

MULTI-RESIDUE METHOD FOR THE DETERMINATION OF FLAME RETARDANTS IN INDOOR DUST

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Introduction

Flame retardants (FRs) such as polybrominated diphenyl ethers (PBDEs) have been used for years as additives to reduce the flammability of furniture, electronics, foams, building materials, vehicles, textiles etc. Recent bans and restrictions in use of PBDEs^{1,2} have led to the increased use of alternative FRs such as novel brominated FRs (NBFRs) and organophosphate compounds (OPs). Although it remains important to monitor the presence of PBDEs in household dust, the demand for information concerning the presence of alternative FRs in indoor environments increases. A problem encountered until now is that analysis for two or more groups of compounds has to be done separately, which requires a lot of sample and time. Moreover, many developed extraction procedures are based on Soxhlet extraction requiring high solvent volumes and sometimes sample amounts of one or more grams³⁻⁵. Often destructive clean-up methods are used early in the procedure, limiting the number of groups of compounds which can be analyzed. The principal aim of this study was to develop and validate a simple sample preparation method for the determination of PBDEs, and emerging FRs, such as OPs and NBFRs in indoor dust. This procedure also addresses other issues of practical concern, namely a shorter extraction time, a small amount of sample and reduced consumption of solvents, resulting also in lower costs for analysis. The analysis of purified extracts was performed with gas chromatography coupled to electron impact and electron capture negative ionization mass spectrometry using established separation and detection methods⁶⁻⁸. The method was applied to an indoor dust standard reference material (SRM 2585) which is certified for PBDEs.

Materials and methods

Materials. *n*-Hexane (Hex) was purchased from Acros Organics (Geel, Belgium). Acetone (Ac), dichloromethane (DCM), ethyl acetate (EA), and *iso*-octane were purchased from Merck (Darmstadt, Germany). All solvents used during analysis were of analytical grade. Standards of BDE 28, 47, 99, 100, 153, 154, 183 and 209, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE), Hexachlorocyclopenta-dienyldibromocyclooctane (HCDBCO), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH) and labeled internal standard ¹³C-BDE 209 were purchased from Wellington Laboratories (Guelph, ON, Canada). Internal standards (IS) BDE 77 and 128 were obtained from AccuStandard Inc. (New Haven, CT, USA). Standards of triethyl phosphate (TEP), tri-*n*-propyl phosphate (TnPP), tri-*iso*-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), triphenyl phosphate (TPP), tris(2-chloroethyl) phosphate (TCEP), tricresyl phosphate (TCP, (mixture of 4 isomers), and tris(1,3-dichloropropyl) phosphate (TDCPP, (mixture of 2 isomers) were purchased from Chiron AS (Trondheim, Norway). Triamyl phosphate (TAP; IS) was purchased from TCI Europe (Zwijndrecht, Belgium). Labeled TPP-d₁₅ (IS) and tris(2-butoxyethyl) phosphate (TBEP) were purchased from Sigma Aldrich. Tris(1-chloro,-2-propyl) phosphate (TCPP, mixture of 3 isomers) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Purity of analytical standards was >98%, except for TBEP (>94%).

SRM 2584 and 2585 were purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3mL Supelclean™ ENVI™ Florisil® cartridges were purchased from Supelco (Bellefonte, PA, USA). Silica gel, anhydrous sodium sulfate (Na₂SO₄), and concentrated sulfuric acid (H₂SO₄, 98%) was purchased from Merck.

Sample preparation. The method was based on existing methods for OPs⁶ and for NBFRs⁷. Initial tests for fractionation and clean-up were performed by spiking 1g of acid silica (44%, w/w) and Florisil with standard solutions. Ultrasonic extraction was tested with two solvents, namely DCM and Hex-Ac (3:1, v/v), on three replicas of SRM 2584.

Dust was spiked with IS and extracted using three times 2 mL of hexane-acetone (3:1, v/v). Extraction was based on a combination of vortexing and ultrasonication, which was done for 1 min and 5 min, respectively, two times per extraction cycle. After each cycle, extracts were centrifuged and the supernatant was transferred and combined with the other supernatants in a clean tube. Before loading the extracts on Florisil cartridges the solvent was exchanged to Hex. PBDEs and NBFs (except TBPH) were eluted using 8 mL of Hex (F1). OPs and TBPH were eluted using 10 mL of ethyl acetate (F2). BDE 128, used for quantification of TBPH, was added to the F2 eluate. F1 was cleaned up by loading it on acidified silica (44%, w/w) and eluting with 10 mL of Hex-DCM (1:1, v/v). F1 and F2 were then evaporated until dryness, and resolubilized in 100 μ L *iso*-octane.

Instrumentation. The determination of NBFs and PBDEs was done on an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electron capture negative ionization (ECNI) mode. The GC system was equipped with electronic pressure control and a programmable-temperature vaporizer (PTV). Two μ L of cleaned extract was injected on a DB-5 column (15 m \times 0.25 mm \times 0.10 μ m) using solvent vent injection mode. The GC temperature program was 90 $^{\circ}$ C, hold 1.50 min, ramp 10 $^{\circ}$ C/min to 300 $^{\circ}$ C, hold 3 min, ramp 40 $^{\circ}$ C/min to 310 $^{\circ}$ C, hold 5 min. Helium was used as a carrier gas with a ramped flow. The initial flow was 1.0 mL/min (for 20 min), then ramp 6 mL/min to 2.0 mL/min. The mass spectrometer was employed in selected ion monitoring (SIM) mode, BDE 28 to 183 were monitored by m/z 79 and 81, m/z 487 and 485 were monitored for BDE-209. Monitored m/z values for NBFs can be found elsewhere⁷. Dwell times were set on 35 ms. The ion source, quadrupole and interface temperatures were set at 250, 150 and 300 $^{\circ}$ C, respectively and the electron multiplier voltage was at 2200 V. Methane was used as moderating gas. BDE 28 to BDE 154, TBB and HCDBCO were quantified on BDE 77 as IS and BDE 183, BTBPE and TBPH were quantified on BDE 128. BDE 209 and DBDPE were quantified on ¹³C-BDE 209.

Determination of OPs in F2 was done on an Agilent 6890 GC coupled to an Agilent 5973 MS operated in electron impact ionization (EI) mode as described elsewhere⁶. TEP, TnPP, TiBP, TnBP, TCEP, TCPP, TBEP were quantified on TAP. TPP, TDCPP and TCP were quantified on TPP-d₁₅.

Method validation was carried out by spiking a dust sample having a low concentration of FRs with two concentrations of FRs (Qlow and Qhigh) over three days (Table 1). Analysis of SRM 2585 was done using 50 mg per replica over six days.

Results and discussion

Optimization. When spiking the two sorbents it was found that TBPH and OPs degraded on acid silica, but eluted in the EA fraction of Florisil and could be analyzed when using acid silica only for the hex fraction. Both extraction solvents DCM and Hex-Ac (3:1, v/v) gave similar concentrations of SRM 2584 replicas thus both solvents provided a similar extraction efficiency. Less variability was observed when using the Hex-Ac (3:1, v/v) mixture.

Spiking experiments. Relative recoveries were calculated based on the injection of a standard solution with the same concentration compared to the Qlow and Qhigh spiked samples. Accuracy was generally acceptable and ranged between 81 and 131%. Losses of TEP and TnPP in F2 occurred mostly during evaporation and were due to their high volatility³. Accuracy of TBEP and TCEP was less good (> 160%) at the Qlow level (20 ng, equivalent to 267 ng/g dust). Minor matrix effects were observed for TBB with relative recoveries rising from 100 at Qlow and 110% at Qhigh to 131% and 130%, respectively (Table 1). For other compounds, matrix effects were also observed, namely TCEP with a positive influence: Qlow recovery decreased from 164 to 142%. Relative recovery of TBEP rose from 166% to 235%, although no influence of matrix interferences on these two compounds were seen at Qhigh level. Method precision for between days (Table 1) at Qhigh was acceptable for all compounds with maximum RSD of 11% for DBDPE, except for TEP (30%) and TiBP (20%), resulting from variable losses during evaporation and variable blanks, respectively. For Qlow, precision between days was acceptable with RSD below 24% for all compounds except again for TEP (52%), and TiBP (315%). The precision and accuracy for NBFs and PBDEs with this analytical method is similar to other published methods⁹⁻¹¹. Analytical methods for OPs often do not measure TiBP, they show the same precision and also a similar accuracy at the Qhigh level^{12,13}.

Method limits of quantification (LOQm) (Table 2) were based on three times the standard deviation of blank values and divided by a typical amount of dust for analysis (75 mg). LOQms ranged between 0.04 ng/g (BDE 28) and 17 ng/g (BDE 209). These values demonstrate a good sensitivity of the method for NBFs and

PBDEs⁹⁻¹¹. For OPs, LOQms were typically higher and varied between 10 ng/g (TPP) and 370 ng/g (TiBP). TCEP and TBEP had calculated LOQms of 110 and 50 ng/g, respectively, although results would be inaccurate at this concentration as recoveries exceeded 140% at 267 ng/g. Nevertheless, the sensitivity for most OPs is close to other analytical methods^{5,12,13}.

Table 1. Spiking experiments on dust matrix. Each level consists of three replicate measurements on three different days. RSD : Relative Standard Deviation within (w) and between (b) different days.

Compound	Q low				Qhigh			
	Spiked amount (ng)	Recovery (%)	RSD _w (%)	RSD _b (%)	Spiked amount (ng)	Recovery (%)	RSD _w (%)	RSD _b (%)
BDE 28	0.60	98	1	2	4	94	3	4
BDE 47	0.60	98	2	2	4	94	2	2
BDE 99	0.60	91	9	10	4	93	8	8
BDE 100	0.60	113	1	1	4	97	2	2
BDE 153	0.60	104	1	2	4	102	2	2
BDE 154	0.60	102	1	1	4	101	2	2
BDE 183	0.60	103	2	5	4	95	2	2
BDE 209	30.6	99	2	2	378	100	6	5
BTBPE	5	93	2	2	25	87	2	2
DBDPE	6.3	93	17	24	21	102	6	11
HCDBCO	5	100	2	2	25	95	3	4
TBB	5	131	4	4	25	130	4	4
TBPH	5	107	3	6	25	111	2	6
TEP	20	89	39	52	250	84	39	35
TnPP	20	109	9	13	250	102	6	5
TiBP	20	81	246	315	250	99	10	20
TnBP	20	93	3	4	250	96	2	2
TCEP	20	142	4	6	250	110	2	3
TCPP	20	103	2	3	250	99	1	1
TBEP	20	235	12	13	250	108	1	2
TPP	20	111	12	10	250	90	6	8
TDCPP	20	125	9	8	250	99	6	10
TCP	20	124	8	7	250	94	6	8

Analysis of SRM 2585. The comparison of concentrations according to the above described analytical procedure with the certified values and previously reported concentrations showed some divergence (Table 2). OP values were similar to those reported previously⁶ except for TDCPP and TBEP. In either case, the extraction solvent could not be the cause, as no differences were seen during method optimization. A possible explanation for the higher value of TBEP is the extrapolation of the calibration curve. TiBP values are not displayed because of the irreproducible blanks. Concentrations measured with the new analytical method range between 69% (BDE 28) to 91% (BDE 154) of the certified values. Relative standard deviations were 3% for lower PBDEs (BDE 28 to 154) and below 14% for BDE 183 and BDE 209.

No certified values for NBFRs exist and therefore results were compared to data from previous analyses⁷. HCDBCO and DBDPE were again not detected, and no significant differences were seen for concentrations of TBPH and BTBPE. However, mean value TBB 26 ng/g was different from 40 ng/g reported earlier, although the latter value is based on duplicate measurements only.

It was observed further that HBCD isomers were divided over F1 and F2. Initial experiments showed that by combining both fractions and exchanging the injection solvent to methanol HBCD isomers can be measured with LC/ESI-MS, but validation of this step has not been performed yet.

Table 2. Mean values and standard deviations (ng/g dust) of flame retardants measured in SRM 2585 (n = 6). LOQ_m is the method limit of quantification.

Compound	LOQ _m	Mean value (SD)	Indicative or Certified value (SD)	Percentage of indicative or certified value
BDE 28	0.04	32.8 (1.1)	46.9 (4.4)	69
BDE 47	0.13	409 (11)	497 (46)	81
BDE 99	0.18	742 (23)	145 (11)	79
BDE 100	0.24	116 (3)	892 (53)	81
BDE 153	0.18	97 (2)	83.5 (2.0)	91
BDE 154	0.71	77.2 (2.7)	119 (1)	80
BDE 183	1.6	32.3 (4.8)	43 (3.5)	73
BDE 209	17	2,150 (231)	2,510 (190)	84
BTBPE	1.1	39 (14)	32*	122
DBDPE	7.1	< 7.1	< 20	
HCDBCO	2.8	< 2.8	< 2	
TBB	9.0	26 (2)	40*	65
TBPH	0.1	574 (49) [†]	652*	88
TEP	30	< 30	< 50	
T _n PP	50	< 20	< 20	
T _i BP	370	-	-	
T _n BP	10	190 (10)	180 (20)	106
TCEP	110	680 (60)	700 (170)	97
TCPP	10	860 (70)	820 (100)	105
TBEP	50	63,000 (2000)	49,000 (9 600)	129
TPP	10	1,160 (140)	990 (70)	117
TDCPP	10	3,180 (70)	2,020 (260)	157
TCP	40	1,140 (30)	1,070 (110)	107

Acknowledgments

NVDE and NA acknowledge university of Antwerp for PhD scholarships. ACD acknowledges financial support from GOA project at the UA. AC acknowledges FWO for a postdoctoral fellowship.

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