

## DETERMINATION OF 40 PBDE IN RIVER SEDIMENTS FROM PORTUGAL

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### Introduction

Much concern is nowadays given to monitor the levels of polybromodiphenylethers in several environmental samples such as sediment (1) or fish (2) due to the widespread use of such compounds as flame retardants. These compounds are considered as endocrine disrupting chemicals and its survey in the environment is needed to determine the detrimental effects they may cause. At the present moment, most works are directed to determine either the single legislated congeners (PentaBDE) or the most abundant ones (BDE #47, 99 and 100). However, there is a lack of the complete characterization of all PBDE in environmental samples. The present work was aimed to determine 40 PBDE congeners in river and coastal sediments collected in Portugal in the frame of a monitoring program directed to survey priority pollutants in water, sediments and biota. For such purpose, an analytical method based in Soxhlet extraction, followed by a clean-up using alumina solid phase extraction cartridges and analysis by gas chromatography-mass spectrometry with negative chemical ionization was optimized and applied for the analysis of 32 sediment samples. This paper reports the quality parameters obtained with such methodology and reports the levels of all 40 PBDE congeners detected in Portuguese sediments.

### Materials and Method

#### *Chemicals and reagents*

The Polybrominated Diphenyl Ether Analytical Standard Solution EO-4980 was purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). The components of this solution were: 3 monoBDEs (BDE # 1,2 and 3), 7 diBDEs (BDE # 7,8,10,11,12,13 and 15), 8 triBDEs (BDE # 17,25,28,30,32,33,35 and 37), 6 tetraBDEs (BDE # 47,49,66,71,75 and 77), 7 pentaBDEs (BDE # 85,99,100,105,116,119 and 126), 6 hexaBDEs (BDE # 138,140,153,154,155 and 166) and 3 heptaBDEs (BDE # 181,183 and 190). Moreover, the mixture also contain 5 <sup>13</sup>C-labeled BDE congeners: 2 tetraBDEs (<sup>13</sup>C-BDE # 47 and <sup>13</sup>C-BDE # 77) and 3 pentaBDEs (<sup>13</sup>C-BDE # 99, <sup>13</sup>C-BDE # 100 and <sup>13</sup>C-BDE # 126). The concentrations of each compound ranged from 100 pg/μL for the mono congeners to 250 pg/μL for the hepta congeners. This solution was used to draw the calibration curve (from 5 pg/μL to 200 pg/μL) and also to spike the sediment samples at a concentrations varying from 2.5 to 10 ng/g, depending on the compound, to study the recoveries.

#### *Sampling strategy*

Selected sampling points chosen covered the main river basins and coastal areas of Portugal. In the sampled areas, there is a high industrial and agricultural activity, and during the last two decades, industrial effluents were directly discharged untreated to the river bed. This situation has changed with

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the introduction and appliance of new EU Directives, but historical contamination is expected in all these sites. Coastal sediment samples were collected from the river bed using a drag Smith-McIntyre with a midcorer Mark II-400. In such way, the external layers (0-2 cm) were not altered. For river sampling, a Petit-ponar drag was used. All samples were stored in aluminium foil and kept at 4 °C until transported to the laboratory.

## *Sample preparation*

Samples were stored at -18 °C and lyophilized at -50 °C during 36 hours. Prior to analysis, samples were sieved through 100, 50 and 2.5 µm sieve in order to obtain a homogenized material. The TOC of these samples were between 0.49 and 6.25 mg/g with a total organic load between 4 to 6079 ng/g.

Prior to extraction, 1 g of sample was spiked PCB 209 which was used as surrogates. Samples were Soxhlet extracted in hexane:dichloromethane (1:1) during 18 hours. The extract was rotaevaporated to almost dryness and the clean-up was performed with alumina cartridges of 2 g. The cartridges were placed on a Baker SPE 12G apparatus connected to a vacuum system. Prior to clean-up, the cartridges were conditioned with hexane and dichloromethane (19:1). Afterwards, 1 mL of sample extract was placed on the top of the cartridge and by gravity, it was let down and collected in a balloon. Elution was performed with 20 mL hexane:dichloromethane (19:1), with 20 mL hexane:dichloromethane (1:1) and 20 mL dichloromethane:methanol (1:1). Fraction 1 and 2 were mixed and fraction 3 was disregarded since no traces of any BDE were present. Following, the extract was rotaevaporated to almost dryness and finally reconstituted to 200 µl of isoctane.

Recovery studies were performed by spiking 1 g of sediment with a mixture of all 40 BDE congeners at a concentration levels between 2.5 ng/g and 10 ng/g. Extraction was performed as depicted above.

## *GC-NCI-MS analysis*

GC-NCI-MS was performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network (Agilent). A HP-5ms (30 m x 0.25 mm i.d., 0.25 µm film thickness) containing 5 % phenyl methyl siloxane (model HP 19091S-433) capillary column was used with helium as the carrier gas at 10 psi. The temperature program was from 110 °C (held for 1 min.) to 180 °C (held for 1 min.) at 8 °C/min., then from 180 °C to 240 °C (held for 5 min.) at 2 °C/min., and then from 240 °C to 280 °C (held for 6 min.) at 2 °C/min., using the splitless injection mode during 1 min. 2 µl of sample were injected.

The GC-NCI-MS operating conditions were as follows: ion source temperature between 130 and 250°C, methane as chemical ionization moderating gas at an ion source pressure between  $1.2 \cdot 10^{-4}$  torr and  $2.7 \cdot 10^{-4}$  torr, according to previous work (3).

Quantification was performed by external standard calibration and results were corrected by the recovery factor. Recovery values, standard deviations (n=3) and method detection limits using a signal to noise ratio of 3 were calculated.

## **Results and discussion**

### *Quality parameters*

The present work was aimed to develop an extraction and a simplified clean-up method for the analysis of 40 BDE, covering all the bromination levels (from mono to hepta). Emphasis was given to the detection of minority BDE, for which an extraction method and analysis in environmental samples had not been previously described. Extraction was performed using the classical Soxhlet which is specially suitable and widely applied to determine persistent organic pollutants in general.

**Table 1.** Quality parameters (recovery and coefficient of variation) of the studied compounds after extracting 1 g of sediment spiked between 2.5 and 10 ng/g.

Compound	Rt (min)	% recovery	CV
BDE #1	11.290	49.9	4.6
BDE #2	11.528	59.6	7.0
BDE #3	11.818	49.9	3.3
BDE #10	15.810	77.0	6.8
BDE #7	17.265	84.5	7.6
BDE #11	17.919	81.3	7.4
BDE #8	18.066	83.7	8.3
BDE #12+13	18.466	83.1	7.4
BDE #15	19.167	51.2	6.7
BDE #30	22.655	86.5	7.9
BDE #32	25.019	89.4	8.4
BDE #17	25.820	88.9	7.5
BDE #25	25.928	87.6	7.2
BDE #28+33	26.998	90.5	7.6
BDE #35	27.737	88.3	7.6
BDE #37	28.685	88.8	7.3
BDE #75	33.659	90.6	8.9
BDE #71	34.383	86.1	7.9
BDE #49	34.737	85.2	7.6
BDE #47	35.884	60.9	9.0
BDE #66	37.139	87.9	7.3
BDE #77	39.165	89.9	6.3
BDE #100	42.945	85.8	7.09
BDE #119	43.731	85.8	6.4
BDE #99	45.371	81.9	6.2
BDE #116	46.365	76.3	10.6
BDE #85	50.014	74.7	8.2
BDE #126+155	50.792	120.7	13.7
BDE #105	51.589	81.0	7.5
BDE #154	52.559	79.9	8.6
BDE #153	55.875	100.4	8.8
BDE #140	57.969	80.1	9.7
BDE #138	60.064	78.2	10.3
BDE #166	60.310	72.3	10.5
BDE #183	64.953	80.5	12.3
BDE #181	69.412	92.4	11.0
BDE #190	70.012	67.7	14.4

However, the clean-up procedure chosen consisted in the use of solid-phase extraction cartridges packed with alumina. The use of this cartridges has many advantages, among others the quicker and easy handling, they can be disposed after used so no external contamination can take place, there is no

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need of tedious glassware cleaning and avoids activation/deactivation procedure. Table 1 shows the quality parameters obtained after spiking raw sediment with a mixture of 40 BDE. Recovery values were generally around 80 % with the less brominated congeners showing lower values due to the fact that these compounds were at the lowest concentration level in the spiked sediment. The limits of detection were at 0.05-0.1 ng/g level due to the high sensitivity and selectivity obtained with GC-NCI-MS in selected ion monitoring. By performing triplicate analysis, the coefficient of variation of the method was for all congeners below 12 %, generally of 8 %, indicating a good performance of the method. In order to unequivocally confirm the presence of any BDE, 3 ions were selected by compound and their relative intensities should be within 10 % of the corresponding standard. In addition, the retention times could not vary more than 0.1 min of their theoretical value. The base peak at  $m/z$  79 was chosen for quantification. PCB 209 was used as internal standard for quality control of the MS, but could not be used for quantification due to a high dispersion of the response factors.

## *Environmental samples*

With the method developed, it was possible to determine PBDE in river sediments from different parts over Portugal. In general, the sampled areas were highly industrial (e.g. close to the city of Porto) or river effluents such as the estuary of the Tajo, in Lisbon. Out of 32 samples analysed, all of them contained at least one BDE. The most common BDE detected were BDE# 47, 99, 100 and 153 and generally the concentrations varied from 0.4 to 18 ng/g dry weight. However, out of the minority BDE analysed, BDE #2, 3, 8, 30 and 49 were detected at concentration levels at the 0.5-3 ng/g level. The presence of these compounds in environmental samples reveal the importance of their monitoring and survey to get a better knowledge of the persistence, degradation and fate of this chemicals in the environment

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