Determination of polybrominated diphenyl ethers at trace levels in environmental waters using hollow-fiber microporous membrane liquid-liquid extraction and gas chromatography- mass spectrometry

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Abstract

In this study, we present a simple and easy-to-use extraction method that is based on a hollow-fiber microporous membrane liquid-liquid extraction (HF-MMLLE), as an extraction technique, followed by gas chromatography–mass spectrometry (GC-MS) to determine a group of brominated flame retardants, polybrominated diphenyl ethers (PBDEs), at trace levels in aqueous samples.

The hollow-fiber membrane (HF) filled with organic solvent was immersed into the aqueous sample, spiked with the analytes at ng l^{-1} level, and stirred for 60 minutes. The proposed method could attain enrichment factors (E_e) up to 5200 times, after optimising parameters, such as organic solvent, stirring speed and extraction time, that affect the extraction.

The HF-MMLLE-GC-MS method was successfully applied to the extraction of PBDEs from tap, river and leachate water samples with spike recoveries ranging from 86% to 110%. The method validation with reagent and leachate water samples provided good linearity, detection limits of 1.1 ng l^{-1} or lower, both in reagent and leachate water, as well as satisfactory precision in terms of repeatability and reproducibility with values of % relative standard deviation (%RSD) lower than 8.6 and 10.5, respectively.

1. Introduction

During the last decades, polybrominated diphenyl ethers (PBDEs) have been among the group of most commonly used brominated flame retardants (BFRs), which are exploited as additives in polymers (such as plastics, textiles, electronic equipments and building materials) to prevent ignition and decrease the rate of combustion [1-3]. The environmental concern regarding these compounds has risen because they are released into the environment during production and use, as well as leach out from the products in which they are used. In addition, the physicochemical properties of PBDEs are similar to other well-known environmental contaminants, such as polychlorinated biphenyls (PCBs). PBDEs are toxic, persistent and liphophilic, so that they have a tendency to bioaccumulate in biota and reach humans via the food chain [1,2]. Some reviews [3-8] have reported the presence of PBDEs in air, water, sediments, marine mammals, birds, fish and humans.

As a consequence of the occurrence of PBDEs in the environment, there has been a growing interest in recent years in developing analytical methods to determine these persistent pollutants in different matrices [6,9-11].

The extraction of PBDEs from environmental aqueous samples has been usually carried out by using conventional liquid-liquid extraction (LLE) [10], which is time-consuming and requires large volumes of organic solvents. This is the basis for the draft US Environmental Protection Agency (EPA) method 1614 for analysis of PBDEs [12]. Recently, headspace solid-phase microextraction (HS-SPME) has been proposed for the extraction of PBDEs from aqueous samples [13,14]. However, the sample has to be heated up to nearly its boiling point in order to allow partitioning of the non-volatile compounds, such as PBDEs, between the aqueous (i.e. sample) and the gaseous phases. Other drawbacks of this technique are the fragility and cost of the fibers, in addition to possible sample carry-over effects between runs.

Microporous membrane liquid-liquid extraction (MMLLE) is a suitable technique for extracting and concentrating hydrophobic compounds from aqueous samples. MMLLE is a two-phase membrane extraction technique based on an aqueous phase (donor or sample phase) and an organic (acceptor) phase. The organic phase is supported by a hydrophobic membrane, which keeps the solvent in position. The organic phase fills the membrane pores and the acceptor channel (in case of a flat membrane is used) or the lumen (in case of a HF membrane is used) [15]. Therefore, MMLLE can be carried out by using either flat membranes, which can be incorporated into a miniaturised extraction card that is fixed into an automated device for extraction and analysis [16] or by using single, low-cost, disposable, and porous HF membranes [17].

HF-MMLLE, also called liquid phase microextraction (LPME) or solvent bar microextraction (SBME) by other researchers, has been applied to the determination of different groups of pollutants, including polycyclic aromatic hydrocarbons (PAHs) [18-20], triazine herbicides [21], organochlorine pesticides (OCPs) [20,22], PCBs [23] and penta- and hexachlorobenzene [24]. However, this extraction technique has never been applied to the determination of PBDEs.

This paper explores the potential of a simple procedure based on HF-MMLLE to totally extract a group of PBDEs from aqueous complex samples followed by GC-MS analysis. The method was optimised to achieve higher enrichment factors, so that the sensitivity is enhanced and, thus, determination of low ng l^{-1} levels of PBDEs is possible. The optimised conditions were validated for quantitative purposes in reagent and leachate water samples.

2. Experimental

2.1. Reagents and standards

The standards of polybrominated diphenyl ethers were purchased from Accustandard (New Haven, CT, USA) and consisted of: 2,4,4'-tribromodiphenyl ether (BDE-28), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154), 2,2',3,4,4',5,6-heptabromodiphenyl ether (BDE-183) at 50 mg l^{-1} in isooctane. They are mainly those proposed in the EPA method 1614 [12]. 4,4'-dibromodiphenyl ether (BDE-15) was from Sigma-Aldrich (Steinheim, Germany) and decachloro biphenyl (PCB-209), used as internal standard (I.S.), was from Dr. Ehrenstorfer (Augsgburg, Germany). Properties of these compounds are given in Table 1. Octane and n-undecane were purchased from Sigma-Aldrich and the rest of solvents (all analytical grade or above) from Merck (Darmstadt, Germany). Sodium chloride, hydrochloric acid and sodium hydroxide were all from Merck. Ultrapure reagent water purified by a Milli-Q gradient system (Millipore, Bedford, MA, USA) was used through out. The Q3/2 Accurel PP polypropylene hollow-fiber (HF) membranes (200 μm wall-thickness, 600 μm inner diameter, 0.2 μm pore size) were obtained from Membrana (Wuppertal, Germany).

Standard stock solutions of BDE-15 at 1000 mg l^{-1} and further diluted to 50 mg l^{-1} were prepared in isooctane. A standard solution containing 2 mg l^{-1} of all PBDE, was also prepared in isooctane. Standard stock solution of PCB-209 at 1000 mg l^{-1} was prepared in toluene. Working solutions were prepared by appropriate dilution in isooctane, toluene, n-undecane or acetone and stored at –20 °C. Water solutions of PBDEs were prepared by using a spiking solution (100 μg l^{-1}) in acetone.

2.2. Sample collection

Tap water was sampled from the main area of the water supply network of Lund, Sweden. River water was collected at Höje River in the south suburb of Lund, Sweden. Leachate water was collected from the Härlöv landfill (the Kristianstad municipal solid waste deposit) and from an industrial landfill in Halmstad, Sweden. All samples were collected in amber glass containers and maintained in the dark at 4 °C until analysis. No filtration or any further treatment was applied in any of the samples before extraction.

2.3. GC-MS analysis

All the analyses were performed using a 6890 Series gas chromatograph equipped with a split/splitless injector, autosampler and a 5973-N mass spectrometry detector (Agilent Technologies, Palo Alto, CA, USA). Analytes were separated using a HP-5ms fused silica capillary column (5% phenyl-methylpolysiloxane) of 30 m x 0.25 mm with a phase thickness of 0.25 μm. The temperature program was: 150 °C, hold 1 min, rate 15° C min^{-1} to 220 °C, rate 4 °C min^{-1} to a final temperature of 300 °C, hold 2 min. Helium was used as carrier gas at flow rate of 1.2 ml min^{-1}. The injector temperature was set at 280 °C with a splitless time of 2 min. The MS was operated in the electron impact ionisation (EI) mode (70 eV). The transfer line, quadrupole and ion source temperatures were 280 °C, 150 °C and 230 °C, respectively. Samples were analysed in selective ion monitoring (SIM) mode. Scan runs were made with range from *m/z* 100 to 800. Specific ions were selected for each PBDE congener and the most abundant ion was selected as a quantitative ion, while two other ions were used as qualifiers (Table 1). Quantification was carried out with the internal standard (I.S.) procedure with the PCB-209 (100 μg l^{-1}) as I.S..

2.4. Hollow-fiber microporous membrane liquid-liquid extraction (HF-MMLLE)

Prior to extraction, HF pieces of ~ 3.7 cm length were heat-sealed at the two ends using a hot surface, and then cleaned with acetone and dried. After this preparation, the obtained sampling membrane had an effective length of ~ 3.5 cm with sampling phase volume of ~ 10 μl in the lumen and ~ 12 μl in the pores of the wall (taking into account that the porosity in the HF wall is ~ 70%). Then, a number of pre-sealed HFs, enough for one day of experiments, were filled by sonication for about 1 hour (while the sample solutions and extraction set-up were prepared) with the organic solvent spiked with PCB-209 (I.S.) at 100 μg l^{-1}, which is a concentration in about same order of magnitude as the enriched analytes. The ratio between the area of the analyte peak and the I.S. peak was monitored and considered for all analysed samples. Before starting the extraction procedure, one filled HF was taken from the organic solvent, immersed and briefly shaken in reagent water to wash away any excess organic solvent from the surface. Then one HF was placed in the aqueous sample (100 ml) for extraction. During the extraction, the solution was stirred at 1200 rpm (previously optimised). After the extraction, the HF was taken out and the solvent in the lumen was collected by just puncturing one end of the HF with a 10 μl GC syringe. Normally, 10 μl of solvent could be obtained of which 2 μl volume was manually injected into the GC.

2.5. Definitions

The enrichment factor, E_e, which was selected as response variable for the optimisation of the extraction process, is defined as the ratio of the concentration of analyte in the acceptor (C_A) after the extraction to that in the sample before extraction (C_S): $E_e = C_A / C_s$. C_A was calculated by using the peak area ratio and the calibration curve of the standards by direct injection into GC-MS.

Another variable is the extraction efficiency, E, which is calculated from the product of E_e and the volume ratio of the organic solvent in the acceptor (V_A) to the aqueous sample volume (V_S), and V_A considers the volume in the lumen (V_L, i.e. 10 μl) plus the volume of the pores (V_P, i.e. 12 μl): (%) $E = E_e \times (V_A/V_S) \times 100$. E indicates the percentage of the total analyte present initially in the sample that was extracted into the organic solvent, present in the lumen and in the pores.

3. Results and discussion

3.1. Method optimisation

Since the extraction in MMLLE is based on an equilibrium distribution process, the amount of analyte extracted at a certain time depends on the mass transfer of the analyte from the aqueous sample to the organic solvent in the HF. There are several parameters such as type of organic solvent, stirring speed, extraction time, addition of salt and sample pH that can enhance this distribution process. Thus, we first optimised all the above mentioned factors affecting the extraction efficiency. To evaluate the significance of these factors, a series of 100-ml aqueous samples spiked at 50 ng l^{-1} of each PBDE was extracted in triplicate.

a) Selection of organic solvent

The selection of organic solvent was based on the selectivity of the solvent to extract the analytes and its evaporation during the extraction process. For this purpose, toluene, isooctane, octane and n-undecane were examined.

We first attempted to use toluene because of its selectivity towards the analytes and GC performance. However, this solvent (b.p. 110 °C) partially evaporated after the extraction had finished, and after that, upon manual handling of the hollow-fiber, this solvent had completely evaporated. Other solvents with similar properties, such as octane (b.p. 125 °C) and isooctane (b.p. 99 °C) were also tested, but the results were similar to those for toluene. Then, n-undecane with higher boiling point (196 °C) was tested. This solvent showed good stability after the extraction and good selectivity for extraction of highly hydrophobic compounds as PBDE (see log K_{ow} values of the PBDEs in Table 1). Therefore, n-undecane as extraction solvent can be easily handled and it is also suitable for a good GC performance for PBDE analysis.

b) Stirring speed

The stirring speed used in the extraction procedure was investigated since agitation of the sample reduces the time to reach thermodynamic equilibrium, especially for the analytes with higher molecular mass. Fig. 1 shows the E_e values, for all PBDE congeners studied, at stirring speeds between 400 and 1200 rpm. As expected, stirring speed enhanced extraction with E_e reaching its maximum at 1200 rpm, the highest speed attainable by the magnetic stirrer used. Therefore, we selected 1200 rpm as stirring speed for subsequent experiments.

c) Extraction time

To determine the influence of the extraction time, aqueous standard solutions were extracted for different extraction times ranging from 5 min to 300 min at the stirring rate of 1200 rpm. Fig. 2 shows the extraction time profile for all the analytes. The enrichment factors obtained for the extraction increased with the extraction time up to 60 min, and then stayed almost constant, indicating that equilibrium was attained for most compounds, with the exception of BDE-15 and BDE-28. The behaviour of BDE-15 and BDE-28 could be explained by that they are the less hydrophobic analytes of the studied compounds and might diffuse from the aqueous sample to the organic solvent more slowly. The prolongation of the extraction time more than 60 min at this high stirring speed (1200 rpm) might produce some solvent losses, which results in poor precision in the analysis (data not shown). On the basis of these findings and also considering the high E_e for all analytes after 60 min, we selected 60 min as optimum extraction time for the subsequent experiments.

d) Salt addition and sample pH.

NaCl is often added to the sample in order to increase the ionic strength and enhance the analyte extraction; however, some discrepancies have been reported about the effect of salt addition [14,25,26]. On one hand, the addition of salt may change the activity coefficients of analytes in the aqueous phase and thus the extraction into the organic phase is enhanced. On the other hand, it could increase the viscosity and density of the aqueous phase and negatively affects the kinetics of the process and, consequently, the extraction efficiency [27].

The possible salting-out effect was evaluated by adding different amounts of NaCl (0 – 20 % w/v) to the aqueous solution spiked at analyte concentration of 50 ng l^{-1}. Fig. 3 depicts that the optimal extraction was achieved when no NaCl was added. These results are in agreement with other studies, where PBDEs were extracted using SPME, and the addition of salt did not improve the extraction of these compounds [14,27].

The effect of the pH of the sample solution was also investigated in the range from pH 2 to 9. Similarly, as expected, no effect of sample pH was observed.

3.2. Enrichment factor and extraction efficiency

After evaluating the different parameters that might affect the extraction, the following optimised conditions were selected for all further experiments: 3.5 cm HF filled (10 μl) and impregnated (~12 μl in membrane pores) with n-undecane solution containing PCB-209 (I.S.), and put in 100 ml aqueous sample (without salt addition and pH adjustment) stirred at 1200 rpm for 60 min.

Fig. 4 depicts E_e values for all studied compounds under the above optimised conditions. We can observe that the E_e values range from 2800 times for BDE-15 to 5200 times for BDE-153.

The high E_e values are at least one magnitude of order higher than those achieved (typically a few hundreds) in several previous reports (since in the present study V_s is at least 10 times smaller than those described in previous studies). In those studies, different classes of analytes with different polarity and hydrophobicities, such as PCBs (E_e from 67 to 241) [23], hexachlorocyclohexanes (221 to 538) [28], PAHs (166 to 234) [29] or endocrine disrupting compounds and pharmaceuticals (13 to 415) [30] were extracted using a similar two-phase extraction system. Moreover, it should be pointed out that the E_e values in the present study were obtained by spiking the samples at low ng l^{-1} levels, which are the levels that can be more probable to be found in the environmental waters. It might be anticipated that this HF-MMLLE method in combination with GC-MS would be capable to reach low detection and quantification limits.

Another feature of the extraction method presented is that it is capable to completely extract all analytes with extraction efficiency (E) near to 100% for all the compounds (see the corresponding values close to the bars of each analyte in Fig. 4).

3.3. Method validation

a) Analytical performance in reagent water samples.

To validate the analytical method using reagent water samples spiked at low ng l^{-1} levels, linearity, method detection limits (MDL) and quantification limits (MQL), and method precision were investigated. The performance parameters are tabulated in Table 2. Linearity was tested with PBDE spiked samples with concentration ranging from 1 to 100 ng l^{-1}, with different lower concentration in the linear range depending on the MQL of each congener (Table 2). Each level of concentration was analysed in triplicate. All the analytes exhibited good linearity with squared regression coefficient (r^2) ranging from 0.9968 to 0.9998. The MDL and MQL were determined according to the EPA method 136 [31], i.e. as three and ten times, respectively, the standard deviation of eight replicate extractions of spiked reagent water at 2 ng l^{-1} of each analyte. The MDL ranged from 0.2 ng l^{-1} for BDE-15 to 0.9 ng l^{-1} for BDE-99. These detection limits are lower than those reported for PBDEs extracted by SPME with GC-MS analysis [14] in which, for instance, the MDL for BDE-99 in reagent water was 9.7 ng l^{-1}. However, the obtained MDL for the proposed HF-MMLLE method is higher than given in EPA method 1614 [12] (e.g. 40 pg l^{-1} for BDE-99). But there the quantification was made by high resolution mass spectrometry (HR-MS), dramatically deceasing the MDL. As E_e in the EPA method is about 1000, it could be expected that the MDL for the HF-MMLLE method would be about three to five times lower than in the EPA method using a similar HR-MS detection. The repeatability and reproducibility (three consecutive days with triplicate analyses every day) were tested with water samples spiked at 10 ng l^{-1}. The precision of the experimental procedure, expressed as relative standard deviations (%RSD), was 0.9 – 8.5 % for repeatability, and 2.5 – 10.3 % for reproducibility. Thus, the method shows good precision at such low concentration levels.

b) Application to real samples.

To assess sample matrix effects, the optimised extraction method was then applied to three environmental water samples: tap water, river water and leachate water. All water samples were used without any pre-treatment. Tap, river and leachate water from Halmstad did not show any trace of any PBDE; however, in leachate water from Kristianstad two peaks appeared at the retention time corresponding to BDE-153 and BDE-183. The two peaks were indeed those of the two PBDEs, which were confirmed by relative abundance of the three ions selected. Fig. 5 shows the chromatogram for contaminated leachate water from Kristianstad, in which BDE-153 and BDE-183 appeared. The concentrations of BDE-153 and BDE-183 were determined to be 3.5 and

23 ng l^{-1} (n = 3), respectively. In fact, these two PBDE congeners were already found at ng l^{-1} levels in leachate water in earlier samples from the same source [32,33]. BDE-153 and BDE-183 might be present in this leachate water because some plastic manufacturing companies, which might have been using mixtures containing these two PBDEs as plastic additives, are settled nearby the sampling point.

Although contaminated environmental water could be used for validation analysis by properly subtracting the areas in the blank chromatograms from the areas obtained in working solutions spiked at different levels of concentration, we decided to use the non-contaminated leachate water to avoid misleading results. Therefore, leachate water from Halmstad was used for further experiments.

100 ml of each water sample spiked at 10 ng l^{-1} with the mixture of PBDEs were analysed in triplicate by the proposed method. Relative recoveries, determined as the ratio of concentration in environmental water samples to reagent water sample at the same concentration level, were evaluated and the results are listed in Table 3. The relative recoveries were between 85% and 110% for all the analytes in the three different matrices studied. The precisions obtained in all the real water samples (Table 3) were similar to those of reagent water samples (Table 2) spiked at the same level of concentration. These facts clearly indicate that there is no significant influence of the sample matrix. Fig. 6 shows the chromatograms after the extraction of 100 ml tap (a), river (b) and leachate (c) water spiked at 10 ng l^{-1}. As can be seen, the chromatogram profile for any of the sample analysed is comparable, which indicates that the HF-MMLLE-GC-MS system is suitable for analysis of

different types of environmental matrices and it also shows the effective clean-up of the system. In addition, HFs are cheap and disposable, thus eliminating possible carry-over effects or any contamination between the real sample analyses.

In view of the high relative recoveries as well as the good precision obtained with leachate water, the method was also validated using this water. The same performance parameters and the same experimental procedure as described for reagent water were used. Table 4 summarises the linearity, MDL, MQL and precision of the method with leachate water samples. Linearity was excellent (r^2 0.9943 – 0.9984), MDL lower than 1 ng l^{-1} for all the congeners, with the exception of BDE-99 (1.1 ng l^{-1}). The method repeatability and reproducibility were evaluated at two different concentration levels. At 50 ng l^{-1}, the RSD values were lower than 10%, and at 10 ng l^{-1} the RSD values were somewhat higher with values up to 16.9%, which are still reasonable in such samples of low concentration of analytes and high complexity. From the above results, we can conclude that the overall method performance with leachate water is comparable to that with reagent water.

Thus, the HF-MMLLE-GC-MS system shows a great potential for analysing trace levels of PBDEs in environmental water samples.

4. Conclusions

In this study we have demonstrated the applicability of the HF-MMLLE technique followed by GC-MS for trace-level determination of PBDEs in environmental waters. The extraction technique under the optimised conditions combines high enrichment factors (up to 5200 times), allowing optimal sensitivity, and efficient sample clean-up of complex dirty samples.

The analysis of different environmental aqueous samples such as tap, river and leachate water showed no matrix influence. The method was successfully validated for reagent water and for leachate water. Low MDLs (values not higher than 1.1 ng l^{-1}) for all congeners in both matrices were obtained with a relatively small effort and negligible solvent consumption. It is worth noting, that the MDL can be further enhanced by GC-MS-MS or GC-HR-MS as in EPA method 1614.

The most relevant features of the extraction device are the simplicity to prepare and very low cost, making it suitable for single use, and thus avoiding carry-over effects, and also promotes high sample throughput. In addition, the HF–MMLLE method is shown to be very effective in sample clean-up, resulting in very good chromatographic behaviour for the extracts. The proposed HF-MMLLE technique with GC-MS analysis is well suited as a potential method in routine analysis to determine trace levels of PBDEs in environmental matrices.

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Table 1. GC-MS-SIM conditions for PBDEs' analyses, boiling point (b.p.) and octanol/water partition coefficient (log K_{ow}) of the PBDE congeners studied.

Analyte	t_R (min.)	target ion (*m/z*)	confirmation ions (*m/z*)	b.p. (°C)	Log K_{ow}
BDE-15	6.8	327.9	325.9, 168	339	6.0 ± 0.6 [a]
BDE-28	9.1	405.8	407.8, 247.9	370	6.7 ± 0.7 [a]
BDE-47	12.2	485.7	483.7, 325.8	396	7.4 ± 0.7 [a]
BDE-100	14.9	403.7	563.6, 405.7	434	8.0 ± 0.8 [a]
BDE-99	15.8	403.7	563.6, 405.7	416	8.2 ± 0.8 [a]
BDE-154	18.2	483.6	643.5, 485.6	471	9.0 ± 0.7 [a]
BDE-153	19.5	483.6	643.5, 485.6	453	8.9 ± 0.7 [a]
BDE-183	23.3	561.6	721.5, 563.5	491	9.7 ± 0.7 [a]
PCB-209 (I.S.)	17.3	497.7	495.6, 427.7	466	8.1 ± 0.4 [b]

[a] Value calculated using a computer program, ACD/Labs for Chemistry, Advanced Chemistry Development Inc., Canada. [b] Value from ref. 34

Table 2. The analytical performance of the HF-MMLLE-GC-MS system in reagent water samples.

	Linearity		**Limits (ng l^{-1})**		**Precision [a] (%RSD, n = 3)**	
Analyte	**Range (ng l^{-1})**	**r^2**	**MDL**	**MQL**	**Repeatability**	**Reproducibility**
BDE-15	1 - 100	0.9968	0.2	0.8	0.9	10.3
BDE-28	2 - 100	0.9988	0.3	1.1	2.8	4.0
BDE-47	1 - 100	0.9995	0.2	0.6	4.1	9.6
BDE-100	5 - 100	0.9998	0.7	2.3	8.1	9.6
BDE-99	5 - 100	0.9998	0.9	2.9	8.5	10.4
BDE-154	2 - 100	0.9995	0.3	1.1	6.1	6.3
BDE-153	2 - 100	0.9994	0.6	2.0	5.9	6.1
BDE-183	5 - 100	0.9997	0.7	2.3	2.5	5.6

[a] Spiked at 10 ng l^{-1}

Table 3. Mean % relative recoveries (%RSD, n = 3) of PBDEs in environmental water samples with HF-MMLLE-GC-MS system.

	% Relative recovery [a] (%RSD, n = 3)		
Analyte	**Tap**	**River**	**Leachate**
BDE-15	108.6 (1.5)	110.4 (6.3)	106.7 (2.4)
BDE-28	100.1 (2.0)	101.4 (9.8)	100.1 (2.7)
BDE-47	99.9 (6.8)	94.9 (13.9)	92.7 (7.6)
BDE-100	97.4 (4.2)	86.1 (11.4)	90.0 (8.2)
BDE-99	101.7 (7.0)	103.4 (4.0)	87.3 (7.9)
BDE-154	99.7 (8.0)	94.1 (6.4)	92.1 (5.2)
BDE-153	96.1 (7.4)	90.1 (5.1)	85.4 (3.9)
BDE-183	107.4 (3.0)	98.8 (4.1)	94.7 (3.9)

[a] Spiked at 10 ng l^{-1}

Table 4. The analytical performance of the HF-MMLLE-GC-MS system in leachate water samples.

Analyte	**Linearity**		**Limits (ng l^{-1})**		**Precision at 50 ng l^{-1}[a] (%RSD, n = 3)**		**Precision at 10 ng l^{-1}[a] (%RSD, n = 3)**	
	Range (ng l^{-1})	**r^2**	**MDL**	**MQL**	**Repeatability**	**Reproducibility**	**Repeatability**	**Reproducibility**
BDE-15	2 - 100	0.9984	0.3	1.1	2.7	3.1	2.4	12.3
BDE-28	2 - 100	0.9984	0.3	1.1	2.2	2.9	2.7	15.2
BDE-47	1 - 100	0.9983	0.3	0.8	5.7	2.7	7.6	16.9
BDE-100	5 - 100	0.9943	1.1	3.6	7.4	8.8	8.2	11.4
BDE-99	5 - 100	0.9949	1	3.2	8.8	9.1	7.9	12.0
BDE-154	2 - 100	0.9965	0.5	1.5	8.6	8.5	5.2	2.9
BDE-153	2 - 100	0.9952	0.6	1.9	6.6	10.0	3.9	7.5
BDE-183	5 - 100	0.9958	0.8	2.5	3.8	9.0	3.9	8.4

[a] Spiked 100 ml sample

Figure captions

Figure 1. Effect of stirring speed on E_e of PBDEs. Extraction conditions: organic solvent, n-undecane; sample volume, 100 ml; spiked concentration of the analytes, 50 ng l^{-1}; extraction time, 60 min.

Figure 2. Effect of the extraction time on E_e of PBDEs. Stirring speed 1200 rpm. For other extraction conditions, see Figure 1.

Figure 3. Effect of salt addition on E_e of PBDEs. For the extraction conditions, see Fig. 2.

Figure 4. E_e (depicted in the bars) and E (indicated by the number) values of PBDEs achieved by HF-MMLLE under the optimised extraction conditions (at concentration 50 ng l^{-1} of each analyte).

Figure 5. Total ion chromatogram from GC-MS analysis of the extract from 100 ml of contaminated leachate water sample from Kristianstad.

Figure 6. Total ion chromatogram from GC-MS analysis of the extract from 100 ml of tap (a), river (b) and leachate from Halmstad (c) water samples spiked at 10 ng l^{-1} of each analyte under the optimised HF-MMLLE conditions. Peak designation corresponds to the BDE congener numeration used along the text; I.S. = PCB-209 at 100 μg l^{-1}.

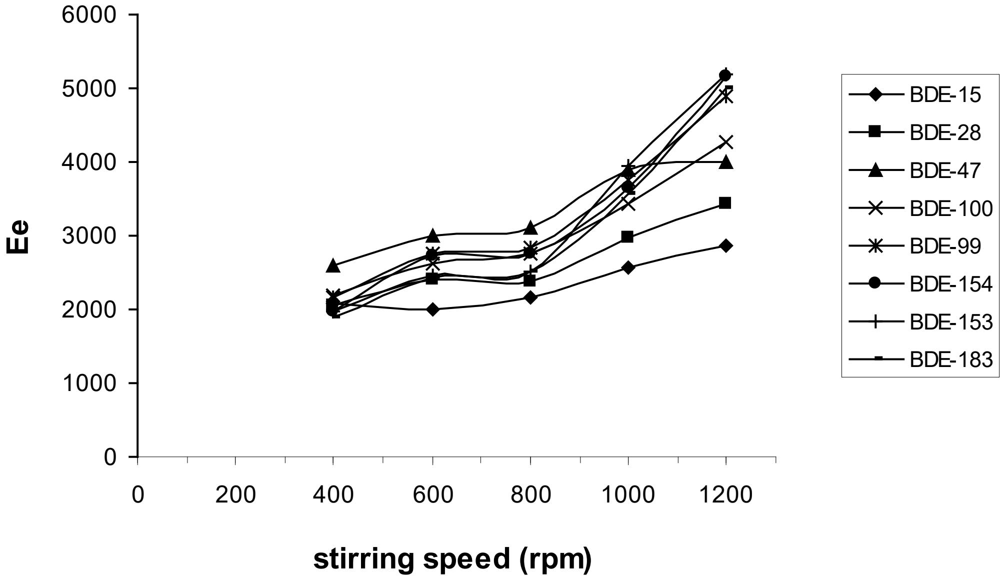
6000
5000
4000
3000
2000
1000
0
Ee
0
200
400
600
800
1000
1200
stirring speed (rpm)
BDE-15
BDE-28
BDE-47
BDE-100
BDE-99
BDE-154
BDE-153
BDE-183

Figure 1

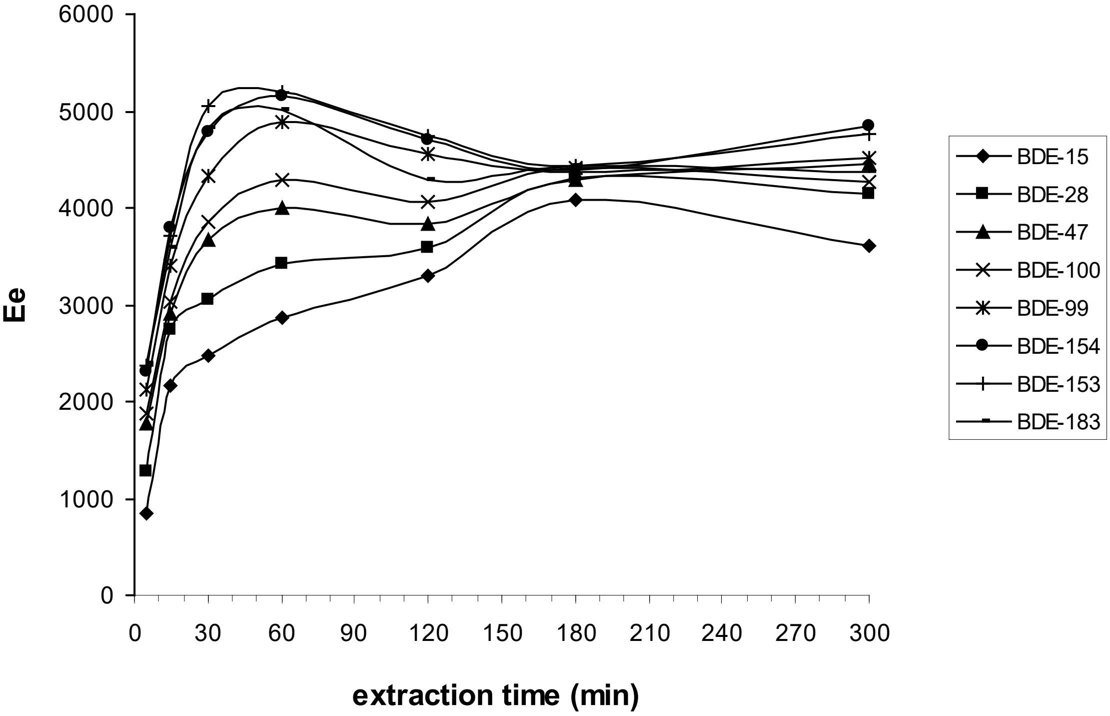
6000
5000
4000
3000
2000
1000
0
Ee
0
30
60
90
120
150
180
210
240
270
300
extraction time (min)
BDE-15
BDE-28
BDE-47
BDE-100
BDE-99
BDE-154
BDE-153
BDE-183

Figure 2

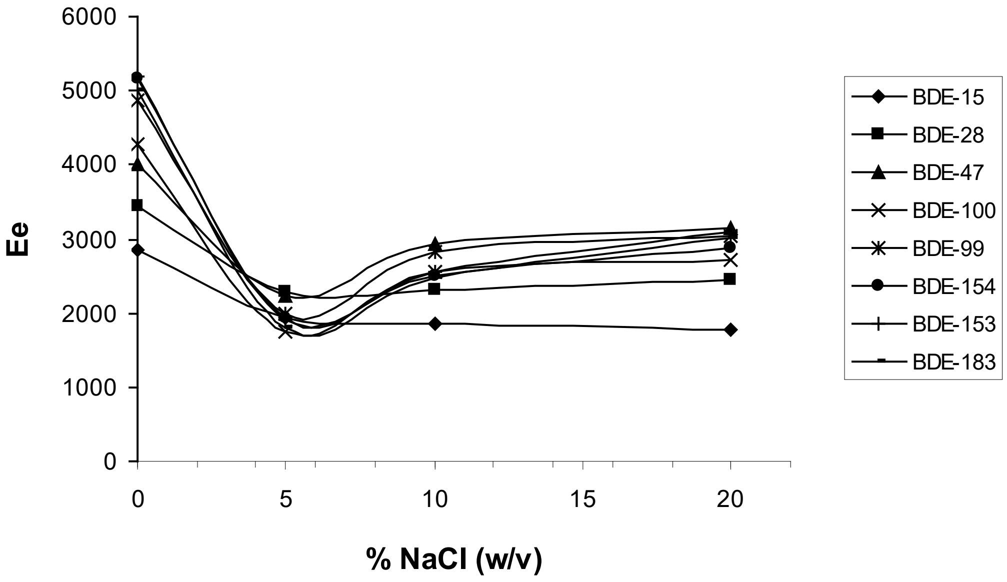
6000
5000
4000
3000
2000
1000
0
Ee
0
5
10
15
20
% NaCl (w/v)
BDE-15
BDE-28
BDE-47
BDE-100
BDE-99
BDE-154
BDE-153
BDE-183

Figure 3

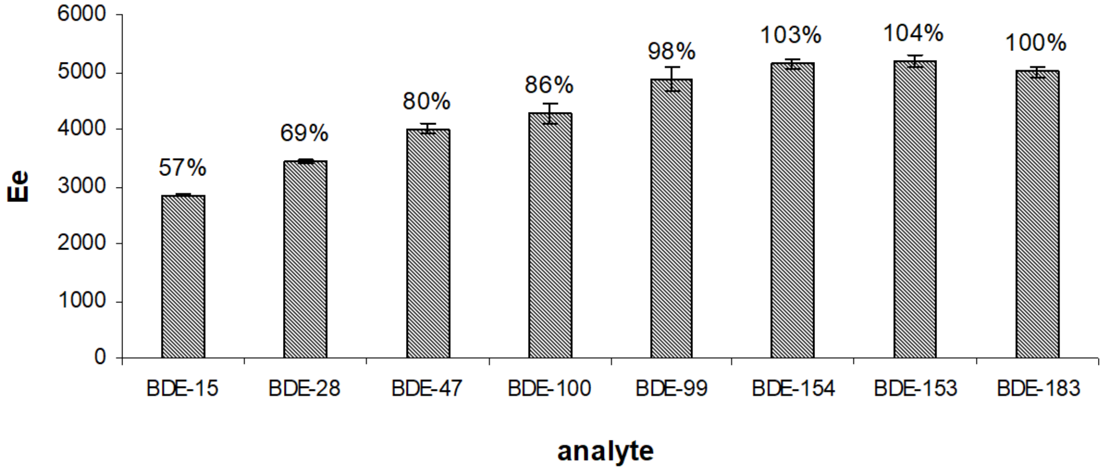
6000
5000
4000
3000
2000
1000
0
Ee
57%
69%
80%
86%
98%
103%
104%
100%
BDE-15
BDE-28
BDE-47
BDE-100
BDE-99
BDE-154
BDE-153
BDE-183
analyte

Figure 4

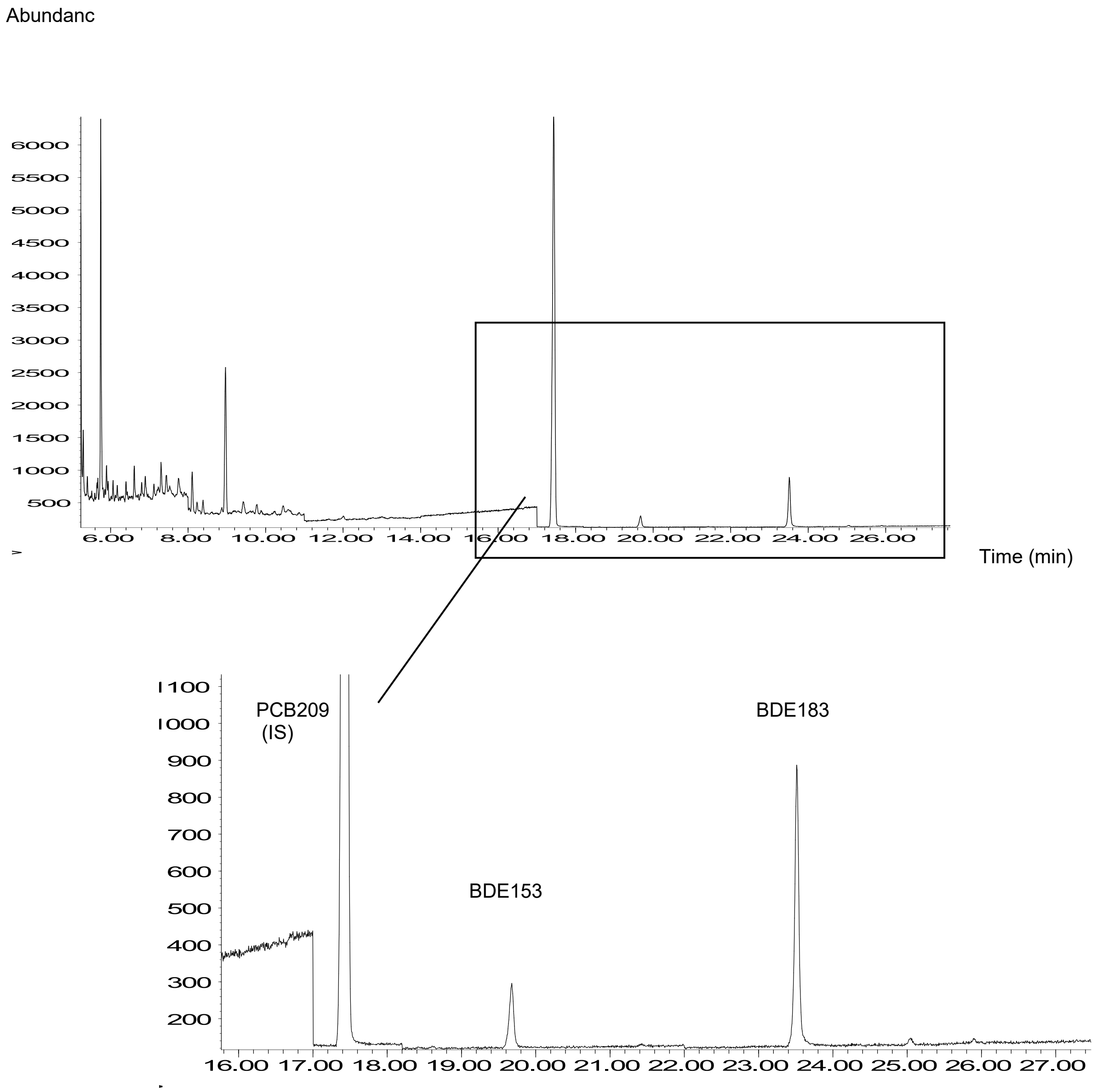
Abundanc
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time (min)
1100
1000
900
800
700
600
500
400
300
200
PCB209
(IS)
BDE153
BDE183
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
27.00

Figure 5

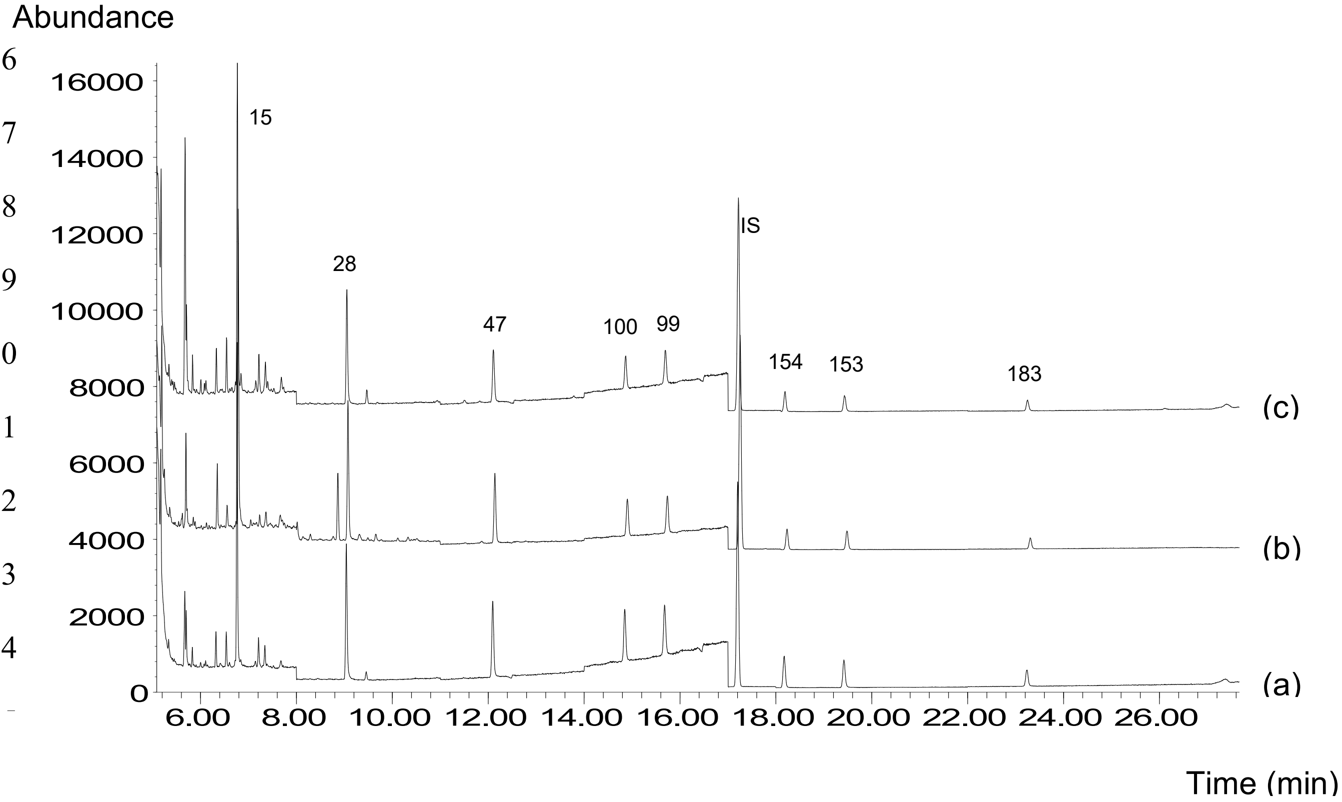
Abundance
16000
14000
12000
10000
8000
6000
4000
2000
0
15
28
47
100
99
IS
154
153
183
(c)
(b)
(a)
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
Time (min)

Figure 6