RAPID ANALYSIS OF NOVEL AND LEGACY BROMINATED FLAME RETARDANTS IN SOIL

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Introduction

A range of brominated flame retardants (BFRs) have been incorporated into plastics, electronic equipment, foams and textiles. The most common of these, polybrominated diphenyl ethers (PBDEs), have been banned and restricted in a number of countries[1-3] due to their long-range atmospheric transport potential, persistence in the environment, and toxicity.[4] Replacement products known as "novel" brominated flame retardants (NBFRs) share many of the structural and physicochemical properties of PBDEs and have been shown to be subject to similar environmental release and fate.[5]

Gas chromatography coupled to mass spectrometry (GC-MS) has been the most commonly employed instrumental technique for quantifying BFRs in environmental matrices. Traditional methods of BFR sample preparation typically utilize separate extraction and clean-up steps to achieve clean extracts for analysis.[5] These processes have been employed successfully for the extraction of combinations of PBDEs and NBFRs from soil, but can be slow and inefficient. Recently, methods described as "selective" pressurized liquid extraction (S-PLE) have been developed for extraction of analytes with minimal co-extraction of interfering compounds by incorporating chromatographic media into extraction cells.[6-8] S-PLE methods achieve faster and simpler sample preparation as no further clean-up steps are required following extraction.

S-PLE has been shown to be an appropriate technique for the extraction of PBDEs and other established flame retardants from a variety of matrices[9] but has rarely been used to extract NBFRs in combinations of more than two or three. The objective of this study is to develop a sensitive, rapid and accurate method for the simultaneous quantification of PBDEs and NBFRs in environmental soil samples using one-step S-PLE and GC-(EI)-MS/MS.

Materials and methods

Target analytes are listed in Table 1. All S-PLE trials were carried out with a Dionex Accelerated Solvent Extractor (ASE-200) using an oven temperature of 100 ˚C and cell pressure 1500 psi. Samples were heated for 5 min followed by a static time of 5 min, flush volume of 60% and purge time of 120 s. Three cycles were performed on each sample. Various combinations of acetone, hexane and dichloromethane (DCM) were assessed as extraction solvents. A range of adsorbent media were prepared in order to test different clean-up procedures. Adsorbent preparations included activated Florisil, deactivated Florisil (5% w/w H_2O), acid silica (5 and 10% w/w H_2SO_4) and basic silica (20% w/w NaOH).

The test soil for use in spiking experiments (TOC = 19.6 ± 0.2% w/w) was collected from parkland northeast of Melbourne and verified to contain only trace levels of target BFRs. Recovery and repeatability of the optimized method were assessed by repeated analysis of 3 g of test soil spiked with all target analytes at three concentration levels. Five extra samples were collected from industrial and background locations within the Greater Melbourne area to assess the performance of the optimized method on real environmental samples.

All quantitative analyses were performed using an Agilent 7000C gas chromotograph - triple quadrupole mass spectrometer (GC-MS/MS) operated in electron ionization (EI) mode. Injections of 2 µL were executed in pulsed splitless mode and separated on a DB-5MS column (15 m x 180 µm internal diameter, 0.18 µm film thickness).

Results and discussion

A GC-MS/MS acquisition method was successfully developed for the quantitation of all analytes from a single injection with run time of 13.5 min. The response sensitivity of DBDPE was insufficient to quantitate all but the two highest calibration standards and, therefore, spike tests were not assessed for this compound. A 2:1 ratio of acid silica (10% w/w) and activated Florisil proved to be the only combination of adsorbents tested to deliver an acceptably clean extract for use in solvent trials. The optimized cell packing arrangement entailed, from bottom to top, a single cellulose filter, 3 g activated Florisil, 6 g acid silica (10% w/w), 3 g Na_2SO_4, another cellulose filter, 2 g activated copper powder and 3 g soil sample dispersed in 2 g Na_2SO_4 and 1 g of Hydromatrix. Equal parts hexane and DCM (1:1) was found to be the most appropriate combination, delivering clean extracts with adequate analyte recovery (Figure 1, Table 1). BEH-TEBP could not be recovered using DCM proportions less than 80% and was, consequently, excluded from the final method. Good recoveries were observed for most analytes at each of the spiking levels with RSD values generally below 20% (Table 1). MDLs ranged

Table 1. Percentage recovery and percentage relative standard deviation (%RSD) of analytes from optimized S-PLE method validation spikes.

	Low Spike (n=3)		Medium Spike (n=5)		High Spike (n=3)	
Compound	**Recovery**	**RSD**	**Recovery**	**RSD**	**Recovery**	**RSD**
BDE-28	96	2	98	2	98	2
BDE-47	98	4	98	2	99	3
BDE-99	95	11	100	5	101	<1
BDE-100	99	3	97	1	100	1
BDE-153	98	<1	98	1	96	7
BDE-154	116	5	93	2	92	2
BDE-183	53	11	68	3	104	47
BDE-209	N/A	N/A	101	19	91	1
PBT	106	9	93	2	86	2
PBEB	116	11	92	2	88	2
HBB	66	47	95	5	106	3
EH-TBB	N/A	N/A	88	7	91	16
BTBPE	N/A	N/A	110	9	108	2
DBDPE	N/A	N/A	N/A	N/A	N/A	7

N/A= data not available

from 0.01 to 4.8 ng/g dw for PBDEs and 0.01 to 0.55 ng/g dw for NBFRs (excluding BEH-TEBP and DBDPE). PBDEs were detected in all five of the environmental soil samples with BDE-209 recording the highest concentrations (89 to 190 ng/g dw in samples 1-4 and exceeding the upper calibration range of 330 ng/g dw in sample 5). Each of the NBFRs was detected at low levels in at least one of the soil samples, except for EH-TBB.

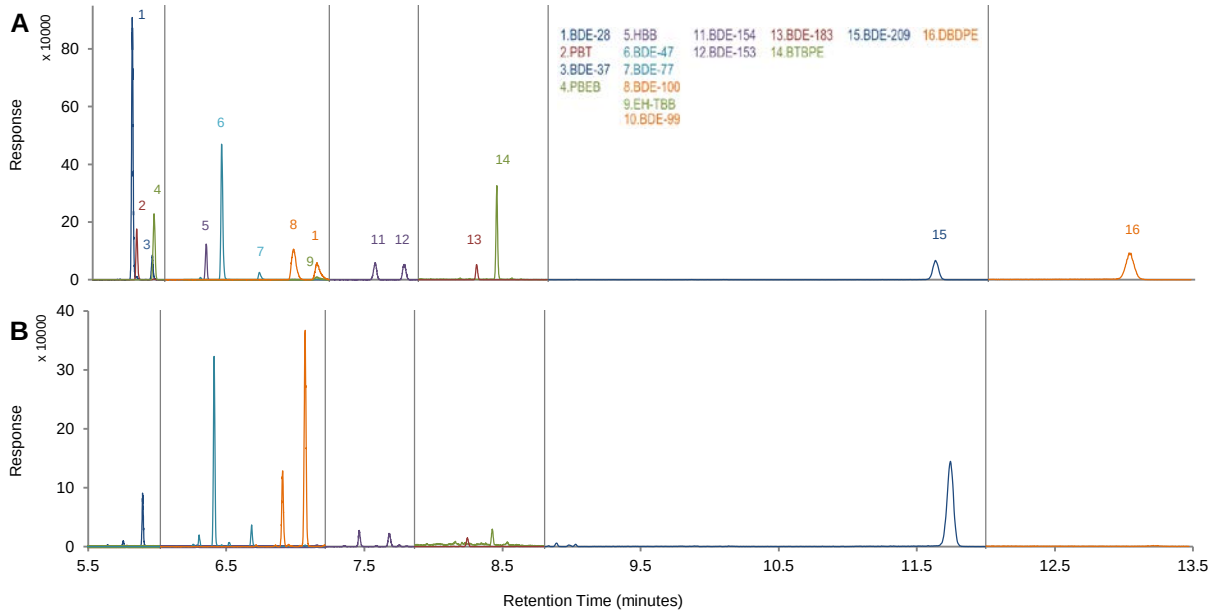

Figure 1. MRM chromatograms of quantitation transitions for target analytes and recovery surrogates in A) spiked soil and B) real environmental soil sample.

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