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DEVELOPMENT AND VALIDATION OF A METHOD FOR DETERMINATION OF SELECTED POLYBROMINATED DIPHENYL ETHER CONGENERS IN HOUSEHOLD DUST

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ABSTRACT

Background. Polybrominated diphenyl ethers (PBDEs) belong to group of so-called persistent organic pollutants (POPs). These compounds occur in nearly all elements of the environment, including household dust which constitutes one of a major route for human exposure. Their main adverse effects on human health are associated mainly with endocrine disruption – they interfere with thyroid function exhibit anti-androgenic action.

Objectives. To develop and validate analytical method for determination of BDE-47, BDE-99, BDE-153, and BDE-209 congeners in household dust.

Material and methods. Household dust was sampled in residences from Warsaw and the surrounding areas. An automated Soxhlet extraction of samples was then performed and PBDE congeners were subsequently measured in cleaned-up extracts by GC-μECD. The identity of quantified compounds was confirmed by GC/MS.

Results. Household dust samples were fortified at levels of 2.88, and 28.8 ng g^{-1} for BDE-47, BDE-999, and BDE-153, and for BDE-209 at levels of 101.2, and 540 ng g^{-1}. Recoveries ranged between 72 – 106%. The relative standard deviations (RSD) were less than 16% for all PBDE congeners analysed. The relative error determined on the basis of multiple analyses of certified reference material ranged from 1.07 – 20.41%. The method's relative expanded uncertainty varied between 16 – 21%.

Conclusion. The presented method was successfully validated and can be used to measure concentrations of BDE-47, BDE-99, BDE-153 and BDE-209 congeners in household dust.

Key words. *PBDEs, dust, method validation, recovery*

STRESZCZENIE

Wprowadzenie. Polibromowane difenyloetery (PBDE) zaliczane są do trwałych zanieczyszczeń organicznych. Wykrywane są praktycznie we wszystkich elementach środowiska, także w kurzu. Kurz jest istotnym źródłem pobrania polibromowanych difenyloeterów przez człowieka. Szkodliwy wpływ PBDE na zdrowie człowieka wiązany jest głównie z zaburzaniem równowagi układu hormonalnego – zaburzają one m.in. funkcjonowanie hormonów tarczycy oraz działają antyandrogennie.

Cel badań. Opracowanie i walidacja metody analitycznej umożliwiającej oznaczanie kongenerów BDE-47, BDE-99, BDE-153 i BDE-209 w kurzu domowym.

Materiał i metody. Materiał do badań stanowiły próbki kurzu pochodzące z domów osób zamieszkałych w Warszawie i okolicach. PBDE ekstrahowano z kurzu z wykorzystaniem aparatu do automatycznej ekstrakcji Soxhlet. Ekstrakt oczyszczano i poddawano analizie instrumentalnej. Oznaczenia zawartości analizowanych kongenerów PBDE prowadzono na GC-μECD, a tożsamość potwierdzano na GC-MS.

Wyniki. Próbki kurzu były wzbogacane na poziomie 2,88 ng g^{-1} i 28,8 ng g^{-1} dla BDE-47, BDE-99, BDE-153 oraz 101,2 ng g^{-1} i 540 ng g^{-1} dla BDE-209. Odzysk mieścił się w zakresie 72 - 106%. Względne odchylenie standardowe (RSD) było mniejsze niż 16% dla wszystkich analizowanych kongenerów PBDE. Błąd względny wyznaczony na podstawie wielokrotnej analizy certyfikowanego materiału referencyjnego wynosił od 1,07% do 20,41%. Względna niepewność rozszerzona zawierała się w zakresie 16-21%.

Wniosek. Metoda została zwalidowana i może być wykorzystywana do oznaczania zawartości kongenerów BDE-47, BDE-99, BDE-153 i BDE-209 w próbkach kurzu domowego.

Słowa kluczowe: *PBDE, kurz, walidacja metody, odzysk*

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INTRODUCTION

One of the negative consequences of a modern lifestyle is the plethora of harmful chemical compounds present in the environment. Those environmental contaminants that are of particular concern are ones with long persistence, the ability to readily migrate and ones which are lipophilic. such persistent organic pollutants (POPs) include the aforementioned polybrominated diphenyl ethers (PBDEs) which consist of 209 congeners that differ in the numbers and position of bromine substitutions on the two aromatic rings of the diphenyl ether moiety. All of these congeners have an octanol: water partition coefficient (Log_{OW}) greater than 5, thereby showing their high fat solubility [12, 14]. PBDEs were first used in the 1960s of the previous century as flame retardants. They are commercially available as three mixture types known as penta-BDE, octa-BDE and deca-BDE. The former mainly consists of BDE-47, BDE-99 and BDE-100, whilst the middle type is principally composed of BDE-183, BDE-190, BDE-197 and BDE-196, but the latter is practically only made up of BDE-209 (making up 97% of the content) [31].

Since 15th August 2004 there has been a ban in force throughout the EU on penta-BDE and octa-BDE. Furthermore, from 2008 the European Union Court of Justice extended this ban to include deca-BDE used in electric and electronic goods. Some USA states, like California in 2006, banned the use of penta-BDE and octa-BDE products which thus abolished their manufacture from the USA. At the end of 2013 the manufacture of deca-BDE also became banned [4, 9, 40]. Despite this stepwise withdrawal of PBDE and its manufactured flame retardant products, such products will be nevertheless still present on the market for a long time yet, as well as in the immediate environment [32].

It is estimated that the PBDEs as flame retardant component may constitute up to 30% of the plastic casings of computers, televisions, fabrics (automobile seats and air), together with flooring and polyurethane foams (in household furniture, mattresses or car seats) [29]. As non-permanently chemically bonded components of products, they can be readily released into the environment during the operation of electrical devices when heating is generated. A 5 °C rise in temperature has been shown to increase the emission of PBDEs from television casings to the environment from 40 to 70% [37]. Another factor responsible for such PBDE release is by UV irradiation [38].

PBDEs can in fact be found throughout the environment that includes plant and animal tissue [10, 16, 25], together with human specimens [15, 34]. Many published studies demonstrate that a significant source of human exposure to PBDEs are various foodstuffs and dust [5, 18, 27], where those particularly vulnerable to exposure are small children aged 6 months to two years [19, 41]. It has been shown that these compounds are human endocrine disruptors altering thyroid, pituitary and hypothalamic function as well as having neurotoxic effects, that lead to behavioural changes and thought process disorders [3, 17, 20, 21, 28]. The non-respirable fraction of inhaled dust is a heterogeneous mixture of dander, skin, hair, food debris, sand, fragments of fibres from carpets, clothes and cigarette ash etc. [41]. PBDEs in dust are mainly determined by gas chromatographic (GC) methods with various means of detection eg. GC/MS (mass spectrometric) or GC-ECD (electron capture) [23, 24].

The aim of the study was to develop a simple method for measuring PBDE congeners in dust, serving as a basis to thereby determine human exposures from this source. Through performing a literature review, four congeners were chosen, namely: BDE-47 (2,2’,4,4’- tetrabromodiphenyl ether), BDE-99 (2,2’,4,4’,5-pentabromodiphenyl ether, BDE-153 (2,2′,4,4′,5,5′-hexabromodiphenyl ether) and BDE-209, (2,2’,3,3’,4,4’,5,5’,6,6’-decabromodiphenyl ether) [8, 13, 30, 33, 35, 39].

MATERIAL AND METHODS

Reagents and Standards

Certified standard solutions of PBDEs (ie. BDE-47, BDE-99, BDE-153 and BDE-209) were commercially obtained in 1.2 mL aliquots, each at 50 µg/mL concentrations (in nonane), from Cambridge Isotope Laboratories (Andover, USA). Merck (Darmstadt, Germany) supplied the following; *n*-hexane and acetone for GC/ECD and GC/FID, dichloromethane (for analysing pesticide residues), *n*-dodecane (for synthesis), silica gel (60 extra pure 70-230 mesh ASTM; for column chromatography), activated aluminium oxide 90 neutral (also for column chromatography) and florisil. Cellulose extraction thimbles (43 x 123 mm) were bought from Munktell (Bärestein, Germany) whilst certified reference material SRM 2585 (NIST-2585) was provided by the LGC Standards.

Test sample material

Dust samples obtained from households in Warsaw and the surrounding areas constituted the test material on which the method was developed and validated. These were taken using a vacuum cleaner at each place of residence and, as quickly as possible, were gathered at the laboratory so that a visual segregation of large object could be done to eliminate any plastics, wood, metal or hair and then sieved on 150 µm vibrational steel sieving (Retsch AS 200 basic). Samples were then placed into closed aluminium vessels and stored at -20 °C ready for further use.

This was necessary to prevent photolytic debromination of any PBDE occurring in the dust samples [1, 2].

Extraction

Before use, Florisil was heated for 2 hours at 130 °C and left in an exsiccator until cooled, followed by deactivation through adding 2% of distilled water. Next, 1 g dust samples were placed into cellulose extraction thimbles to which 3 g of deactivated florisil were added. Automated extraction was then performed in a *Soxhlet* B-811 (Büchi) extractor by adding a 100 mL mixture of *n*-hexane:acetone (3:1, v:v). The details of extraction conditions are shown in Table 1. To each extract, 50 µL of *n*-dodecane (keeper) was added, which due to its high boiling point (200 °C) prevents any analytical losses in later stages of evaporation and changing of solvent [9]. The extract was then evaporated to almost dryness and the residue reconstituted in 2 mL *n*-hexane.

Table 1. Parameters for Soxhlet's extraction method (Büchi B-811 system)

Parameter	setting
Soxhlet warm mode:	
Lower heating level	10
Upper heating level	2
Number of cycles	30
Rinse:	
Lower heating level	8
Time	15 min

Column clean-up

Prior to use, the aluminium oxide and silica gel were heated at 130 °C for 24 hours, after which each were respectively deactivated by adding 6% and 4.5% water. Extracts were then purified on columns containing 10 g silica gel and 5 g aluminium oxide that had been pre-conditioned with 50 mL *n*-hexane. Samples were then eluted with 75 mL mixture of dichloromethane:*n*--hexane (1:9, v:v) and collected eluates were evaporated to dryness followed by reconstitution in 1 mL *n*-hexane. Using glass *Pasteur* pipettes, samples were transferred into glass amber vials ready for instrumental analysis.

Chromatography

Concentrations of the chosen PBDEs in the dust samples were measured using a GC with µECD (electron capture detection) instrument; Agilent Technologies 6890N with automated sample injection (Agilent 7863) controlled by Agilent ChemStation. Chromatographic run conditions were as follows; DB-5MS column (30 m x 0,32 mm i.d. and film thickness 0.25 µm. The GC oven temperature ramp programme was 70 ºC (1.7 min) – 30 ºC min^{-1} – 210 ºC (0 min) – 5 ºC min^{-1} – 300 ºC (28 min). The PTV injector temperature ramp programme in 'solvent vent' mode was 40 ºC (0.2 min) – 700 ºC min^{-1} – 220 ºC (1 min) – 700 ºC min^{-1} – 260 ºC (2 min). Detector temperature was 330 °C, sample volume 1 µL with helium as the carrier gas. Retention times of the chosen PBDEs were; BDE-47 – 13.077 min, BDE-99

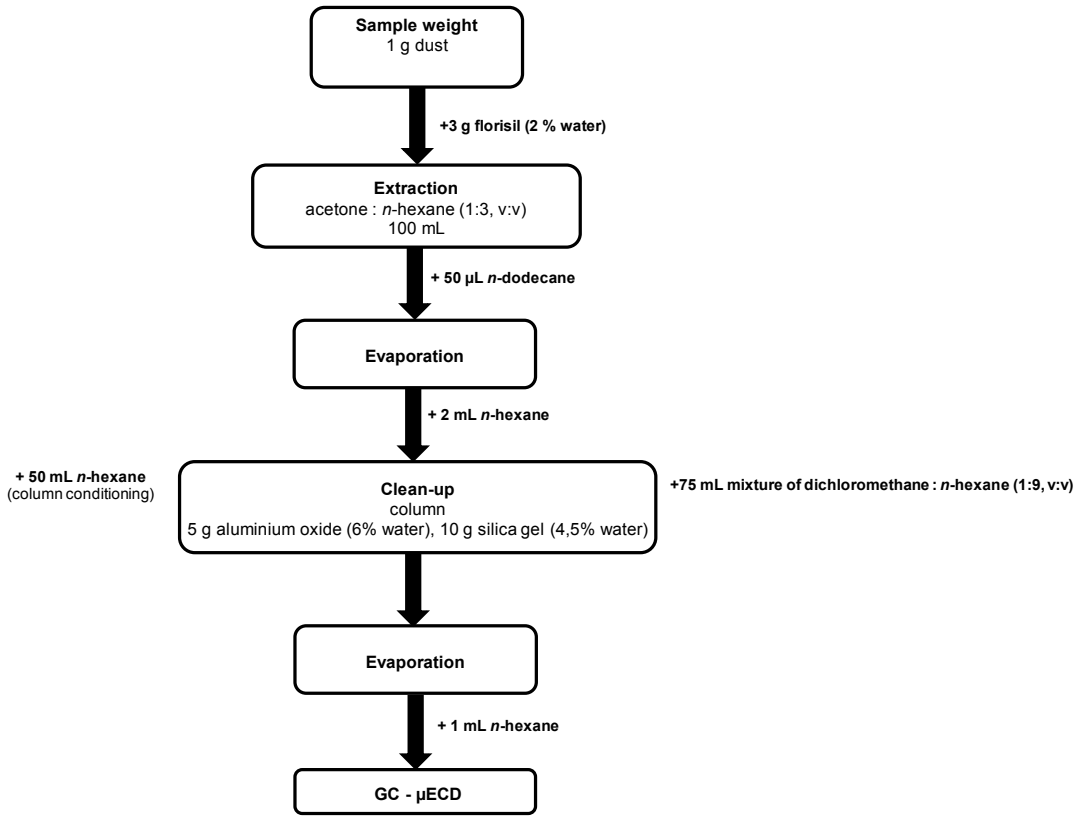

Figure 1. Diagram of the analytical method for the determination of selected PBDE congeners in the dust samples

– 15.942 min, BDE-153 – 19.034 min and BDE-209 – 46.026 min The detailed scheme is shown in Figure 1.

The identity of quantified PBDE congeners was confirmed by means of gas chromatography coupled with mass spectrometric detector with the exception of BDE-209, because of its thermal instability. The detector was an ion-trap Varian 4000 and run conditions of the GC system, using the same column, were as follows; 70 ºC (1 min); 30 ºC min^{-1} – 170 ºC, 8 ºC min^{-1} – 300 ºC (15 min), with temperatures of the detector and injector at 200 °C and 250 °C, a sample volume of 2 µL with helium again being the carrier gas. Characteristic ions of the PBDE congeners were chosen: BDE-47 – 326 and 486 *m/z*, BDE-99 – 406 and 564 *m/z* and BDE-153 – 484 *m/z*.

RESULTS AND DISCUSSION

Validation of a given analytical method enables the assessment of possibility of an accurate and precise measurement of analyte concentration to be made. The present study was carried out in accordance with the published recommendations [6, 7, 11, 22]. The limits of quantification (LOQ) corresponding to the lowest points on the calibration curve were 1 ng mL^{-1} for BDE-47, BDE-99 and BDE-153, and 20 ng mL^{-1} for BDE-209 (equal to 1 and 20 ng per gram of dust). However due to the influence of co-extracting matrix complex components, an approach applied by *Król* et al. (2012) has been applied, and LOQs were finally estimated at 2 ng g^{-1} for BDE-47, BDE-99, and 30 ng g^{-1} for BDE-209. Parameters characterizing the method are shown in Table 2.

Recoveries were determined at two PBDE levels as follows; 2.88 ng g^{-1} and 28.8 ng g^{-1} for BDE-47, BDE-99 and BDE-153 whilst at 101.2 ng g^{-1} and 540 ng g^{-1} for BDE-209. For this purpose, a test portion of the dust inserted in the cellulose thimble was spiked with known volume of standard solution containing mixture of PBDEs and was followed by the adopted scheme. The fortification levels were adopted through performing a review of scientific papers describing levels of these compounds in dust [8, 13, 30, 33, 35].

Recoveries for BDE-47, BDE-99 and BDE-153 ranged from 75% – 82%. The method's relative expanded uncertainty for both fortification levels was estimated to vary between 16 – 21%. In the case of BDE-209, similar recoveries were found at 73 and 72% respectively at levels of 101.2 ng g^{-1} and 540 ng g^{-1} with the relative expanded uncertainty in both cases being 18%. In estimating the method's uncertainty, only the intra-laboratory analytical procedure was taken into account that included the PBDE congeners recoveries. Precision of the method was also estimated and expressed as the repeatability limit (r) of measurement.

During the validation, each stage of the method was checked to determine which contributed to the greatest measurement uncertainty; this was found to be the solvent evaporation. The *n*-dodecane, as a keeper, was checked for its effects on PBDE recoveries during evaporation in the following manner; two sets of five test tubes containing 1 mL of mixture of standards in *n*-hexane (BDE-47 – 50.6 ng mL^{-1}, BDE-99 – 51.2 ng mL^{-1}, BDE-153 – 51.2 ng mL^{-1} and BDE-209 – 253 ng mL^{-1}), were prepared with 50 µL of *n*-dodecane being added to only the first set. Both sets were then evaporated to dryness and then reconstituted with 1 mL *n*-hexane. As shown in Table 3, *n*-dodecane reduces recovery losses in the lower-brominated PBDE congeners (e.g. BDE-47) but reduces recoveries in decabromodiphenyl ether. For BDE-47, BDE-99 and BDE-153 congeners an intra-laboratory reproducibility was checked for dust samples (n=6) spiked with 28.8 ng^{-1} of these compounds. Recoveries of the PBDEs varied from 78 – 95%, with RSDs (relative standard deviation) ranging 11 – 15% that were lower than the 27% RSD_R value (relative standard deviation of reproducibility) calculated according to the *Horwitz* equation [26].

Table 2. Summary of validation parameters for the method

Parameters	PBDE congeners			
	BDE-47	BDE-99	BDE-153	BDE-209
Working range [ng g^{-1}]	2- 506	2 - 512	2 - 512	30 - 759
Fortification level [ng g^{-1}]	**2.88**			**101.2**
Average recovery [%] (n=6)	106	104	95	73
SD [ng g^{-1}]	0.49	0.29	0.38	8.81
RSD [%]	15.98	9.93	13.74	11.97
Repeatability limit (r)	1.36	0.82	1.05	24.66
Relative expanded uncertainty [%]	16	15	21	18
Fortification level [ng g^{-1}]	**28.8**			**540**
Average recovery [%] (n=6)	82	76	74	72
SD [ng g^{-1}]	3.65	3.23	2.72	35.26
RSD [%]	15.38	14.8	12.77	9.10
Repeatability limit (r)	10.23	9.04	7.60	98.74
Relative expanded uncertainty [%]	20	16	19	18

Table 3. The role of keeper (*n*-dodecane) addition at the stage of solvent evaporation

PBDE congeners	Concentation [ng mL^{-1}]	Evaporation with keeper (n=5)		Evaporation without keeper (n=5)	
		Measured concentration [ng mL^{-1}]	SD [ng mL^{-1}]	Measured concentration [ng mL^{-1}]	SD [ng mL^{-1}]
BDE-47	50.60	52.12	0.47	25.83	6.65
BDE-99	51.20	55.42	1.26	46.07	3.39
BDE-153	51.20	54.83	1.48	54.47	1.96
BDE-209	253.00	215.02	11.48	251.34	22.70

The certified reference material SRM 2585 (NIST) was used also for validation which is the sieved dust contained numerous contaminants, including analysed PBDEs [31]. Results of analysis of 6 such reference dust samples are shown in Table 4.

Table 4. Results of standard reference material NIST SRM 2585 analyses (n=6)

PBDE congener	Certified concentration [ng g^{-1}]	Measured concentration ± SD [ng g^{-1}]	Relative error [a] (%)
BDE-47	497	491.66 ± 18.17	1.07
BDE-99	892	751,64 ±20.95	15.74
BDE-153	119	94.71 ± 13.46	20.41
BDE-209	2510	2746.54 ± 160.63	9.42

[a] calculated as (|average measured concentration– certified concentration|/certified concentration)*100

The results demonstrate the adequacy of the developed method for measuring the defined analytes. It should however be mentioned that PBDE levels in the certified reference material were very high (especially for BDE-99 and BDE-209) and therefore either dilutions are required at the final stages to fall within the working range of calibration curve or smaller samples of dust need to be taken. Indeed the latter option was used, where only 100 mg amounts of dust were sampled with the final result being accordingly adjusted as per 1 g dust.

Because PBDEs are vulnerable to debromination by photolysis, it is important to limit their exposure to UV light at each stage of the analytical procedure, particularly those involving organic solvents where this process occurs most readily [36, 38]. The speed of photo-degradation also increases with the number of

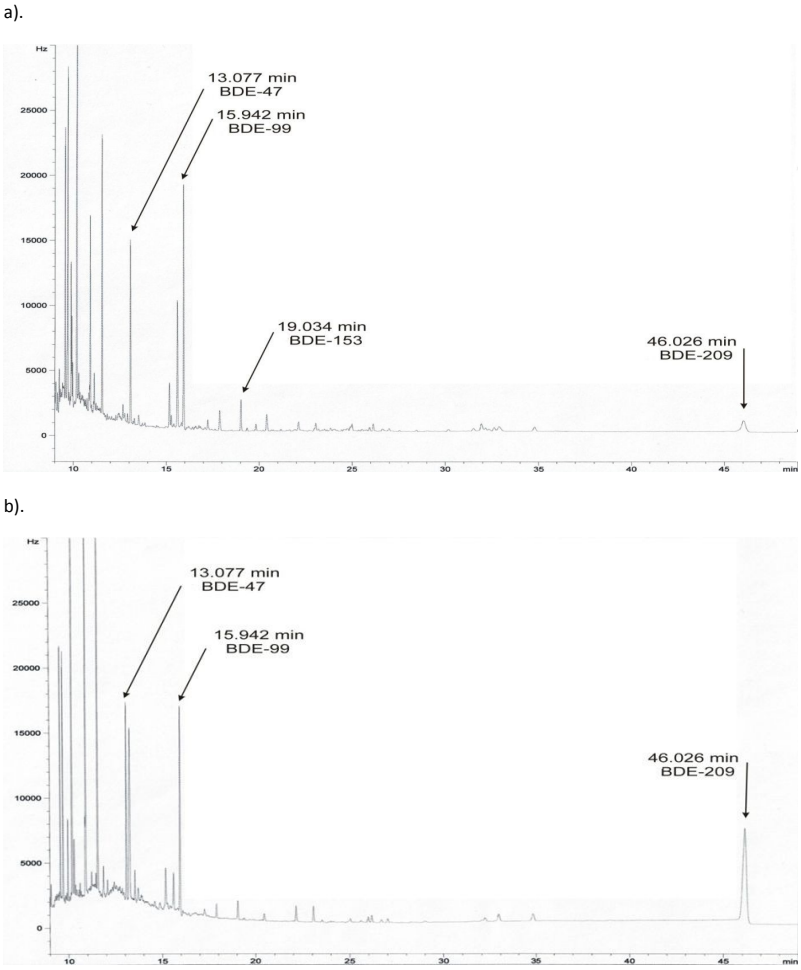

Figure 2. GC- μECD chromatograms obtained from standard reference material NIST SRM 2585 sample (a) and household dust sample (b).

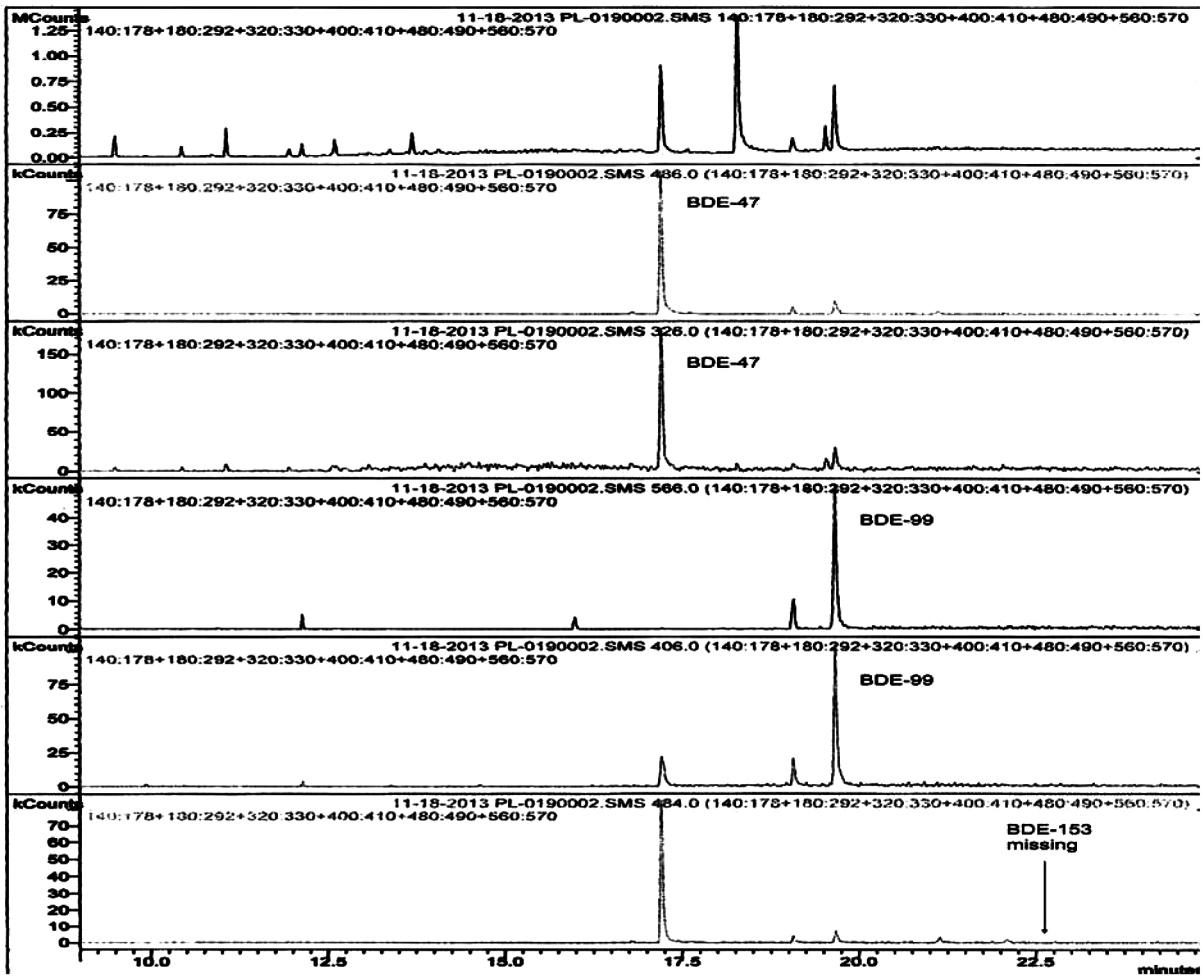

Figure 3. GC-MS chromatogram of household dust sample obtained in SIS mode.

bromine substitutions on the PBDE moiety [1, 2]. By using the 'warm extraction' mode with the automated *Soxhlet*, it was possible to shorten the extraction time by 3 hours as compared to the original procedure [8, 9, 28, 35].

Due to dust being an extremely heterogeneous matrix, the chromatograms of successive samples may differ in the numbers of peaks observed and their intensities. Figure 2 shows chromatograms of a reference SRM 2585 material and a sample of household dust obtained by GC-μECD.

Figure 3 demonstrates an example of a chromatogram obtained from a dust sample using GC/MS in the SIS (selected ion storage) mode which increases the sensitivity of detecting specifically chosen ions, and thus enables full identification of test substances. In the presented sample, the presence of BDE-47 and BDE-99 were confirmed, however BDE-153 was absent.

CONCLUSIONS

1. This developed and validated method can be used for measuring the concentrations of the selected polybrominated diphenyl ethers congeners: BDE-47, BDE-99, BDE-153, and BDE-209 in dust samples, thus enabling human exposure to these substances to be assessed within household environments or other similar confined spaces, such as those found in automobiles.
2. Recoveries and relative standard deviations are analytically appropriate as are the repeatability and reproducibility within the working conditions used in the study. The method is also robust to changes in the laboratory environment.

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Conflict of interest

The authors declare no conflict of interest.

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