

# Hollow-Fiber Microporous Membrane Liquid-Liquid Extraction for Determination of Polybrominated Diphenyl Ethers at Trace Levels in Sewage Sludge with Gas Chromatography-Electron Capture Detection

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## ABSTRACT

A two-phase hollow-fiber (HF) liquid-phase microextraction (LPME) method followed by gas chromatography was developed for quantification of 8 major polybrominated diphenyl ethers at trace level in sewage sludge. In this method the porous polypropylene hollow fibers filled with a few microliters of organic solvent, were immersed in aqueous samples of wet sludge which were spiked with the PBDEs at ng/l level. Parameters such as salt concentration, stirring speed, extraction time and pH were optimized and the optimum extraction conditions were then applied to the determination of PBDEs in sewage sludge from Källby sewage treatment plant in Lund. The optimized method allowed detection of  $5.1 \mu\text{g kg}^{-1}$  and  $0.43 \mu\text{g kg}^{-1}$  of BDE-47 and 183, respectively, in dried sludge. The findings were compatible with the results from recent research on PBDEs level in sewage sludge samples from Sweden. Although BDE-209 was expected to have the highest level, it was not detected. Limit of detection, photodegradation or/and biodegradation of BDE-209 during treatment or experiment are major reasons. Low organic solvent consumption, low sample volume requirement, high preconcentration factor, simplicity without using expensive instrument for extraction and excellent sample clean-up are some important factors that make this sample preparation technique very useful for determination of PBDEs in sludge.

**Keywords:** PBDE, Gas Chromatography, Sewage Sludge, Membrane Extraction, LPME

## 1. Introduction

Of all the pollutants released into the environment every year, persistent organic pollutants (POPs) are among the most dangerous chemical pollutants. These are used as pesticides, used by industry, or generated unintentionally as by-products of industrial processes. They accumulate through the food chain in environmental and biota samples [1-9] and pose a risk of causing adverse effect to human health and environment. Polybrominated diphenyl ethers (PBDEs) are a group of persistent organic pollutants, which are used as flame retardants in plastics in consumer products such as computers, television sets and polyurethane foam. Animal studies have shown that PBDEs cause very serious health effects such as estrogenic [10] and, neurobehavioral [8,11] effects, thyroid

dysfunctions [12] and cancer [13,14]. Exponential increase of PBDEs in human [4] and biota samples as well as their adverse health effects on animals have raised concerns over potential health effects of PBDEs in humans and many studies have been conducted to determine these persistent pollutants in environmental samples such as sewage sludge and treatment plant effluents, which are major sources of contamination by PBDEs.

Conventional methods for extraction of PBDEs from sewage sludge such as Soxhlet extraction or accelerated solvent extraction (ASE) need a clean-up step prior to analysis by chromatographic methods and consume a lot of time and extraction solvent, which leads to a significant expense. Hollow fiber microporous membrane liquid-liquid extraction (HF-MMLLE) [15] also known as

liquid phase micro-extraction (LPME) is an alternative technique that can be used for extraction of contamination from different types of matrices.

Depending on the analyte hydrophobicity, a two or three phase extraction system is applied. In two-phase LPME that is also called microporous membrane liquid-liquid extraction (MMLLE), the organic solvent filled in the lumen and the pores of the hollow fiber acts as acceptor phase and is used to extract hydrophobic analytes from an aqueous sample which is donor phase. The acceptor phase can then be analyzed with gas chromatography or HPLC in the normal phase mode. The three phase system (aq/org/aq), or supported liquid membrane (SLM) extraction, involves extraction of polar compounds from an aqueous sample matrix, through an organic phase in the pores of the hollow fiber into a new aqueous phase inside the lumen of the hollow fiber. Analytical techniques such as reversed phase HPLC and capillary electrophoresis can be used for analysis of extracts from three-phase LPME [16,17]. In the present study a two phase hollow fiber microextraction method is applied to extract PBDEs from sewage sludge samples and gas chromatography (GC) with electron capture detector was used as final analysis. The aim was to propose an inexpensive and simple method for environmental laboratories, where thousands of samples are analyzed annually.

## 2. Material and Methods

### 2.1. Reagents and Standards

The PBDE congeners 28, 47, 99, 100, 153, 154, 183 and 209 were obtained from Accustandard (BDE-EPA-SET; New Haven, CT, USA) as stock solutions ( $50 \mu\text{g mL}^{-1}$ ) in isoctane. They were stored in refrigerator and protected against light. Acetone and n-undecane (analytical grade) were from Sigma-Aldrich (Steinheim, Germany). Sulfuric acid (> 95%) and sodium hydroxide were purchased from Acros (New Jersey, USA) and Scharlau (Barcelona, Spain) respectively. Sodium chloride was from Merck (Darmstadt, Germany). Working solutions were prepared by appropriate dilution of stock solutions in acetone. All aqueous solutions for optimization procedure were prepared by using reagent water purified by a Milli-Q system (Millipore, Bedford, MA, USA). A standard solution containing  $4000 \mu\text{g}\cdot\text{L}^{-1}$  BDE-209 and  $2000 \mu\text{g}\cdot\text{L}^{-1}$  of the remaining seven BDEs was prepared in acetone and was used to spike into aqueous sample solutions containing sludge. Solutions were stored in dark at  $4^\circ\text{C}$ .

### 2.2. Instruments

Sample analyses were carried out using a Hewlett-Pack-

ard 6890 series (Agilent, Palo Alto, CA, USA) gas chromatograph system equipped with a Hewlett-Packard 6890 autosampler and a DB-5MS fused silica capillary column  $15 \text{ m} \times 0.25 \text{ mm} \times 0.1 \mu\text{m}$  (J&S Scientific, Folsom, CA, USA) connected to a siltek deactivated retention gap from Restek Corp (Bellefonte, PA, USA) ( $5 \text{ m} \times 0.32 \text{ mm}$ ) by a siltek deactivated universal glass press-fit connector (Restek Corp, Bellefonte, PA, USA). The temperature program was:  $50^\circ\text{C}$  hold 2 min; rate 20 to final temperature of  $325^\circ\text{C}$ , hold 15 min. Injection was made on-column. The injection volume was set at  $3 \mu\text{L}$ . Helium was used as a carrier gas at a flow rate of 30 cm/s. The  $\mu\text{ECD}$  (Hewlett Packard) temperature was  $350^\circ\text{C}$  and nitrogen was used as make-up gas at a flow of 60 ml/min.

The Q3/2 Accurel PP Q3/2 polypropylene hollow-fiber membranes (HF) ( $200 \mu\text{m}$  wall-thickness,  $600 \mu\text{m}$  inner diameter,  $0.2 \mu\text{m}$  pore size) obtained from Membrana GmbH (Wuppertal, Germany) were used to extract PBDEs from sludge. The effective length of the membrane was 5.5 cm. LC Microsyringes with  $50 \mu\text{L}$  volume from Agilent Technology were applied to inject the organic solvent (n-undecane) in the lumen of hollow fibers which were sealed from one side and to keep the membrane in extraction solutions. The membrane pores were impregnated un-decane by dipping the hollow fiber pieces in it for 15 min. The solution pH was measured with a 211 microprocessor pH-meter (Hanna instruments, Kungsbacka, Sweden). A five-position magnetic stirrer (RO 5 power, IKA-WERKE GmbH & Co. KG, Staufen, Germany) was used to stir the samples during extractions.

### 2.3. Sample Collection

The sludge sample was collected during May 2009 from Källby sewage treatment plant which treats sewage from the city of Lund in the south of Sweden and kept in dark condition at  $4^\circ\text{C}$  until analysis. The waste water treatment in STP consists of four steps: a primary mechanical pre-treatment, a biological treatment step, a chemical treatment step and a sludge treatment step. The aim of mechanical treatment is to remove different types of suspended solids. In the biological process activated sludge which contains large amount of microorganisms is added to waste water to degrade organic matter in water and in chemical treatment process phosphate is removed by addition of iron or aluminum salt. Finally in the sludge treatment process, the sludge collected from the first step (sedimentation) undergoes dewatering; an anaerobic digestion process and various dewatering processes for reducing the amount of sludge.

### 3. Results and Discussion

#### 3.1. Analytical Challenges

Analysis of high molecular weight PBDE (nona- and decaBDE) congeners poses some problems. These compounds are sensitive to light and adsorb to glass surfaces and small dust particles. In general, the photochemical reaction rate increases with increasing number of bromine substituent, so PBDE-209 is the most sensitive. To avoid photochemical degradation, samples should be kept in dark and UV filters may be placed at windows and below fluorescent lights. In addition, all glassware should be covered with aluminum foil to prevent adsorption of dust. They are also sensitive to temperature and degrade at high temperature required for GC analysis. Therefore relatively short columns should be used for the GC analysis of nona- and decaBDEs [18].

The injection technique, type of retention gap, press-fit connector and stationary phase also significantly affect the yield of PBDEs from chromatographic systems. Concerning these aspects the recommendations given in the literature were followed. [19].

#### 3.2. Optimization of Extraction Procedure

The optimization step was performed using four variable factors, involving pH of donor phase, salt (NaCl) addition, stirring speed and extraction time. The choice of organic solvent (n-undecane) as the acceptor phase was based on selection of the best solvent with high stability and selectivity in extraction of PBDEs (high hydrophobicity) in a previous study on environmental water [20]. To study the extraction process the variable taken as response was extraction efficiency  $E$ , that is the ratio of the number of moles of analyte in the acceptor phase ( $n_A$ ) after extraction to that initially present in the donor phase ( $n_S$ ).

$$E = n_A/n_S \quad (1)$$

To evaluate the effect of parameters on extraction efficiency, a series of 100 ml aqueous slurry samples containing 1 g of wet sludge were spiked to final concentrations of  $0.100 \mu\text{g}\cdot\text{L}^{-1}$  of BDE-209 and  $0.050 \mu\text{g}\cdot\text{L}^{-1}$  of each the remaining seven BDEs and then pH was adjusted at 5.1 according to a preliminary experiment. Spiked slurry samples were stirred for 5 min before starting the extraction procedure. All determinations and experiments were performed in triplicate and the presented results are the average values of three determinations.

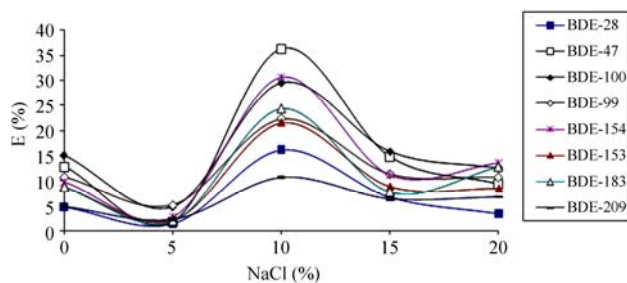
#### 3.3. Influence of Ionic Strength

The use of salting-out effects may greatly enhance the

extraction efficiency of various organic compounds from aqueous solutions and thereby sensitivity and precision of their determination. This effect can be especially significant for hydrophobic analytes, which bind well to particles with high organic carbon content in sewage sludge. In this study different amounts of NaCl (0 - 20% W/V) were added to aqueous solutions containing sludge and spiked with  $0.100 \mu\text{g}\cdot\text{L}^{-1}$  of BDE-209 and  $0.050 \mu\text{g}\cdot\text{L}^{-1}$  of remaining BDEs with pH adjusted at 5.1. **Figure 1** depicts that optimal extraction condition was obtained at 10% NaCl for all analytes.

Addition of NaCl to sample solution will alter the partition coefficient of the analytes between dissolved organic matter content of sludge and water and also between water and acceptor phase based on the change of ionic strength and viscosity [21]. Changes in ionic strength can alter macromolecular structure of humic substances (HSs) which exist in sewage sludge. At lower ionic strength HSs have long and flexible structure with available region for binding to hydrophobic organic molecules (HOMs) whereas at higher ionic concentrations HSs forms rigid spherical shape molecules with the hydrophilic surface and hydrophobic interior where is less accessible for binding of hydrophobic organic molecules (HOCs). Therefore an increase in ionic strength results in a decrease in sorption of HOMs [22,23].

Moreover the high content of salt in water affects hydration and causes decrease in water solubility. It seems that in 5% NaCl, the solution does not have sufficient ionic strength required for efficient partitioning to the organic solvent in the fiber and increased viscosity of the aqueous phase negatively influences the kinetics of the process. Lower extraction efficiency at higher ionic strength (15% and 20% of NaCl) can also be related to high viscosity and adsorption of analytes to glassware or polymer [24]. Therefore, the maximum extraction efficiency in selected concentration for experiments at 10% of NaCl is due to the combined effects of ionic strength and viscosity.



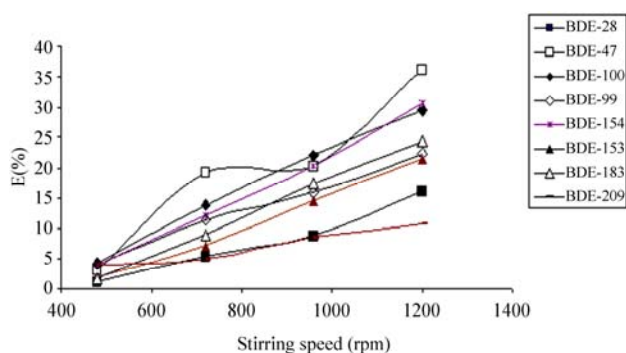
**Figure 1.** Effect of donor salt addition on  $E$  (%). Stirring speed 1200, extraction time 60 min, pH 5.1.

### 3.4. Stirring Speed

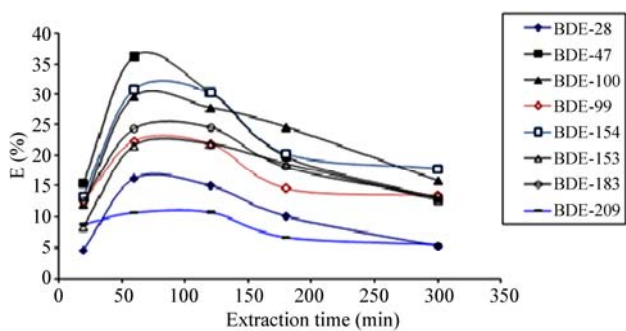
The stirring speed has an important effect on transport of analytes in LPME system thereby reducing extraction time to reach thermodynamic equilibrium. The stirring of donor phase was carried out from dial settings 4 to 10 (480 to 1200 rpm). **Figure 2** shows the E value for all PBDE congeners studied and indicates that extraction efficiency decreases at lower speeds. Therefore, the highest speed was selected as optimum for subsequent experiments.

### 3.5. Extraction Time

The effect of extraction time was evaluated for slurry solutions stirred with stirring at 1200 rpm and adjusted to pH at 5.1 with 10% NaCl during 20, 60, 120, 180 and 300 min. As seen in **Figure 3**, the concentration in the fiber increased with time for all PBDEs up to 60 min and then remained rather constant during an hour, indicating that equilibrium was attained. A decrease in extraction efficiency observed during prolonged extraction time most probably was due to solvent losses at the high stirring speed (1200 rpm). On the basis of these finding, we selected 60 min as optimum extraction time.



**Figure 2.** Effect of stirring speed on E (%). Extraction time 60 min, 10% NaCl, pH 5.1.



**Figure 3.** Effect of extraction time on E (%). Stirring speed 1200 rpm, 10% NaCl, pH 5.1.

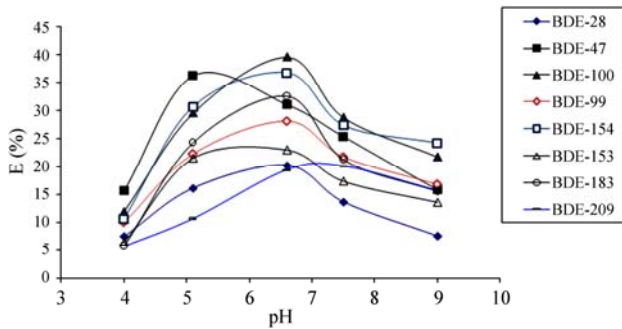
### 3.6. Effect of Sample pH

The pH can be an important factor in membrane extraction especially when analytes of interest are ionisable. It was found that sludge pH increases with stirring, especially at lower pH. So to determine the influence of pH on extraction efficiency, the initial pH of samples was adjusted to pH 4, 5, 6.6, 7.5 and 9 using H<sub>2</sub>SO<sub>4</sub> and NaOH. **Figure 4** shows the effect of initial pH on the extraction efficiency of all analytes. Samples with acidic and basic pH showed lower recoveries but higher and similar results were achieved for samples with pH values of 5, 6 and 7.5. Lower recoveries at acidic and basic conditions can be related to changes in sludge properties. The chromatogram is shown in **Figure 5**. Among the analytes, the more hydrophobic compounds (BDE-183, BDE-209) showed a significant increase in extraction efficiency when the pH was changed from 5 to 6.6. Therefore pH 6.6 was selected as optimum pH for sample preparation of real samples.

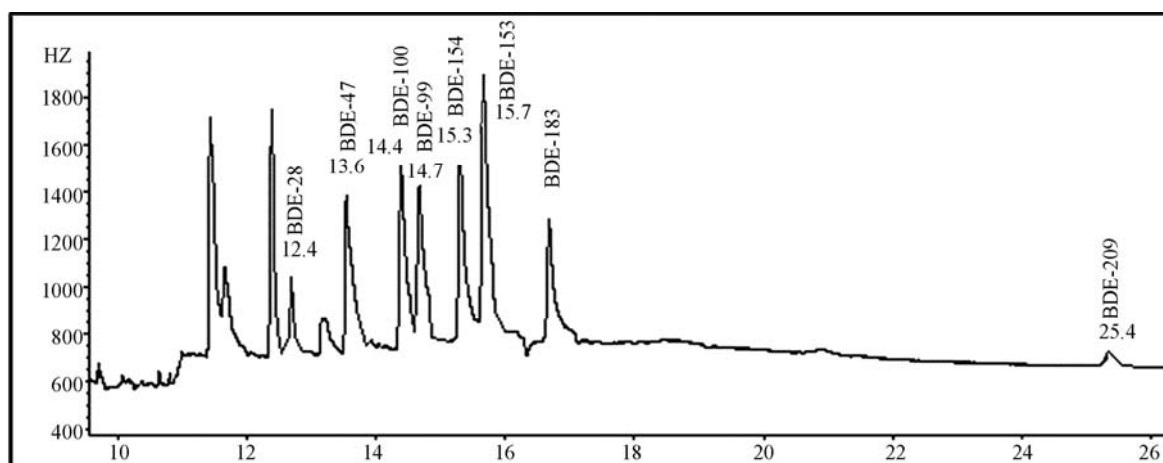
### 3.7. Application to Real Sample

The extraction method developed in this study was applied to sewage sludge from Källby sewage treatment plant in Lund (Sweden). 100 ml of spiked and non spiked aqueous samples containing 1 g of wet sludge (considering of 70% water content) and 10% NaCl (w/v) were prepared and pH was adjusted at 6.6 for each sample. Extractions were performed with 5.5 cm polypropylene hollow-fiber at 1200 rpm stirring speed for 1 hour and the amounts of PBDEs per dry weight were calculated on the basis of 70% water in wet sludge using a standard addition calibration procedure. It was found that the sludge contained 5.1 µg·kg<sup>-1</sup> of BDE-47 and 0.43 µg·kg<sup>-1</sup> of BDE-183. No other congeners were found. The relative standard deviation of the results was about 15%.

Also, the extraction efficiency of the native PBDE in the sludge was calculated from the standard addition data. It was found to be 23% - 32%, which is compensated for by the standard addition procedure.



**Figure 4.** The effect of pH on E (%). Stirring speed 1200 rpm, extraction time 60 min, 10% NaCl.



**Figure 5.** Chromatogram obtained by the developed method for sludge sample spiked with  $0.100 \mu\text{g L}^{-1}$  of BDE-209 and  $0.050 \mu\text{g L}^{-1}$  of remaining BDEs. Stirring speed 1200 rpm, extraction time 60 min, 10% NaCl, pH 6.6.

An overview of distribution and levels of brominated flame retardants in sewage sludge samples from 22 wastewater treatment plants in Sweden shows that the concentration of PBDEs were in the range of n.d. – $450 \mu\text{g}\cdot\text{kg}^{-1}$  wet weight [25]. Previous studies on 9 sewage sludge samples in Germany also showed total amounts of tri- to hepta BDEs between  $0.49$  and  $16.25 \mu\text{g}\cdot\text{kg}^{-1}$  dry weight sludge [26]. Extraction techniques applied to these analyses were centrifugation and Soxhlet extraction respectively, and the concentrations of PBDEs are compatible with the results obtained for BDE-47 and 183 by membrane extraction in this study although BDE-209 which was expected to have the highest level was not detected. The major reason may be the limit of detection but photodegradation or/and biodegradation during treatment or experiment are other explanations. On the other hand there is a correlation between PBDE levels and vicinity of industrial areas, especially textile and electrical industries (which is not the case in Lund) as significant local sources of PBDEs. This causes important variation among different municipal wastewater treatment plants.

#### 4. Conclusions

A simple and novel method has been developed for determination of 8 major polybrominated diphenyl ethers at trace level in sewage sludge. The method was based on two phase HF-MMLLE for extraction and gas chromatography analysis. The investigation was focused on the optimization of the extraction parameters such as salt concentration, stirring speed, extraction time and initial pH of donor phase. The employed extraction method minimizes the consumption of organic solvents (microliters) which are expensive and toxic for environment. In addition, cheap piece of hollow fiber, no additional

preconcentration prior to final analysis and no requirement for sample clean-up step by expensive instruments make the method simple and more economic for determination of PBDEs in sewage sludge.

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