Horizontal Standardisation of Brominated Flame Retardants (BFRs)

Analysis of Polybrominated Diphenyl Ethers (PBDEs) in sewage sludge

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Introduction

Polybrominated diphenyl ethers (PBDEs), which are used as flame retardants. They are measured in several matrices and for environmental purposes it is necessary that the methods applied in these matrices are comparable and making use of the same principles and instrumentation. The project HORIZONTAL has been started to develop horizontal and harmonised European standards in the field of sludge, soil, contaminated soil and treated biowaste. The suggested method is here described. However, depending on the properties of the matrix, different or slightly different steps in the method can be necessary. In the earlier study, "Report of the Phase II Ruggedness" (April, 2005), two methods, one based on Soxhlet extraction and one based on pressurized liquid extraction (PLE) were developed for the analysis of PBDEs in sediment. These methods should also be practicable on many types of soil samples since soil generally is a cleaner matrix. In this work we describe the Soxlet method applied on sewage sludge. However, the PLE method is under investigation for the sewage sludge samples and is going to be presented in the completed experimental report.

The analysis method of PBDEs in sewage sludge are described in the following steps;

- Pre-treatment
- Extraction
    - Pressurized liquid extraction (PLE)
    - Soxhlet
- Clean-up
- Gas chromatography/mass spectrometry
- Requirements for identification, limits of detection (LOD), limits of quantitation (LOQ) and recoveries.

23 PBDE congeners, from tri- to decaBDEs are included in the analytical work with sewage sludge: one triBDE (BDE-28), three tetraBDEs (BDE-47, BDE-49, BDE-66), four pentaBDEs (BDE-85, BDE-99, BDE-100, BDE-119), six hexaBDEs (BDE-138, BDE-139, BDE-140, BDE-153, BDE-154, BDE-155), one heptaBDE (BDE-183), four octaBDEs (BDE-194, BDE-196, BDE-197, BDE-203), three nonaBDEs (BDE-206, BDE-207, BDE-208) and the decaBDE (BDE-209).

The sewage sludge sample used was "Horizontal SL 11", sewage sludge, electronic industry, ball-milled < 125 μm, Turin, Italy.

Pre-treatment

Samples are transferred to the laboratory at a temperature of 4ºC, and then frozen at -20ºC before being frozen dried. The lyophilised samples are ground and homogenized by sieving through a stainless steel 2-mm sieve, and stored in sealed containers at -20ºC until analysis. Before extraction, surrogate standard are added to 0.5 g or 1.0 g of dry weight sample. Samples were spiked with 15 ng of the tri- to heptaBDEs and 30 ng of the octa- to decaBDEs. Spiked samples are kept over night to equilibrate.

Extraction

Soxhlet extraction

Soxhlet extraction is accomplished in cellulose thimbles containing 0.5 g or 1.0 g of sewage sludge. To remove sulfur interference 1.0 g and 2.0 g of copper are added to sewage sludge 0.5 g and 1.0 g, respectively. Triplicate extractions are done on both blanks and spiked samples using 100 mL of a mixture of hexane:dichloromethane (1:1) for 24 h. After extraction, the extracts and the rinses of the Soxhlet are combined and then subjected to the clean-up procedure.

Pressurized liquid extraction (PLE)

PLE are carried out using a fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA). For the sewage sludge samples, cooper is selected as sorbent in the extraction cell. The final optimised method is as follows: a 22 mL extraction cell is loaded by inserting two cellulose filters into the cell outlet and spiked samples of 0.5 g and 1 g of sewage sludge are ground with cooper (1:2). The mixture is loaded into the extraction cell on top and the dead volume is filled with Hydromatrix, and the cell is sealed with the top cell cap. The extraction cell is filled with hexane:dichloromethane (1:1) mixture until the pressure reached 1500 psi, and heated to 100ºC. After an oven heat-up time of 5 min under these conditions, two static extractions of 10 min. at constant pressure and temperature are developed. After this static period, fresh solvent is introduced to flush the lines and cell, and the extract is collected in the vial. The flush volume amounted to 100% of the extraction cell. The extraction is cycled twice. The volume of the resulting extract is about 35 mL. The extracts are then subjected to the clean-up procedure.

Clean-up

After extraction with Soxhlet and PLE, crude extracts are subjected to purification steps. Both 0.5 g and 1.0 g sewage sludge samples extracts were treated with concentrated sulfuric acid (2 × 25 mL) and subsequently purified with two and five grams of alumina cartridges (Table 1). The conditioning parameters, sample loading volume and elution parameters were optimised. Solid-phase extraction (SPE) cartridges are conditioned with 20 mL hexane. The sample volume loaded are ~ 1 mL, and the elution step is performed with 30 mL hexane:dichloromethane (1:2). Samples are finally concentrated to incipient dryness and re-dissolved in isooctane (50 µL) containing the recovery standards PCB-209, 15 ng and 4'-chloro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether (Cl-BDE-208), 30 ng, prior to the analysis by GC-NCI-MS.

Gas chromatography-mass spectrometry

GC-NCI-MS analyses are performed on a gas chromatograph Agilent 6890 connected to a mass spectrometer Agilent 5973 Network (Agilent). A HP-5MS (30 m × 0.25 mm i.d., 0.25 µm film thickness) containing 5% phenyl methyl siloxane (model HP 19091S-433) capillary column is used for the determination of congeners from of tri- to heptaBDEs. The temperature program is from 110ºC (hold for 1 min) to 180ºC (hold for 1 min.) at 8ºC/min., then from 180ºC to 240ºC (hold for 5 min) at 2ºC/min., and then from 240ºC to 265ºC (hold for 6 min) at 2ºC/min., using the splitless injection mode during 1 min. The operating conditions are as follow: ion source temperature = 250ºC, ammonia as chemical ionisation moderating gas at an ion source pressure of 1.9 10^{-4} torr. The injection volume was 2 µL, injector temperature = 275ºC and the interface temperature = 250ºC. The experiments are carried out monitoring the two most abundant isotope peaks from the mass spectra corresponding to m/z = 79 and 81 ($[Br]^-$).

For octa- to decaBDEs, a DB-5MS (15 m × 0.25 mm i.d., 0.10 µm film thickness) containing 5% phenyl methyl siloxane capillary column is used with helium as the carrier gas at 6 psi. The temperature program are from 140ºC (hold for 2 min.) to 325ºC (hold for 10 min.) at 10ºC/min., using the splitless injection mode during 1 min. The interface temperature was set at 270ºC on these 15 m colounm.

Requirements for identification, limits of detectation and recoveries

Confirmation criteria for the detection and quantification of PBDEs should include the following: (i) retention time for all m/z monitored for a given analyte should maximize

simultaneously ± 1 s, with signal to noise ratio ≥ 3 for each; (ii) the ratio between the two monitored ions should be within 15% of the theoretical. Quantification of tri- to hepta-BDEs are carried out by internal standard procedure with the PCB-209 as internal standard, whereas octa- to decaBDEs are quantified using the external standard method and Cl-BDE-208 as internal standard in the sewage sludge samples.

The recoveries of tri- to nonaBDEs of the sewage sludge samples using Soxhlet extraction ranged from 59-84% when 0.5 g sample and a 2 g alumina column were employed, 62-93% when 0.5 g sample and a 5 g alumina column were employed, 60-98% when 1.0 g sample and a 2 g alumina column were employed and 59-84% when 1.0 g sample and a 5 g alumina column were employed (Table 3). In these analyses, recoveries of BDE-209 ranged from 198-208%. Consequently, further measurements on the recoveries of BDE-209 are going to be preformed.
So far, the recoveries of tri- to heptaBDEs of the sewage sludge samples using PLE extraction need to be done. The recoveries for the octa- and nonaBDEs ranged from 70-98% when 0.5 g sample and a 2 g alumina column were employed and 62-89% when 0.5 g sample and a 5 g alumina column were employed. For BDE-209, recoveries of 172-178% were obtained in the latter analyses. Also here, further measurements on the recoveries of BDE-209 are going to be preformed.

Of the four different Soxhlet methods presented in Table 1, best recovery results of the analysis of the sewage sludge, were obtained starting with 1 g of sample and the use of five grams of alumina cartridges (Table 1). Ranges of limits of detection (LOD) and limits of quantitation (LOQ) of tri- to decaBDEs in sewage sludge obtained with the best Soxhlet method is shown in Table 2 and LOD as well as LOQ of some common PBDE congeners are shown in Table 3.

Table 1. PBDE recoveries in sewage sludge, obtained using the Soxhlet-SPE method.

	Soxhlet mean recovery (%RSD)			
	0.5 g sample		1.0 g sample	
	alumina		alumina	
	2 g (n=3)	5 g (n=2)	2 g (n=3)	5 g (n=3)
triBDE				
BDE-28	61 (8)	78 (12)	78 (5)	94 (7)
tetraBDEs				
BDE-47	69 (8)	82 (7)	86 (7)	92 (3)
BDE-49	68 (8)	80 (7)	85 (7)	91 (3)
BDE-66	71 (9)	86 (7)	91 (7)	98 (3)
pentaBDEs				
BDE-85	77 (7)	91 (7)	98 (5)	105 (5)
BDE-99	72 (5)	82 (7)	83 (6)	92 (5)
BDE-100	71 (5)	79 (7)	82 (6)	88 (5)
BDE-119	74 (6)	82 (8)	86 (6)	92 (5)
hexaBDEs				
BDE-138	82 (10)	93 (9)	93 (6)	103 (6)
BDE-139	81 (8)	90 (8)	91 (6)	99 (5)
BDE-140	84 (7)	92 (8)	91 (6)	101 (6)
BDE-153	73 (7)	82 (9)	82 (8)	91 (4)
BDE-154	80 (6)	88 (6)	91 (7)	100 (5)
BDE-155	73 (6)	78 (5)	75 (7)	80 (4)
heptaBDE				
BDE-183	77 (9)	93 (5)	86 (6)	94 (5)
octaBDEs				
BDE-194	84 (8)	89 (3)	79 (9)	80 (3)
BDE-196	59 (9)	65 (3)	59 (9)	62 (6)
BDE-197	79 (12)	86 (5)	72 (5)	75 (3)
BDE-203	74 (7)	65 (1)	72 (9)	61 (9)
nonaBDEs				
BDE-206	59 (7)	62 (2)	60 (8)	62 (4)
BDE-207	74 (5)	81 (3)	75 (7)	76 (2)
BDE-208	77 (6)	85 (4)	77 (6)	79 (0)
decaBDE				
BDE-209	203 (7)	198 (3)	208 (8)	203 (9)

Table 2. Limits of detection (LOD) and limits of quantitation (LOQ) of PBDEs obtained by and Soxhlet-SPE-GC-NCI-MS in sewage sludge using 1 g of sample and five grams of alumina cartridges (Table 1).

		LOD pg/g d.w.	LOQ pg/g d.w.
Tri-BDEs	(n = 1)	400	1340
Tetra-BDEs	(n = 3)	30-440	90-1480
Penta-BDEs	(n = 4)	180-290	610-970
Hexa-BDEs	(n = 6)	160-250	530-830
Hepta-BDEs	(n = 1)	380	1280
Octa-BDEs	(n = 4)	200-410	660-1370
NonaBDEs	(n = 3)	160-340	540-1140
Deca-BDE	(n = 1)	1230	4100

Table 3. Limits of detection (LOD) and limits of quantitation (LOQ) of some common PBDEs obtained by and Soxhlet-SPE-GC-NCI-MS in sewage sludge using 1 g of sample and five grams of alumina cartridges (Table 1).

PBDE congener	LOD pg/g d.w.	LOQ pg/g d.w.
BDE-47	30	90
BDE-99	180	610
BDE-100	230	760
BDE-153	170	570
BDE-154	180	610
BDE-183	380	1280