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Development and Validation of a Multi-residue Method for the Analysis of Brominated and Organophosphate Flame Retardants in Indoor Dust

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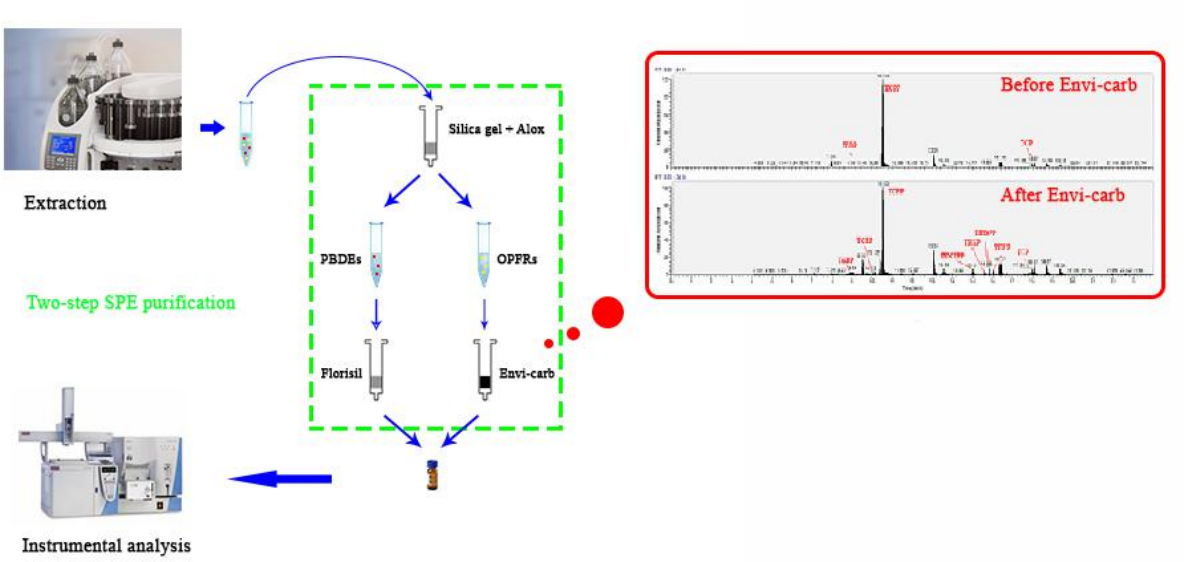
Abstract

Flame retardants are associated to numerous adverse health effects, can accumulate in humans and have been used intensively worldwide. Recently, dust has been identified as a major human exposure route for flame retardants. The aim of this study was to develop a multi-residue method using a two-step SPE purification. It enabled us to effectively limit co-extracted matrix/interferets and therefore a simultaneous analysis of brominated and organophosphate flame retardants for indoor dust was achieved. The optimized method was validated according to standard protocol and achieved good accuracy and reproducibility (percent error ranged from -29 % to 28 %). Standard Reference Material (SRM) for dust was also analysed, and good agreement was found with reported brominated and organophosphate flame retardants (OPFRs) concentrations. The applicability of the validated method was demonstrated by the analysis of ten indoor dust samples from ten Australian homes. Overall 89 % of the analytes were detected in these samples. The average concentrations of ∑OPFRs and ∑PBDEs in those samples were 41 and 3.6 μg/g, respectively. Tris(2-butoxyethyl) phosphate and tris(2-chloroisopropyl) phosphate were the most abundant OPFRs, accounting for 57-92 % ∑OPFRs, while decabromodiphenyl ether dominated the Polybrominated diphenyl ethers (PBDE) congeners contributing between 71-94 % to the ∑PBDEs.

Graphical abstract



Keywords: Polybrominated diphenyl ethers (PBDEs); organophosphate flame retardants (OPFRs); indoor dust; solid phase extraction; GC-MS/MS; Envi-Carb SPE.

1 Introduction

Flame retardants are widely used industrial chemicals that are added in plastics, textiles and electronic circuitry to meet flammability standards worldwide [1]. Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs) have been widely used for decades. However, concerns regarding the bioaccumulation in human tissues and potential adverse health effects of PBDEs have resulted in their phase-out in some countries, leading to an increase in the production and use of alternative flame retardants, including OPFRs [2, 3]. Global demand for flame retardants is projected to increase by 4.6 % per year until 2018 to reach a volume of 2.8 million tonnes [4]. The OPFRs account for 20 % of total flame retardant usage in Europe [2], and are expected to have the fastest market gains by 2018 [5].

Both BFRs and OPFRs have been detected in various environmental matrices [6, 7]. High detection frequencies and high concentrations of both BFRs and OPFRs were reported in indoor dust which is an important route of exposure, especially for children, since their more frequent hand-to-mouth contact and close-to-ground behaviour could lead to higher amount of dust ingestion, and their lower body weigh results in a higher daily exposure [8]. This has led to an increased interest in levels and distributions of BFRs and OPFRs in indoor dust [9-12]. Thus, a method capable of simultaneously analysing OPFRs and BFRs in dust is required.

Typically, PBDEs and OPFRs are analysed using separate methods. For PBDEs determination, dusts are commonly extracted using Soxhlet apparatus, ultra-sonication, accelerated solvent extraction (ASE) or microwave-assisted extraction (MAE), and purified by sorbents, such as silica gel, alumina or florisil, before instrumental analysis by gas chromatography-mass spectrometry (GC-MS) [13]. For example, Harrad et al. [14] presented a method for 8 PBDEs in dust using ASE extraction, florisil purification, and GC-EI-MS analysis, where they reported method detection limits (MDLs) around 0.03 ng/g. Similarly methods for OPFRs analysis include ultra-sonication [15, 16] or Soxhlet extraction [17, 18], purification steps using solid phase extraction (SPE) [16, 19, 20], and GC-MS [21] or liquid chromatography-mass spectrometry (LC-MS) [19]. For example, a method involving an ultra-sonication and vortex extraction, florisil clean-up and GC-MS analysis was developed by Van den Eede et al. [16], which provided low MDLs for 10 OPFRs (20-500 ng/g).

Recently several multi-residue methods combining PBDEs and OPFRs, and some typical analytical methods for OPFRs are summarized in Table S1. Van den Eede [22] reported an ultrasonic extraction coupled with a two-stage SPE clean-up method for simultaneous analysis of PBDEs and OPFRs. The first fraction was then purified by a 44% acidified silica cartridge with no further clean-up for the latter fraction, which was analysed by GC-MS directly. The limits of quantitation (LOQs) were 0.04-17 ng/g for PBDEs, and 10-370 ng/g for OPFRs. In most proposed methods, many matrix interferents were co-extracted and co-eluted along with PBDEs and OPFRs due to the inherent complexity of dust, even after an additional pre-cleanup by florisil [23-25]. Such interferences could possibly lead to an increase in the background in the mass spectrum, decrease instrumental selectivity and sensitivity, and in addition contaminate the GC system. To avoid such issues, some studies report dilution of the OPFR fraction, which consequently decreased the limits of detection (LODs) for most of the compounds of interest [26, 27]..

Therefore, this study aimed to develop a multi-residue method for an efficient and reliable extraction, purification and the simultaneous analysis of 8 PBDEs and 11 OPFRs using GC-MS techniques. The optimisation of the purification of the dust extracts was assessed by testing 5 solid phase extraction adsorbents. The determination of OPFRs and most PBDEs was performed by gas chromatography triple quadrupole mass spectrometry (GC-QqQ-MS/MS) and BDE 209 was determined by gas chromatography mass spectrometry. The method was fully validated through the evaluation of recoveries, linearity, LOD & LOQ, and precision. Method accuracy and applicability was tested for a SRM (SRM 2585) and real dust

samples collected from Australian indoor environments. Our study for the first time reports the extraction and clean-up for the simultaneous analysis of OPFRs and PBDEs, which also meets the clean-up requirement for GC-MS.

2 Materials and methods

2.1 Chemicals

A mixed solution of PBDE congeners (BDE 28, 47, 99, 100, 153, 154, 183, and 209) was purchased from AccuStandard Inc (New Heaven, CT, USA). Tris(2-chloroethyl) phosphate (TCEP), tris(1,3-dichloroisopropyl) phosphate (TDCIPP), tripropyl phosphate (TPrP), tri-n-butyl phosphate (TnBP), tri-iso-butyl phosphate (TiBP), tris(2-ethylhexyl) phosphate (TEHP), tris (2-butoxyehyl) phosphate (TBEP), triphenyl phosphate (TPhP), tri-cresyl phosphate (TCP) standards were purchased from Sigma Aldrich (St Louis, MO, USA), tris(2-chloroisopropyl) phosphate (TCPP) were purchased from Dr. Ehrenstorfer (Augsburg, Germany), 2-ethylhexyl diphenyl phosphate (EHDPP) were purchased from AccuStandard. ^{13}C-PBDE mixture solution and ^{13}C-BDE 209 were purchased from Wellington Laboratories Inc (Guelph, ON, Canada), TCPP-d18, TnBP-d27 and TPhP-d15 were purchased from Cambridge Isotope laboratories, Inc (Andover, MA, USA).

Strata™ empty SPE tube (12 cc), Strata™ W-AX (100 mg/3 mL) and Strata™ FL-PR (500 mg/3 mL) cartridges were obtained from Phenomenex (Torrance, CA, USA), Oasis® HLB (6 cc, 1500 mg) and Supleclean™ Envi-Carb (0.25 g/3 mL) were obtained from Waters (Milford, MA, USA) and Supleco (Bellefonte, PA, USA), respectively. Dust SRM 2585 (Organic Contaminants in House Dust) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). All solvents were of liquid/gas chromatography grade. Acetone, *n*-hexane, dichloromethane (DCM) were purchased from Merck (Darmstadt, Germany), while ethyl acetate (EtAc) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Ultra-pure water was obtained from a Milli-Q filtration unit (Merck Millipore, MA, USA). Hydromatrix was purchased from Agilent Technologies (Santa Clara, CA, USA). Silica gel (40 – 63 μm, Sigma Aldrich) and alumina (150 mesh, Sigma Aldrich) were activated (at 140 ºC and 180 ºC, respectively) and deactivate (with 3 % and 6 % Milli-Q water, respectively) before use. Sodium sulphate anhydrous (AR grade, Fisher Scientific) was baked at 400 ºC, and then stored in desiccator.

2.2 Standards and Internal standards

Stock individual solutions (>100 ng/μL) of OPFRs and PBDEs were prepared in methanol and toluene, respectively, and stored at -20 ºC in amber glass vials. Working solutions of native OPFR (1 ng/ μL) and PBDE (500 pg/μL for BDE 209, and 50 pg/μL for other congeners) were prepared in methanol and isooctane respectively. Internal standards (100 pg/μL) were prepared from isotopically-labelled compounds in the same solvents of native standards. Working standards were stored at 4 ºC in amber glass vials. Carbon-13 labelled PBDE congeners were used for PBDE quantification, while deuterated TnBP, TCPP, and TPhP were used for all OPFRs. Internal standard used for each compound was given in Table S2.

2.3 Dust sampling

Dust samples were collected in Brisbane Australia, from January to March 2015, using a clean nylon sampling sock that was inserted into the entry hose of a vacuum cleaner. Dust was vacuumed typically along the edges of walls where it naturally gathers. The dust from living areas, and bedroom areas was combined into a single sample to gain an overall dust profile of the investigated home. The sampling sock was sealed in a zip lock bag. The dust samples were sieved using a pre-cleaned 1 mm mesh sieve to remove larger particles and to ensure the homogeneity of the sample. For this project, all the samples have been collected with ethics approval from University of Queensland (approval number: 2015000153).

House dust from a private house was collected to generate quality control samples. The dust was spiked with native chemicals at two different levels, to create a low-concentration (QCL) (10 μg/g for TBEP, 1 μg/g for other OPFRs, 5 μg/g for BDE 209, and 0.5 μg/g for other PBDEs) and high-concentration (QCH) samples (50 μg/g for TBEP, 5 μg/g for other OPFRs, 25 μg/g for BDE 209, and 2.5 μg/g for PBDEs).

2.4 Optimized sample preparation

Optimized sample preparation is shown in Fig 1. Weighed dust samples (100 mg) were placed into 33 mL ASE cells and spiked with internal standards (1 ng $^{13}C_{12}$-PBDE mixture, 30 ng $^{13}C_{12}$-BDE 209, 10 ng TCPP-d18, 10 ng TPhP-d15 and TnBP-d27). Samples were extracted using *n*-hexane and acetone (1:1, v:v) on a Thermo Scientific™ Dionex™ ASE™ 350 system. The ASE program parameters were: temperature 100 °C, pressure 1500 psi, 3 static cycles of 5 min, flush volume 60 % and purge time 120 s. The extracts were blown

down to 1 ml before purification on a self-packed silica gel and alumina cartridge (containing, from bottom to top, frit, deactivated neutral alumina 3.0 g, deactivated neutral silica gel 2.5 g, and Na_2SO_4 2.0 g, frit). The adsorbents were conditioned with 20 mL *n*-hexane:DCM mixture (1:1, v:v), EtAc 20 mL and then 50 mL *n*-hexane and DCM mixture, respectively. Once the samples were quantitatively transferred to the column, *n*-hexane and DCM mixture was added. The first 4 mL eluent was discarded, and the following 42 mL was collected into Fraction 1 (F1). Finally, the column was eluted with 24 mL EtAc and collected into Fraction 2 (F2). The F1 was purified on a Strata™ FL-PR cartridge (conditioned with 20 mL *n*-hexane:DCM, and eluted using 10 mL *n*-hexane:DCM). An Envi-Carb cartridge was applied for a further clean-up of F2, with conditioning and eluting by 50 mL and 42 mL EtAc, respectively. The cleaned F1 and F2 were then combined and concentrated to near dryness using a gentle stream of nitrogen. The residues were then reconstituted with 50 μL of instrument standards (10 ng $^{13}C_{12}$-BDE 77 in isooctane).

Figure 1 Optimized procedurals of sample preparation for PBDE and OPFR analysis

To select the optimal sample preparation conditions, the clean-up efficiency and the recoveries of the targeted chemicals were evaluated for different solid phase sorbents. A discussion of these results is provided in section 3.2.

2.5 Instrumental method

All compounds were analysed using a TSQ Quantum GC (Thermo Fisher Scientific) system coupled with triple quadrupole mass spectrometer Quantum (QqQ) and a TRACE GC Ultra equipped with a TriPlus autosampler, except for BDE 209, which was analysed on a Shimadzu QP2010 gas chromatography mass spectrometer (GC-2010 coupled with a GCMS QP-2010).

2.5.1 GC-QqQ-MS/MS

A DB-5MS column (30 m × 0.25 mm i.d.; 0.25 μm film thickness, J&W Scientific) was used for separation in the GC. The oven temperature was programmed as follows: initial temperature was 80 °C for 2 min and increased to 180 °C at 20 °C·min^{-1} and held for 0.5 min, then to 300 °C at 10 °C·min^{-1} and held at this temperature for 5 min. The total run time was 25 min at constant flow rate of 1.0 mL·min^{-1}. The programmed temperature vaporization (PTV) injector temperature was held at 80°C during injection for 0.1 min, then ramped at 14.5 °C·s^{-1} to 200 °C and held for 1 min. The volume injected was 1.0 μ L, in splitless mode.

The QqQ mass spectrometer was operated in electron ionization (EI) mode using the multiple reactions monitoring (MRM) mode with an emission current set at 20 μA. The transfer line and ionization source temperatures were set at 280 °C and 270 °C, respectively. The collision gas pressure was set at 1.5 mTorr and the cycle time was set to 0.4 s. Q1 peak width (FWHM) was set to 0.7 amu. MRM transitions, collision energy for each transition, and average retention times (RTs) are presented in Table S1 in supplementary material.

2.5.2 GCMS-QP2010

An Agilent DB-5MS column (10 m × 0.25 mm i.d.; 0.25 μm film thickness) was used for BDE 209 analysis. The oven temperature was programmed as follows: the initial temperature was 100 °C for 1 min and increased to 190 °C at 20 °C·min^{-1} and held for 1.5 min, then to 280 °C at 20 °C·min^{-1} and held at this temperature for 2 min. The volume injected was 1.0 μL, in splitless mode, and temperature for injector was 270 °C. Negative chemical ionization (NCI) was used for MS, and temperatures for ion source and interface are both 270 °C. Mass to charge ratios (*m/z)* of 484.6 and 486.6 were used for BDE 209 quantification, while 494.6 and 496.6 were used for ^{13}C-BDE 209.

2.6 Validation procedure

The optimized method was validated for recovery, linearity, limit of quantification, precision and accuracy [28]. Basically, recovery was determined using the QCL and QCH spiked samples, by comparing the analytical results to unextracted standards spiked sample (same concentration of native and internal standards with QCL and QCH were spiked into solvent directly, without any extraction or purification procedural) that would represent 100 % recovery. Linearity range was checked with spiking a serial amount of targeted chemicals into blank solvent by 9 concentrations, with linear over the entire range studied (listed in Table 2). The LOD was defined as the average procedural blank concentrations (μg/g) plus three times its standard deviation (SD), whilst the LOQ was blank concentration (μg/g) plus ten times its SD. LODs were considered as the lowest concentration that produced a peak signal ten times the background noise from the chromatograms if chemicals were not found in blank samples. Precision was expressed as relative standard deviation percentage (RSD, %), and was evaluated by intra-day and inter-day variability for QC samples. Intra-day precision was assessed by analysing 3X dust samples in the same day, while the inter-day precision was assessed over 5 days. The accuracy was calculated as the differences of the determined value to the spiked values.

3 Results and discussion

3.1 Instrument optimization in GC-QqQ-MS/MS

Instrument method was optimized basing on a previous method [29]. Chromatographic injection and separation conditions were first optimized to maximize signal to noise ratios. Temperature-programmed pulsed splitless injection in a PTV injector was selected as it was suggested to be the best injection method for PBDE analysis, and has also been applied to OPFR analysis [30]. Initial temperature, splitless time and pulse time were optimized to obtain the highest responses for all compounds. The optimization of the MS/MS method consisted of 1) acquisition of respective MS spectra in full scan mode, 2) selection and fragmentation of appropriate precursor ions, 3) product ion scans at different collisions energies of 5, 10, 15, 20, 25 and 30 eV to obtain the best product ion transition signal and different dwell time of 5, 15, 25 and 35 mins to provide a good peak shape, and 4) further fine tuning of collision energies and dwell time in selected reaction monitoring mode [31]. Optimized conditions were listed in Table S1.

3.2 Sample preparation optimization

Ultra-sonication and accelerated solvent extraction were both used for OPFRs with similar recovery [16]. However, ultra-sonication has not been used widely for BFRs because of lower extraction recoveries [13]. Therefore, accelerated solvent extraction was used in this study to achieve good recovery for both groups of chemicals.

As a result of the different properties of PBDEs and OPFRs, a clean-up can be hardly achieved using a single cartridge [25]. Covaci et al. [13] suggested that silica gel, alumina or florisil could be used for dust clean-up, and had achieved high recoveries for PBDEs. Some sorbents, including florisil, alumina, silica gel, and some commercial cartridges, such as Oasis® HLB and Strata™ W-AX, have also been used for OPFR purification [16, 19, 32-34]. To find the optimal sorbents for clean-up, we investigated several SPE cartridges, which were self-packed silica gel and alumina cartridge, Oasis® HLB, Strata™ W-AX, Strata™ FL-PR, Supleclean™ Envi-Carb.

These cartridges were firstly investigated for their capacity to separate OPFRs from PBDEs so they can be eluted and further purified in separate fractions. Loaded into each sorbent, chemicals were eluted and separated into two fractions, where PBDEs were firstly eluted by non-polar solvent, and OPFRs were in the later fraction eluted by polar solvent. Their

concentrations in both fractions were then measured separately. A clear separation was only found from silica gel and alumina cartridges. A similar result was found by Ionas and Covaci [25]. Hence, silica gel and alumina cartridge was used for OPFRs and PBDEs separation in this study. Both fractions, in most cases, were colourful and dark, especially the later fraction, showing that the increase of solvent polarity increased the amount of co-extractives matrix [35], and a further clean-up step was needed.

A wide range of sorbents have been previously used for purification of PBDEs in extracts from dust, among which, florisil is one of the most commonly used with typically high recoveries, and less interference from co-extracted chemical residues. We found that extracts were still dark coloured after further purification on either Oasis® HLB or Strata™ W-AX, suggesting their lower efficiency for purification of PBDEs. In contrast, a clean-up of the extract using Supleclean™ Envi-Carb yielded clear extracts but low recoveries for PBDEs. Thus, florisil was applied for PBDE clean-up in our study.

Clean-up efficiency for OPFRs fractions was tested for all sorbents listed in Table 1. Colourless extracts with good recoveries of the analytes of interest were only achieved using Envi-Carb cartridges. A comparison of the dirtiness of the concentrated extracts from the different SPE cartridges is illustrated in Fig. S1. Recoveries of the OPFRs of interest after purification on Envi-Carb were in the range of 78-126 % (see Section 3.3). Overall we found that Envi-Carb cartridges had a high selectivity for OPFRs and provided good recoveries. Even for samples where the first purification step on the mixed silica gel and alumina column yielded an apparently clear (transparent) OPFR fraction, the further purification step using the Envi-Carb clean up significantly enhanced the chromatography including the signal to noise of the compounds of interest (Fig 2). Thus, Supleclean™ Envi-Carb cartridges were chosen in our study for the latter fraction clean-up.

Table 1. Fitness for purpose of different sorbent types tested in this study

	Recovery (n=6) [a] (%)	LOD (ng/g)	LOR (ng/g)	Calibration range (ng/g)	R^2	Intra-day (n=3) [a]				Inter-day (n=3) [a]	
						QCL		QCH		QCL	QCH
						RSD (%)	Accu (%)	RSD (%)	Accu (%)	RSD (%)	RSD (%)
OPFRs											
TCEP	81±18	5.4	12	0.1-25000	0.999	1.0	15	12	8.4	6.3	20
TCPP	109±9.3	450	1000	0.1-500000	0.997	3.2	5.5	9.3	-3.0	28	10
TDCPP	88±7.5	380	520	0.1-25000	0.999	3.8	8.9	7.4	4.7	3.5	9.3
TPrP	79±8.5	2.2	6.2	0.1-25000	0.997	2.0	13	8.4	8.5	5.6	9.6
TiBP	105±12	23	38	0.1-500000	0.999	9.4	9.5	7.2	6.6	9.9	9.5

	Recovery (n=6) [a] (%)	LOD (ng/g)	LOR (ng/g)	Calibration range (ng/g)	R^2	Intra-day (n=3) [a]				Inter-day (n=3) [a]	
						QCL		QCH		QCL	QCH
						RSD (%)	Accu (%)	RSD (%)	Accu (%)	RSD (%)	RSD (%)
TnBP	94±6.5	110	160	0.1-500000	1.000	1.4	23	5.3	3.7	27	13
TEHP	78±12	200	420	0.1-25000	0.998	3.8	-6.0	10	5.1	16	12
TBEP	126±41	20	35	0.1-500000	0.998	2.9	10	10	-1.9	2.7	7.9
TPhP	107±8.7	13	25	0.1-25000	1.000	5.0	-1.0	6.6	4.4	7.2	4.0
TCP	116±6.0	8.6	14	0.1-25000	0.998	3.5	-17	12	2.5	14	11
EHDPP	83±9.8	54	120	0.1-25000	0.999	4.5	23	4.1	-6.2	14	4.5
PBDEs											
BDE 28	96±7.8	0.20	0.58	0.1-1000	1.000	8.5	17	13	19	30	15
BDE 47	98±2.4	3.3	8.7	0.1-1000	0.999	1.5	-7.9	7.8	7.8	23	4.9
BDE 99	106±15	1.6	3.6	0.1-1000	0.998	2.8	-9.2	9.6	16	26	4.4
BDE 100	108±1.8	1.5	4.2	0.1-1000	0.999	3.3	6.9	9.7	29	15	4.9
BDE 153	82±7.6	0.050	0.14	0.1-1000	0.999	1.6	10	13	27	24	3.3
BDE 154	88±13	2.7	3.1	0.1-1000	0.998	3.8	8.9	8.7	12	10	1.9
BDE 183	124±15	0.30	0.81	0.1-1000	0.999	3.1	-10	31	2.2	12	17
BDE 209	87±9.0	1000	1100	1-10000	0.999	15	-29	3.9	12	21	8.7

a: n indicates the number of analysed samples

Figure 2. TIC Comparison for OPFRs fraction where both A and B were fractionated by silica gel/alumina cartridge, and A was further purified using an Envi-Carb cartridge

3.3 Method performance

After the optimization of sample preparation, the method was validated to prove its reliability and consistency for the identification and quantification of the targeted chemicals. The validation results were obtained from dust QC at two spiking levels (QCL and QCH), and procedural blank samples, and are presented in Table 2.

3.3.1 Recoveries

Recoveries were calculated through comparing the results from the spiked dust samples with those of unextracted standard solution (considered as 100 % recovery) both using high and low spike concentration subtracting the amount found in the (un-spiked) QC sample. As shown in Table 2, all investigated compounds have recoveries between 78 and 126 %. With only one exception, recoveries had less than 20 % standard deviation indicating the good precision of this method.

Table 2 Summary of method performance results

	Present study (n=3)		Certified/ Indicative values		Percent Error (%)
	Mean (µg/g)	SD (µg/g)	Mean (µg/g)	SD (µg/g)	
OPFRs					
TCEP	0.55	0.11	0.79 [a]	0.12	-28
TCPP	1.0	0.20	0.94 [a]	0.26	6.4
TDCPP	1.5	0.24	1.6 [a]	0.53	-3.6

	Present study (n=3)		Certified/ Indicative values		Percent Error
	Mean (μg/g)	SD (μg/g)	Mean (μg/g)	SD (μg/g)	(%)
TPrP	0.010	0.0041		-	-
TiBP	<0.03	-	0.017 [a]	0.015	-
TnBP	0.14	0.020	0.27 [a]	0.019	-44
TEHP	<0.45	-	0.27 [a]	0.11	-
TBEP	63	15	73 [a]	32	14
TPhP	0.87	0.070	1.1 [a]	0.099	-20
TCP	0.95	0.13	0.84 [a]	0.24	-13
EHDPP	1.3	0.17	0.96 [a]	0.20	-24
PBDEs					
BDE 28	0.035	0.0060	0.047 [b]	0.044	-26
BDE 47	0.47	0.029	0.50 [b]	0.046	-6.4
BDE 99	0.66	0.084	0.89 [b]	0.053	-26
BDE 100	0.13	0.020	0.15 [b]	0.011	-16
BDE 153	0.10	0.032	0.12 [b]	0.0010	-15
BDE 154	0.060	0.046	0.084 [b]	0.0020	-29
BDE 183	0.036	0.0057	0.043 [b]	0.0035	-16
BDE 209	3.2	0.20	2.5 [b]	0.19	28

[a]: Brandsma et al. 2013 [36]

[b]: NIST, 2006 [37]

3.3.2 Linearity

Calibration curves covered the entire range of concentration in real dust samples in this study, which is shown in Table 2. The method showed a linear response with determination coefficient (R^2) higher than 0.995 in all cases.

3.3.3 Limits of detection/quantification

Defined as the average procedural blank concentrations plus three times its SD, LODs for the analytes were in the range of 0.20-1000 ng/g depending on the specific compound of interest. LOQs were determined from the blank concentration plus ten times SD, which were 0.14-1100 ng/g for all compounds (shown in Table 2).

3.3.4 Precision

Intra-day precision was assessed by analysing replicate samples on the same day, while the inter-day precision was assessed over 3 days. RSD for intra- and inter-day were between 1.0-31 %, and 1.9-30 %, respectively (shown in Table 3). As shown in Table 2, there was overall good agreement between spiked and measured concentration where all data were within ± 30 % of the certified or Indicative values of the SRM. These values showed good accuracy and reproducibility of the method.

3.3.5 Quality control

Procedural blank samples were included as part of the quality control. Briefly, previously cleaned hydromatrix was spiked with internal standards, and extracted and cleaned as the same process

described above. Two procedural blank samples were analysed in each batch of samples. Blank correction was conducted when > 5% concentration was found in blank samples.

3.4 Application to real dust samples

3.4.1 Dust SRM 2585

In order to demonstrate the efficiency and accuracy of this method, dust SRM samples were analysed. Measured OPFR and PBDE concentrations together with reference concentrations were both shown in Table 3. The differences to certified PBDE concentrations ranged from -29 % to 28 %. Although there was no certified data available for OPFR concentrations in SRM 2585 we are able to compare our results with several studies that also analysed this SRM. Our result showed good agreement with most studies [15, 16, 25].

Table 3 Measured and reference concentrations of selected OPFRs and PBDEs in dust SRM

		TCEP	TCPP	TDCPP	TPrP	TiBP	TnBP	TEHP	TBEP	TPhP	TCP	EHDPP	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
Fan et al [15]	LOQ ng/g	230	350	280	680	1320	230	n.a.	1430	420	120	550	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Accuracy [a] %	92	94	102	90	79	83	n.a.	14	12	5.7	15	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Precision (RSD, %)	8.3	11	7.9	18	16	14	n.a.	88	104	112	60	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
van den Eede et al [16]	LOQ ng/g	80	20	80	20	500	30	n.a.	60	70	40	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Accuracy [a] %	101	97	116	52	119	82	n.a.	98	101	107	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Precision (RSD, %)	6	3	9	9	28	3	n.a.	12	4	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
van den Eede et al[22]	LOQ ng/g	110	10	10	50	370	10	n.a.	50	10	40	n.a.	0.04	0.13	0.18	0.24	0.18	0.71	1.6	17
	Accuracy [a] %	142	103	125	109	81	93	n.a.	235	111	124	n.a.	98	98	91	113	104	102	103	99
	Precision (RSD, %)	6	3	8	13	315	4	n.a.	13	10	7	n.a.	2	2	10	1	2	1	5	2
Ionas et al [25]	LOQ ng/g	n.r.	n.r.	n.r.	n.a.	n.a.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
	Accuracy [b] %	104	127	115	n.a.	n.a.	65	137	81	83	138	95	74	78	76	76	76	83	58	99
	Precision (RSD, %)	4	7	5	n.a.	n.a.	9	51	1	4	34	2	6	9	13	13	13	9	8	20
Cristale et al [27]	LOQ ng/g	79	31.4	3.8	n.a.	44	77	5.4	288	5.4	9.1	27.7	4.3	2.1	5	5.3	2.3	2	4.4	275
	Accuracy [a] %	n.c.	n.c.	113	n.a.	112	13	117	n.c.	n.c.	n.c.	141	82	104	121	89.8	105	89	129	n.c.
	Precision (RSD, %)	n.c.	n.c.	35	n.a.	35	32	33	n.c.	n.c.	n.c.	2.2	1	1	4	0.2	6	3	11	n.c.
This study	LOQ ng/g	12	1000	520	6.2	38	160	200	20	13	8.6	54	0.20	3.3	1.6	1.5	0.050	2.7	0.30	1000
	Accuracy [a] %	115	106	109	113	110	123	94	110	99	83	123	117	92	91	107	110	109	90	71
	Precision (RSD, %)	1	3.2	3.8	2	9.4	1.4	3.8	2.9	5	3.5	4.5	8.5	1.5	2.8	3.3	1.6	3.8	3.1	15

n.a.= not applicable; n.r.=not reported; n.c.=not calculated (due to high concentrations in QC samples)

[a]: accuracy was described by the difference of calculated concentrations to (low) spiked concentrations;

[b]:accuracy was described by the difference of calculated SRM concentrations to indicated/certified concentrations.

3.4.2 Australian indoor dust

We applied the newly validated method to 10 real dust samples to assess its applicability. Fig 3 and Table S3 summarised the concentrations of OPFRs and PBDEs in Australian dust.

Figure 3 Concentrations of OPFRs and PBDEs in Australian indoor dust

TCEP, TCPP, TDCPP, TBEP, TPhP, TCP, EHDPP, BED 47, BDE 99, BDE 153, and BDE209 were detected in all samples, while TiBP, TnBP, BDE 100, and BDE 183 were detected in most samples. TPrP, TEHP, BDE 28 and BDE 154 had lower detection frequencies. TBEP and TCPP were the dominant OPFRs in all samples, with mean concentrations of 20 μg/g and 14 μg/g, respectively. BDE 209 had the highest concentration among all PBDE congeners (mean concentration of 3.4 μg/g). Our results showed a good agreement with both OPFR and PBDE concentrations previously reported in Australian indoor dust [36, 37]. Compared with the concentrations found in other countries, OPFR concentrations here were lower than those in Germany [12], but comparable with those in Netherlands [38], Canada and Kazakhstan [36]. PBDE concentrations in this study were lower than those of the USA [39], but were similar to UK concentrations [40].

4 Conclusions

In this study, we have developed an analytical method for dust that proved to be suitable for 11 OPFRs and 8 PBDEs. Our new purification approach significantly enhanced the sensitivity of the instrument and consequently lowered the LODs of the method. Recoveries for all interested chemicals ranged from 78-126 %; LODs were 0.20-1000 ng/g; and differences of determined concentrations to spiked concentrations were -29-30 %, suggesting the good accuracy and reproducibility of this method. The method was then applied to dust SRM and real dust samples, where a good agreement with certified or indicative results was found. In Australian indoor dust samples, TBEP, TCPP were the dominant chemicals in all samples, with the mean concentrations of 20 μg/g and14 μg/g, respectively.

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Highlights

- PBDEs and OPFRs were analysed in dust samples by one injection only, except for BDE 209.
- The most efficient sorbent for OPFRs purification was found to be Envi-Carb cartridge.
- LORs were 6.2-1000 ng/g and 0.14 -1100 ng/g for OPFRs and PBDEs, respectively.
- Validation studies showed the good accuracy and reproducibility of the method.
- SRM and real dust samples were analysed, with >50 detection frequency for most compounds.

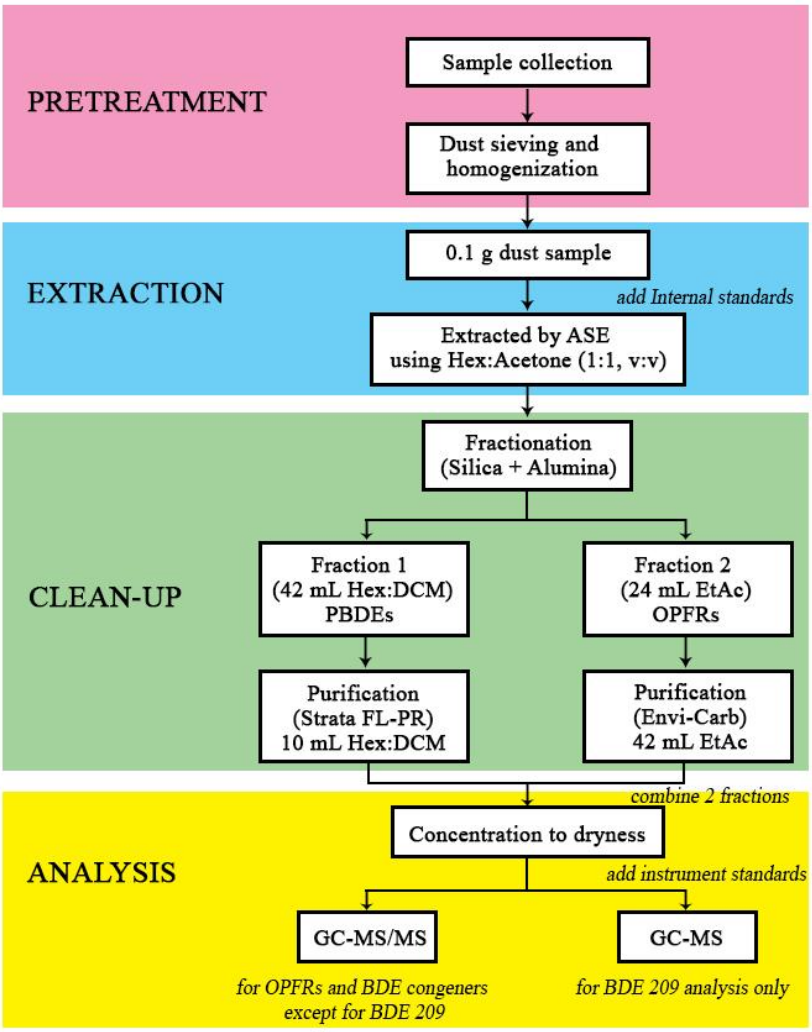

Figure 1 Optimized procedurals of sample preparation for PBDE and OPFR analysis

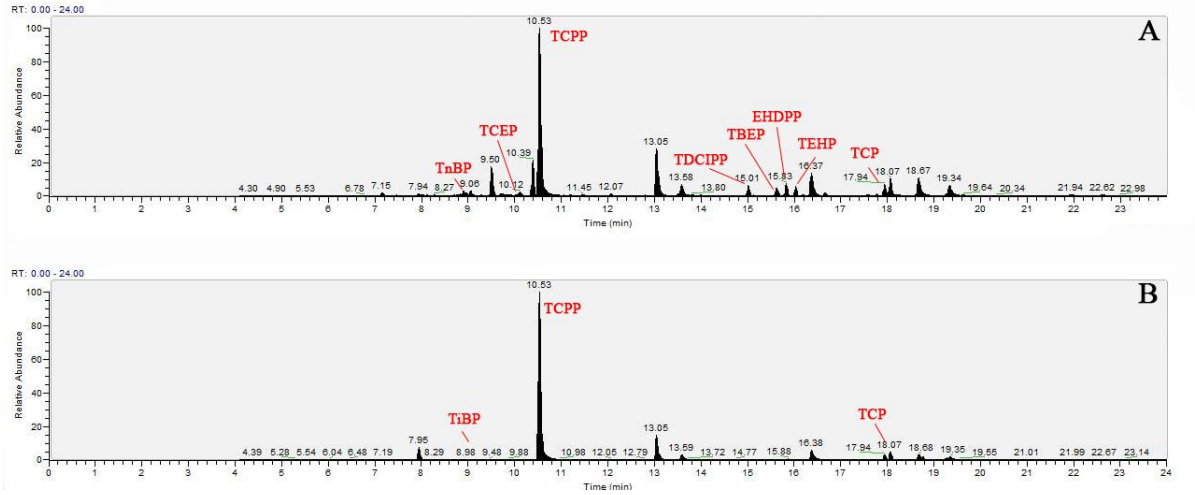

Figure 2. TIC Comparison for OPFRs fraction where both A and B were fractionated by silica gel/alumina cartridge, and A was further purified using an Envi-Carb cartridge

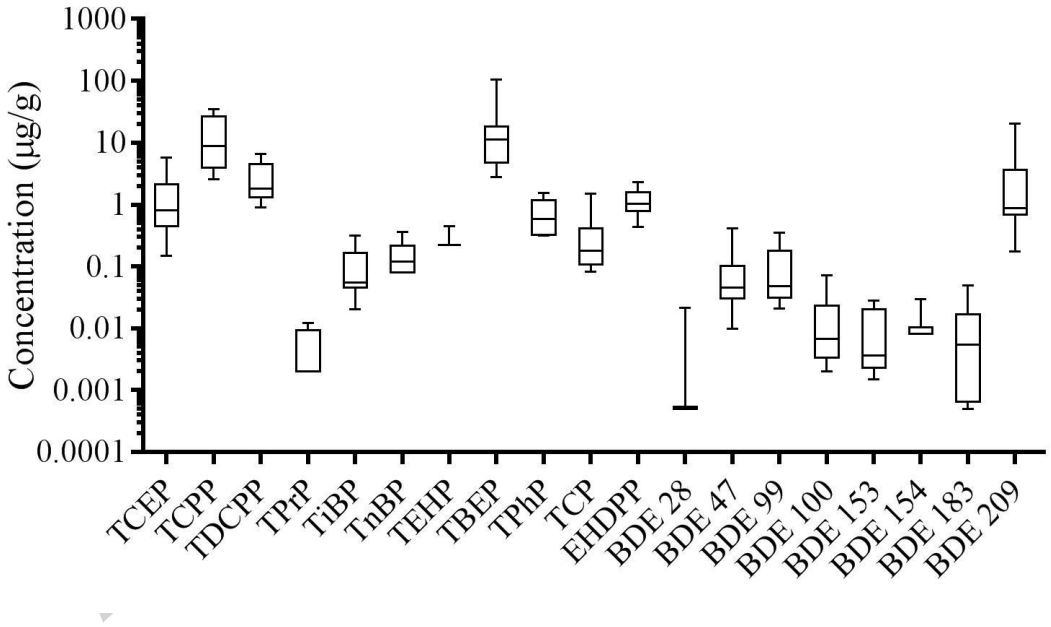

Figure 3 Concentrations of OPFRs and PBDEs in Australian indoor dust