatures were 280, 150 and 230 °C, respectively. Scan range was set from m/z 45 to 450 and sampling rate of two, resulting in scan rate of 3.54 scan s^{-1}. The evaluation of chromatograms was performed using the automatic RTL screener software (Agilent Technologies, G1716AA version A.03.00) in combination with own mass spectral library of selected compounds. The selected ions for the determination are presented in Table 2. The underlined target ions were used as quantifiers. The identification of unknown compounds was carried out by computer matching against Wiley7n and NIST02 mass spectral libraries. For a positive identification of a compound a minimum match factor value of 80% with the MS library mass spectrum was required as well as fulfilment of other requirements described in Kashyap et al. [24].

2.3. SBSE procedure

The stir bars were conditioned in a Gerstel TD glass tube at 300 °C for 4 h in a helium stream at a flow rate of 50 mL min^{-1}.

In the optimised procedure, two 20-mL aliquots of water sample (model sample with addition of tested compounds or the real environmental sample) were placed in two 100-mL glass flasks with slightly concave bottom (this shape of the bottom protects the stir bars from damage during stirring) and closed with a ground joint stopper. To one flask, 6 g of NaCl was added and to the other 4 mL of methanol. To both flasks anthracene-d10 was added as an internal standard. Then stir bars were immersed in water solutions and SBSE was simultaneously performed at room temperature (24 °C) for 2 h while stirring at 900 rpm. After extraction, the magnetic stir bars were removed using a piece of steel wire, dipped briefly in Milli-Q water, dried with a lint-free tissue, placed in the single TD tube and simultaneously analysed by TD-GC–MS.

3. Results and discussion

3.1. Selection of model compounds

Method optimisation was performed using a range of environmentally harmful compounds with different volatilities (boiling points from 193 to 495 °C), polarity (log K_{ow} between 2.17 and 8.54) and acido-basic properties. The majority of model compounds were selected from the EU list of priority substances in the field of water policy [25] and from the US EPA method 625 [26], respectively. The selected compounds are listed in Table 2.

3.2. Optimisation of desorption conditions

Firstly, factors affecting desorption of target analytes from stir bar together with subsequent cryofocusing in the CIS liner were evaluated to achieve the optimum sensitivity of the instrumental method. Initial conditions applied were taken from the previous work of León et al. [8] and Prieto et al. [13]. Desorption temperature of 280 °C was adopted from [8]. Because of great differences in the volatility of tested analytes, the cryofocusing temperature in the CIS was optimised first. The mixture of analytes, containing 50 ng of each compound in 5 μl of acetone, was injected into the glass wool packed TD tube that was then placed in the TD unit. Desorption flow of helium of 75 mL min^{-1} was maintained for 6 min. CIS temperatures of −30, 0 and +20 °C were tested to compare trapping efficiency. For visualisation of the results, responses are shown as average (n = 2) chromatographic peak areas normalised to the highest peak area obtained in the three experiments for each compound (Fig. 1). The best average trapping efficiency for the tested compounds was obtained at CIS temperature of −30 °C.

For helium desorption flow rate optimisation normalised average (n = 2) peak areas were compared for flows 25, 50 and 75 mL min^{-1}, respectively. The mixture of analytes, at 50 ng of each, was injected on the surface of two stir bars inserted into TD tube. During desorption time of 6 min the CIS temperature was maintained at −30 °C. In general, the highest responses were obtained for flow rate of 75 mL min^{-1} (Fig. 2), which is in agreement with [8].

For optimisation of duration of analytes desorption (at 50 ng of each) from PDMS layer of stir bar, desorption times from 4 to 8 min (at desorption flow rate of 75 mL min^{-1}) were tested. In agreement with the results of León et al. [8], desorption was complete for the compounds under study after 6 min.

For the rest of the experiments the optimised conditions were: desorption flow of 75 mL min^{-1}, desorption temperature of 280 °C, desorption time of 6 min and cryofocusing temperature of −30 °C.

3.3. SBSE method development

3.3.1. Addition of modifiers

As mentioned in the introduction of this paper, modifiers are commonly added to the aqueous matrix to improve SBSE conditions towards the extraction of more hydrophilic or more hydrophobic solutes. Addition of NaCl enhances the recoveries of more polar solutes (as a result of decrease of the solutes' water solubility and increase of partitioning coefficients between PDMS and water),

Table 2
Compounds tested, retention times (t_R), octanol–water partitioning coefficients ($\log K_{ow}$), water solubility, pK_a values and selected mass ions.

No.	Compound	t_R (min)	Log K_{ow}[a]	Water solubility (mg L^{-1})[b]	pK_a[b]	Target ion and qualifiers[c] (m/z)
1	*N*,*N*-Dimethylaniline	4.62	2.17	1450 (25 °C)	5.15 (base)	77, 104, 120, 121
2	Isophorone	4.87	2.62	1200 (25 °C)	–	82, 83, 95, 138
3	2,4-Dichlorophenol	5.30	2.80	4500 (20 °C)	7.89 (acid)	63, 98, 162, 164
4	1,2,4-Trichlorobenzene	5.32	3.93	49 (25 °C)	–	74, 145, 180, 182
5	Hexachloro-1,3-butadiene	5.60	4.72	3.2 (25 °C)	–	190, 223, 225, 227
6	2,4,6-Trichlorophenol	6.87	3.45	800 (25 °C)	6.23 (acid)	62, 97, 196, 198
7	Acenaphthene	8.45	4.15	3.9 (25 °C)	–	76, 151, 153, 154
8	2,4-Dinitrotoluene	9.10	2.18	200 (25 °C)	–	63, 89, 90, 165
9	Diethyltoluamide	9.78	2.26	912 (25 °C)	–	91, 119, 190, 191
10	Fluorene	9.94	4.02	1.69 (25 °C)	–	163, 165, 166, 167
11	4-*tert*-Octylphenol	10.21	5.28	5 (25 °C)	–	91, 107, 135, 136
12	Trifluralin	11.64	5.31	0.184 (25 °C)	–	145, 248, 264, 306
13	Hexachlorobenzene	12.36	5.86	0.0062 (25 °C)	–	142, 282, 284, 286
14	Simazine	13.06	2.40	6.2 (20 °C)	1.62 (base)	68, 173, 186, 201
15	Atrazine	13.30	2.82	34.7 (26 °C)	1.7 (base)	68, 173, 200, 215
16	Lindane	13.46	4.26	7.3 (25 °C)	–	181, 183, 217, 219
17	Anthracene	14.09	4.35	0.0434 (24 °C)	–	152, 177, 178, 179
18	4-*n*-Nonylphenol	16.01	5.99	7 (25 °C)	–	77, 107, 108, 220
19	PCB-28	16.13	5.69	0.27 (25 °C)	–	186, 256, 258, 260
20	Chlorpyrifos-methyl	16.60	3.68	4.76 (20 °C)	–	79, 125, 286, 288
21	Heptachlor	16.75	5.86	0.18 (25 °C)	–	65, 100, 272, 274
22	Alachlor	17.03	3.37	240 (25 °C)	–	117, 146, 160, 188
23	PCB-52	17.91	6.34	0.0153 (25 °C)	–	220, 222, 290, 292
24	Aldrin	18.48	6.75	0.017 (25 °C)	–	66, 261, 263, 265
25	Chlorpyrifos	19.22	4.66	1.12 (24 °C)	–	97, 197, 199, 314
26	Isodrin	20.01	6.75	0.0142 (25 °C)	–	66, 193, 195, 263
27	Fluoranthene	20.92	4.93	0.26 (25 °C)	–	101, 201, 202, 203
28	Pyrene	22.30	4.93	0.135 (25 °C)	–	101, 201, 202, 203
29	Endosulfan I	22.61	3.50	0.325 (22 °C)	–	195, 237, 239, 241
30	PCB-101	22.63	6.98	0.0154 (25 °C)	–	254, 256, 326, 328
31	Dieldrin	23.85	5.45	0.195 (25 °C)	–	77, 79, 82, 263
32	*p*,*p*′-DDE	24.03	6.00	0.04 (25 °C)	–	246, 248, 316, 318
33	Endrin	24.73	5.45	0.25 (25 °C)	–	81, 261, 263, 265
34	Endosulfan II	25.17	3.50	0.325 (22 °C)	–	195, 207, 237, 241
35	PCB-118	25.35	6.98	0.0134 (20 °C)	–	254, 324, 326, 328
36	PCB-153	26.19	7.62	0.00095 (24 °C)	–	288, 290, 360, 362
37	*p*,*p*′-DDT	27.00	6.79	0.0055 (25 °C)	–	165, 199, 235, 237
38	PCB-138	27.12	7.62	0.0015 (20 °C)	–	288, 290, 360, 362
39	Benz[a]anthracene	28.46	5.52	0.0094 (25 °C)	–	113, 114, 228, 229
40	Chrysene	28.60	5.52	0.002 (25 °C)	–	113, 227, 228, 229
41	3,3′-Dichlorobenzidine	28.89	3.21	3.1 (25 °C)	3.2 (base)	154, 252, 253, 254
42	PCB-180	29.20	8.27	0.00385 (20 °C)	–	324, 326, 394, 396
43	Di-*n*-octyl phthalate	31.70	8.54	0.022 (25 °C)	–	71, 149, 150, 279
44	Benzo[b]fluoranthene	32.29	6.11	0.0015 (25 °C)	–	125, 126, 252, 253
45	Benzo[a]pyrene	33.29	6.11	0.00162 (25 °C)	–	125, 126, 252, 253

[a] Values calculated by KowWin program [27].
[b] Experimental values obtained from [28].
[c] Underlined target ions were employed for quantification.

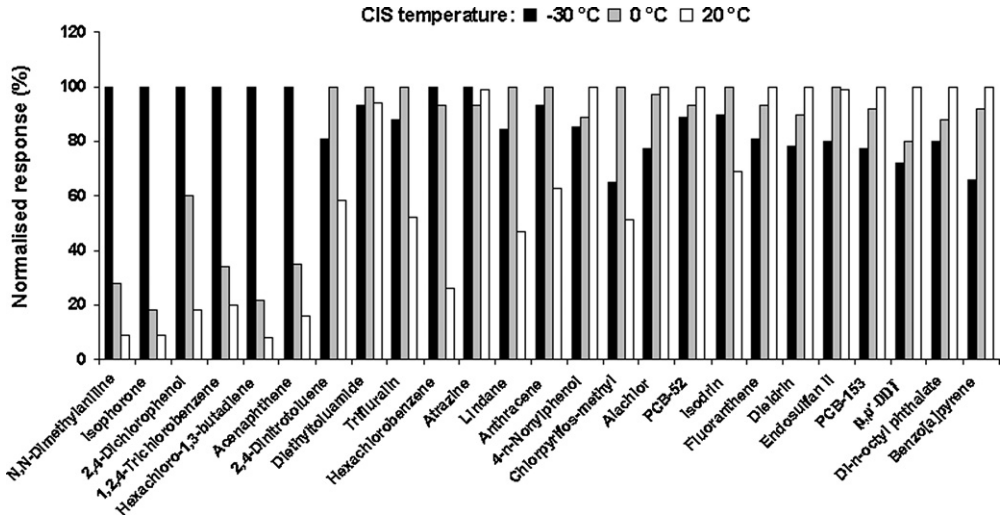


Fig. 1. Optimisation of the cooled injection system (CIS) temperature.

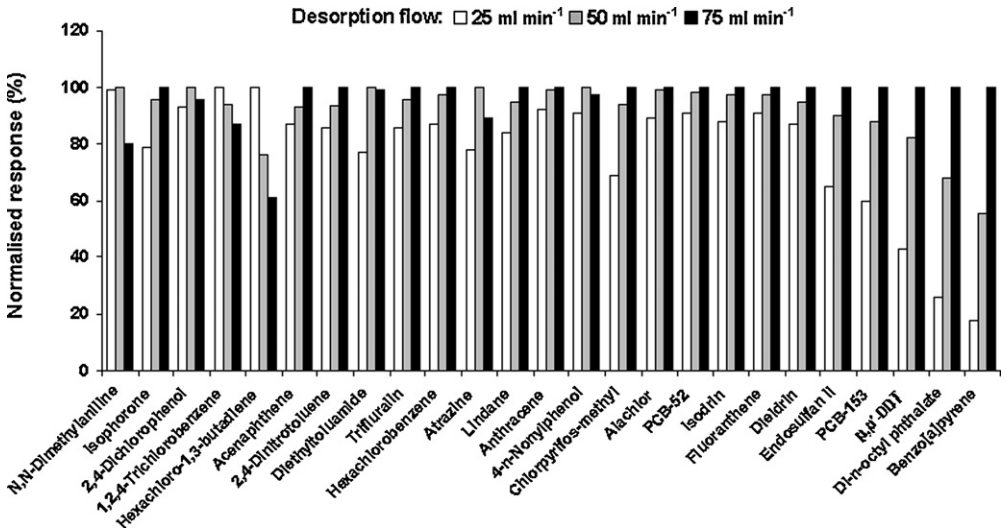


Fig. 2. Optimisation of desorption flow rates.

while it reduces the extraction efficiency of non-polar compounds (explained by various hypotheses) [5]. On the contrary, addition of methanol enhances the extraction of hydrophobic solutes (avoids adsorption of analytes onto the glass walls and suspended particles), while it has a negative effect on the recovery of hydrophilic solutes (as a result of an increase of solutes' water solubility and decrease of the partitioning into the PDMS phase) [5]. In our method we decided to utilize both variants of extraction conditions to enhance the extraction of hydrophilic as well as hydrophobic solutes. One sample aliquot was modified with 23% (w/w) of NaCl, and the other aliquot with 17% (v/v) of methanol, respectively.

The effect of modifiers on the recovery ($n=2$) of selected compounds from 20-mL of test water sample with the solute concentration of 500 ng L^{-1} is presented in Fig. 3. A sample without addition of modifiers was also extracted for comparison. SBSE was performed for 16 h at 900 rpm. The recovery was calculated by comparing peak areas with those of a direct liquid injection of a standard mixture on the surface of two stir bars inserted into TD tube. For the most polar solutes (low log K_{ow} values) the best recoveries were obtained with the addition of salt (Fig. 3). In this case the recoveries were higher than theoretical values, calculated using recovery calculator from Gerstel (Twister recovery calculator 1.0.3.0.). For 2,4-dichlorophenol and 2,4,6-trichlorophenol obtained extraction recoveries were lower than calculated values. This can be explained by the presence of these compounds predominantly in anionic form in solution at neutral pH due to their acidic properties (Table 2). The ionic form has a negligible affinity to the PDMS extraction phase. For the most non-polar solutes (the highest log K_{ow} values) the best recoveries were obtained with methanol addition. In both cases the obtained recoveries were higher than in the case of SBSE without modifier. For solutes with log K_{ow} values between 3.5 and 6.0 the addition of modifiers had no significant effect.

3.3.2. Sample volume

The effect of sample volume on the total amount of solutes extracted by SBSE was investigated. According to the theory [6] the extracted amount increased with the increasing PDMS/sample volume ratio. The extraction efficiency decreases with the increasing sample volume, however, chromatographic response can increase

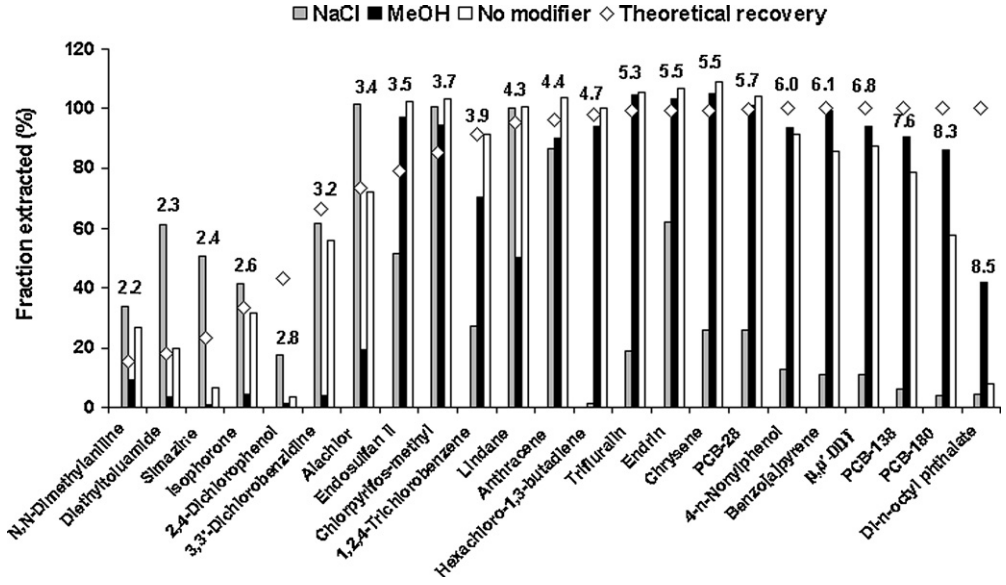


Fig. 3. Effect of modifiers on extraction efficiency of selected compounds (in the upper part of bars log K_{ow} values).

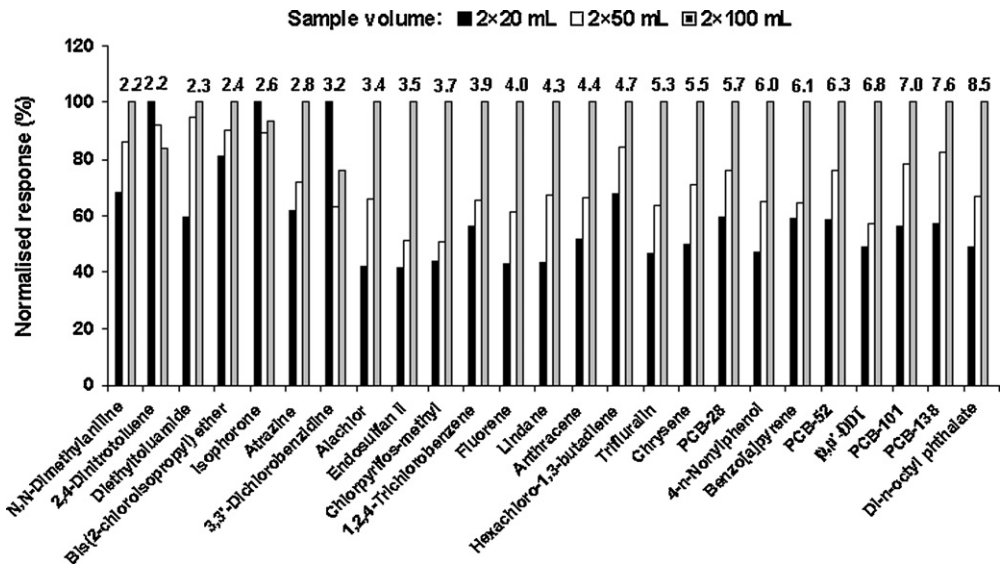


Fig. 4. Optimisation of sample volume (in the upper part of bars log K_{ow} values).

due to an increase of the mass of the extracted analyte [5]. The volumes of 20, 50 and 100 mL, were selected for testing the extraction yield dependence on the sample volume. Two equivalent aliquots of tap water spiked with the concentration of 250 ng L^{-1} of each tested compound were taken for the assay. The first aliquot was modified with 23% NaCl and the second aliquot with 17% MeOH, respectively. After 24 h agitation at 900 rpm the two stir bars were desorbed together and analysed in one chromatographic run.

The effect of sample volume on the chromatographic response for the selected analytes is presented in Fig. 4 as average ($n = 3$) peak areas normalised to the highest peak area obtained in the three experiments for each compound. For non-polar analytes (log $K_{ow} > 3.5$) the increase in sample volume from 2× 20-mL to 2× 100 mL resulted in an average increase in chromatographic response of cca. 50%. For the more polar analytes the increase of sample volume had a minor effect on chromatographic responses. This observation is in agreement with the results of León et al. [8] and also with the theoretical calculation showing that the increase of sample volume from 20 to 100 mL for compounds with log $K_{ow} < 3$ should have a negligible effect on the maximum extracted analyte mass, whereas a strong effect for compounds with log $K_{ow} > 4$ is expected (Supplementary information). Based on this test the 2× 20-mL sample volume was selected as an optimum for the developed SBSE method, which is suitable also for the more problematic polar compounds. The low sample volume required for SBSE has the advantage of demand of smaller samples, smaller consumption of modifiers and faster equilibration.

3.3.3. Stirring rate

The stirring rate is another important parameter that can affect the extraction yield [5]. In our case 20-mL aliquots of model water solution (250 ng L^{-1}) with addition of NaCl (23%) or MeOH (17%) were stirred for 7 h at 500 and 900 rpm, respectively. Higher stirring rates were not tested because of vortex formation and bubbles that were disturbing the homogeneity of stirred solution. The obtained results showed no significant difference in responses obtained at studied agitation rates. The 900 rpm stirring rate was chosen for further experiments.

3.3.4. Effect of extraction time

The extraction time profile of model compounds at concentration of 500 ng L^{-1} was studied at previously optimised conditions: 2× 20-mL sample aliquots with addition of NaCl (23%) or methanol (17%), stirred at 900 rpm at ambient temperature (24 °C). Fig. 5 presents the extraction time profiles for selected compounds obtained over a range of extraction time periods from 1 to 16 h.

In most cases the highest recovery increase was observed after 1-h and 2-h extraction time periods. In many cases the further increase of recovery was very small. In the case of 3,3′-dichlorobenzidine prolonging the extraction time had a negative effect on the recovery, which was possibly caused by a photochemical degradation [29]. Therefore, 2 h was selected as extraction time, which is a favourable time in terms of analysis duration. The selected extraction time together with 20-mL sample volume is in agreement with the SBSE parameters employed in different studies presented in Table 1. From the relation between sample volume and extraction time it is obvious that smaller sample volumes (10–30 mL) require shorter extraction times to reach equilibrium conditions than it is in case of larger sample volumes (e.g. 100 mL).

3.3.5. Dual SBSE-TD-GC–MS method performance

Once desorption and SBSE conditions optimised, the performance characteristics of the whole analytical method were determined (Table 3). The recovery and repeatability of the method was evaluated from six repeated analyses of a fortified tap water sample with tested compounds at 500 ng L^{-1}. The recoveries (Rec.) were in the range of 2.5–89.2%. The lowest recovery values were obtained for ionized acidic 2,4,6-trichlorophenol (2.5%) and 2,4-dichlorophenol (9.1%) and for the most hydrophobic compound di-*n*-octyl phthalate (11.6%) with the highest log K_{ow} of 8.54. For comparison, theoretical recoveries (T. Rec.) are also presented in Table 3. For the most polar compounds the obtained recoveries are close to and in some cases even higher (*N*,*N*-dimethylaniline, 2,4-dinitrotoluene, diethyltoluamide) than the theoretical values. The repeatability, expressed in terms of percent relative standard deviation (RSD, $n = 6$), was found to be in the range of 5.1–16.3%. Only in the case of di-*n*-octyl phthalate the higher RSD (23%) went along with relatively high and fluctuating blank values. The completeness of the thermodesorption process (carryover) was evaluated by a repeated thermal desorption of stir bars. The analyte peak areas of the first and second desorption step were compared, setting the areas of the first desorption to 100%. Carryover was observed only in case of high molecular PAHs (benz[a]anthracene, chrysene, benzo[b]fluoranthene, and benzo[a]pyrene) in the range of 0.4–1.1% and in case of di-*n*-octyl phthalate in average around 5%.

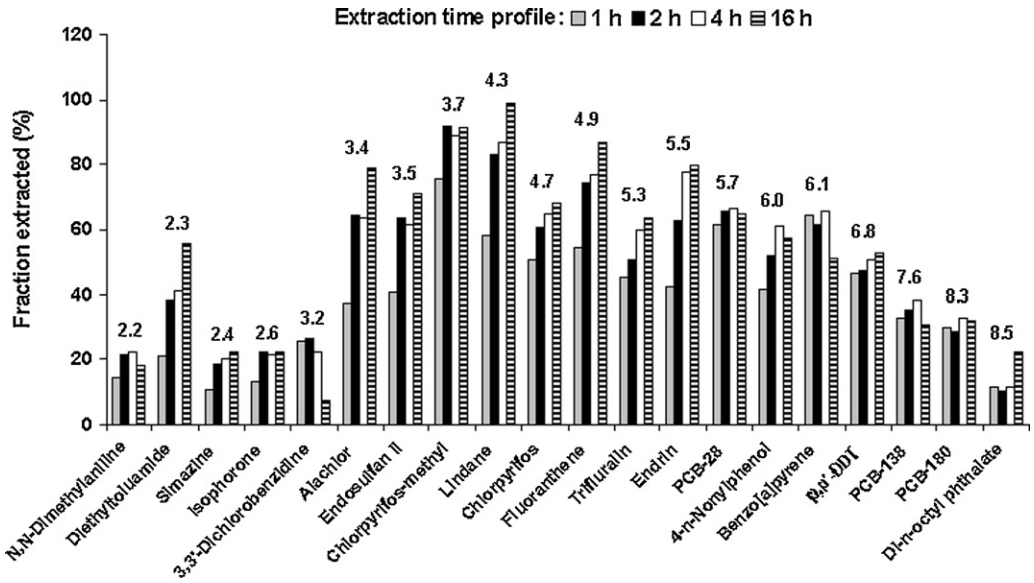
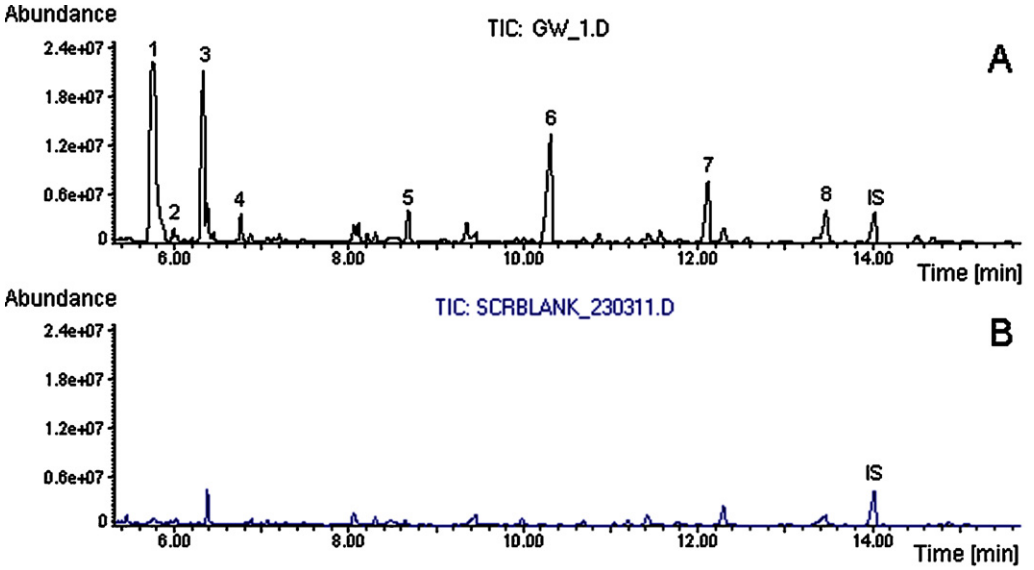


Fig. 5. Extraction time profiles for selected compounds (in the upper part of bars log K_{ow} values).



Peak	R.T. (min)	MW.	CAS#	Formula	Identified compound
1	5.76	135	95-16-9	C_7H_5NS	Benzothiazole
2	5.99	176	1570-65-6	$C_7H_6Cl_2O$	4,6-Dichloro-*o*-cresol
3	6.33	149	120-75-2	C_8H_7NS	2-Methylbenzothiazole
4	6.77	164	2409-55-4	$C_{11}H_{16}O$	2-*tert*-Butyl-*p*-cresol
5	8.68	220	128-37-0	$C_{15}H_{24}O$	4-Methyl-2,6-di-*tert*-butylphenol
6	10.32	181	615-22-5	$C_8H_7NS_2$	2-(Methylthio)benzothiazole
7	12.12	288	319-84-6	$C_6H_6Cl_6$	*alpha*-HCH
8	13.47	288	58-89-9	$C_6H_6Cl_6$	*gamma*-HCH (lindane)
IS	14.03	188	1719-06-8	$C_{14}D_{10}$	Anthracene-d10 (1 $\mu g\ L^{-1}$)

Fig. 6. Total ion chromatogram from dual SBSE-TD-GC–MS analysis (A) of the diluted groundwater sample and (B) of the blank run. (C) Identified compounds.

Table 3
Dual SBSE-TD-GC–MS method characteristics under optimised conditions.

No.	Compound	T. Rec[a] (%)	Rec.[b] (%)	RSD (%)	Lin. range[c] (ng L^{-1})	r^2	LOD (ng L^{-1})	LOQ (ng L^{-1})
1	*N*,*N*-Dimethylaniline	15.1	22.3	8.7	50–1500	0.998	20.9	69.5
2	Isophorone	33.3	24.5	9.9	25–1250	0.994	6.6	22.0
3	2,4-Dichlorophenol	43.1	9.1	11.0	50–1500	0.992	16.0	53.4
4	1,2,4-Trichlorobenzene	91.1	42.2	15.3	25–1500	0.997	1.8	6.0
5	Hexachloro-1,3-butadiene	98.4	19.3	16.3	25–1500	0.994	2.9	9.7
6	2,4,6-Trichlorophenol	77.2	2.5	7.1	500–1500	0.996	431.0	1502.0
7	Acenaphthene	94.4	76.2	6.1	25–1500	0.991	2.3	7.7
8	2,4-Dinitrotoluene	15.4	22.1	11.5	50–1500	0.986	25.3	84.3
9	Diethyltoluamide	17.9	41.7	9.3	25–1500	0.996	2.6	8.8
10	Fluorene	92.6	82.6	8.6	25–1500	0.992	1.2	3.9
11	4-*tert*-Octylphenol	99.6	30.0	11.3	25–1500	0.995	2.3	7.1
12	Trifluralin	99.6	57.6	14.0	25–1500	0.991	0.9	2.9
13	Hexachlorobenzene	99.9	72.5	7.9	25–1500	0.997	0.5	1.7
14	Simazine	23.2	18.0	13.7	50–1500	0.991	19.0	63.3
15	Atrazine	44.2	42.3	8.4	25–1500	0.996	7.6	25.6
16	Lindane	95.6	77.4	7.5	25–1500	0.992	5.8	19.2
17	Anthracene	96.4	80.6	8.1	25–1500	0.995	1.1	3.7
18	4-*n*-Nonylphenol	99.9	55.4	15.7	25–1500	0.995	2.2	7.2
19	PCB-28	99.8	62.6	6.8	25–1500	0.997	0.5	1.6
20	Chlorpyrifos-methyl	82.5	89.2	5.2	25–1500	0.995	2.9	9.7
21	Heptachlor	99.9	58.4	8.5	25–1500	0.994	2.3	7.9
22	Alachlor	73.8	62.6	8.3	25–1500	0.992	5.3	17.7
23	PCB-52	100.0	59.4	7.8	25–1500	0.995	0.8	2.6
24	Aldrin	100.0	64.4	13.7	25–1500	0.997	2.7	9.1
25	Chlorpyrifos	98.2	60.3	6.2	25–1500	0.995	3.1	10.3
26	Isodrin	100.0	62.0	6.5	25–1500	0.998	3.5	11.5
27	Fluoranthene	99.0	78.9	8.6	25–1500	0.995	1.0	3.5
28	Pyrene	99.0	73.0	7.9	25–1500	0.995	1.1	3.6
29	Endosulfan I	79.1	66.6	5.9	50–1500	0.990	19.7	65.7
30	PCB-101	100.0	45.2	11.2	25–1500	0.993	0.9	2.8
31	Dieldrin	99.7	63.0	5.1	25–1500	0.992	6.1	20.3
32	*p*,*p*′-DDE	99.9	44.0	12.7	25–1500	0.992	3.4	11.2
33	Endrin	99.7	65.3	6.9	25–1500	0.990	2.7	8.9
34	Endosulfan II	79.1	63.7	8.8	50–1500	0.993	25.2	83.8
35	PCB-118	100.0	40.9	15.5	25–1500	0.992	0.6	2.1
36	PCB-153	100.0	33.7	13.9	25–1500	0.992	0.9	3.1
37	*p*,*p*′-DDT	100.0	46.8	12.1	25–1500	0.988	10.0	33.5
38	PCB-138	100.0	36.2	11.8	25–1500	0.996	1.0	3.3
39	Benz[a]anthracene	99.7	68.3	6.7	25–1500	0.993	1.8	5.9
40	Chrysene	99.7	67.3	7.1	25–1500	0.993	1.6	5.3
41	3,3′-Dichlorobenzidine	66.1	28.9	16.1	100–1500	0.996	69.1	230.3
42	PCB-180	100.0	29.7	13.2	25–1500	0.993	1.5	5.2
43	Di-*n*-octyl phthalate	100.0	11.6	23.0	50–1500	0.969	19.5	65.1
44	Benzo[b]fluoranthene	99.9	64.5	8.6	25–1500	0.995	2.3	7.7
45	Benzo[a]pyrene	99.9	63.2	8.0	25–1500	0.996	3.6	11.8

[a] T. Rec., theoretical recovery. Theoretical SBSE recovery with 20-mL sample and 24 μl PDMS calculated with Twister Recovery Calculator (1.0.3.0, Gerstel).
[b] Rec., recovery, $n = 6$.
[c] $n = 7$–9 by duplicate determination and $n = 5$ in case of 2,4,6-trichlorophenol.

The linearity of the method was studied at nine concentration levels (25, 50, 100, 250, 500, 750, 1000, 1250, and 1500 ng L^{-1}) in duplicate. Linear ranges and correlation coefficients (r^2) are presented in Table 3. The obtained r^2 values (0.986–0.998) show a good linearity for all tested analytes with exception of di-*n*-octyl phthalate ($r^2 = 0.969$).

Limits of detection (LOD) and quantification (LOQ) were established for signal-to-noise ratios of 3 and 10, respectively, from triplicate analyses of fortified water samples from the Danube river. The limits were evaluated for concentration level of 50 ng L^{-1} for all compounds, except for 3,3′-dichlorobenzidine and 2,4,6-trichlorophenol, in which cases concentrations of 100 ng L^{-1} and 500 ng L^{-1}, respectively, were used. The obtained LOQ values are in a broad range between 1.6 ng L^{-1} for PCB-28 and 1502 ng L^{-1} for 2,4,6-trichlorophenol at neutral pH, respectively (Table 3). This reflects different physico-chemical properties of tested compounds. In general, the sensitivity of the method employing MS full scan mode is very good and in many cases is fulfilling the requirements for environmental quality standards (EQSs) for surface waters according Directive 2008/105/EC [30]. The sensitivity of the method can be further enhanced for target analytes using MS detection in selected ion monitoring (SIM) mode. For compounds with acidic or basic properties, extraction recovery and resulting method sensitivity can be further improved by suppression of their dissociation that can be achieved by pH adjustment.

Fig. 6A shows an example of the method application for the analysis of the contaminated groundwater sample. The sample was diluted 100-times with Milli-Q water and an internal standard (IS) anthracene-d10 in resulting concentration of 1 μg L^{-1} was added. Rubber chemicals and pesticides were identified in the sample (see identified compounds in Fig. 6C). For lindane, concentration of 180 μg L^{-1} was determined. Fig. 6B presents also a chromatogram from the analysis of a sample blank (Milli-Q water).

4. Conclusion

The developed method employing two simultaneous sorptive extractions and one GC–MS analysis run is suitable for fast screening analysis of organic pollutants in aqueous samples without pH adjustment. The selected test analytes included compounds with a range of volatility, polarity and acido-basic properties (Table 2). SBSE extraction of some compounds has been published, but the

selection included also some new compounds. Tuning of extraction conditions had a most significant effect on the recovery rates of more polar analytes, which sometimes exceeded the theoretical values. In general, the obtained sensitivity is comparable and in agreement with LOD and LOQ values from other published studies. The combination of a 2-h SBSE extraction time and a 38-min GC run time facilitate to achieve a favourable sample throughput rate.

For application of the described method to real environmental samples of water, the sampling step should be carefully considered. To minimise changes in sample composition during storage and processing we recommend that the extraction of hydrophobic substances is performed in the original sample container. This will ensure that hydrophobic analytes adsorbed to the walls of sampling vessel are not lost during the sample transfer to the extraction vessel. Alternatively, sample can be collected to two individual bottles or containers that are designed also for the extraction step performed under different conditions. Collection of small volumes of water that are sufficient for SBSE-based analysis is useful also for reduction of sample transportation costs.

Acknowledgement

We would like to thank Eva Figuliová for technical assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.09.055.

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