

Determination of polybrominated diphenyl ethers (PBDEs) in dust samples collected in air conditioning filters of different usage - method development

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Abstract

This study presents the results of studies aimed at the development of an analytical procedure for separation, identification, and determination of PBDEs compounds in dust samples collected from automotive cabin air filters and samples collected from filters installed as part of the air purification system in academic facilities. Ultrasound-assisted dispersive solid phase extraction (UA-dSPE) was found to perform better in terms of extract purification than the conventional SPE technique. GC-EIMS was used for final determination of analytes. The concentrations of PBDEs in car filters ranged from < LOD to 688 ng/g while from < LOD to 247 ng/g in dust from air conditioning filters. BDE-47 and BDE-100 were reported the dominating congeners. The estimated exposure to PBDEs via ingestion of dust from car filters varied from 0.00022 to 0.012 ng/day in toddlers and from 0.000036 to 0.0029 ng/day in adults; dust from air conditioning filters: from 0.017 to 0.25 ng/day in toddlers and from 0.0029 to 0.042 ng/day. In addition, an attempt was made at extracting PBDEs from a dust samples using the matrix solid-phase dispersion (MSPD) technique as a promising alternative to conventional SPE separations.

Keywords

Polybrominated diphenyl ethers; Air conditioning filter dust; Matrix solid-phase dispersion; Dispersive solid-phase extraction; Ultrasound assisted extraction; Gas chromatography

1. Introduction

Mentions of PBDEs being used in industrial production date back as far as the 1960s. The addition of PBDEs reduces the flammability of polymer materials [1]. Therefore, the

compounds were used as flame retardants. Electrical and electronic equipment casings were a particularly popular domain for the use of PBDEs. Due to their high environmental persistence and harmful effects to living organisms, PBDEs were banned by the European Union: the ban was placed on penta- and octa-BDEs in 2004 and extended to include deca-BDEs in 2008. In 2009, the Stockholm Convention classified PBDEs as persistent organic pollutants [2,3]. In the US, ban on the use of penta- and octa-BDEs was introduced by some states in the year 2000 [4]. Eventually, major US-based manufacturers and importers committed to voluntarily withdraw from using PBDEs by the end of the year 2013 [4,5]. However, production of brominated flame retardants (BFRs) has not been banned in Asian countries which continue to export their PBDEs-containing consumer products to Europe. Although the import of these products is driven by economic interests, the imported products should meet the European standards for quality and safety. According to current estimates, the demand for brominated flame retardants is to increase by 4.6 % every year by 2018 [6]. Industrial manufacturers make use of three types of commercial PBDEs mixtures named after the predominant constituents: pentaBDE, octa-BDE, and deca-BDE [7]. PBDEs are classified as additives. This means that they linked to the polymer material by physical interactions rather than by stable chemical bonds. As a consequence, the potential for uncontrolled environmental release of these compounds is increased [8]. As the phase distribution equilibrium of PBDEs is shifted towards media of relatively high lipophilicity, these compounds are characterized by high affinity towards adipose tissues and other body fluids of living organisms. PBDEs are emitted into the air upon production, use, as well as disposal of PBDEs-containing product. An interesting phenomenon consists in PBDEs deposition in house dust. According to the researchers, this is achieved along three hypothetical migration pathways: 1) physicochemical processes – evaporation of PBDEs from the polymeric material into the gaseous phase with subsequent migration into house dust; 2) mechanical processes – migration of PBDEs into gaseous phase due to the abrasion of the polymer materials with subsequent migration into house dust; and 3) migration of PBDEs from the polymer material into house dust upon direct contact [9,10]. Importantly, PBDEs are moderately volatile compounds; in practice, this means that after entering gaseous phase, they become deposited on suspended particulate matter which subsequently settles down under gravity, forming house dust. As an element of indoor environments, house dust is therefore an interesting object of studies aimed at obtaining analytical information on PBDEs-related air quality. The obtained information is of historical value; this, however, may become useful provided that the time of dust deposition is known, e.g. from interviews with the users of a particular facility. Such information may be used for



determination of the scale of PBDEs emission to within a particular period. Simply put, house dust acts as a sort of passive sampler. Dust samples are characterized by complex composition of the matrix depending on the site of origin. Literature contains description of numerous techniques used for the analysis of PBDEs in the samples of dust generated at households, public facilities, means of transportation (e.g. cars, planes), air conditioning filters, or streets. In relation to the extraction of analytes, the most popular techniques include pressurized liquid extraction (PLE) [11–13], ultrasound-assisted extraction (UAE) [11,14–16], Soxhlet extraction (SE) [11,17–20], or microwave-assisted extraction (MAE) [21]. Table 1 shows the basic advantages and disadvantages of each of these techniques in relation to their use in PBDE extraction from dust samples, as well as the features of the techniques being the subject of publication. No information is available in the literature regarding the content of PBDEs in used car filters. Therefore, proposed analytical approach is a pioneer attempt to document this type of analysis. These types of filters may constitute an additional element not yet taken into account, contributing to the knowledge about the occurrence of PBDEs in the environment of car cabins. The literature survey revealed no available data on the possibility of using the relatively novel technique of matrix solid-phase dispersion (MSPD) for preparation of dust samples for PBDEs content determination. This technique was introduced in 1989 by Barker and Long [22] and has since found use in extraction of veterinary drugs [23], polychlorinated biphenyls [24], bisphenol A [25] or progestogens from foodstuffs [26]. In PBDEs analytic assays, MSPD is used mainly in the analysis of biological samples [27,28]. This technique consist of thorough mixing of a sample and a solid matrix (most often an adsorption bed). Next, the obtained mix is put onto SPE columns and the analytes or interfering substances are eluted/extracted as in conventional solid phase extraction technique. This solution allows for significant shortening of the sample preparation stage (while maintaining similar analyte recovery and quantitation limit) as well as reducing the analysis' costs and energy demand. The increasing importance are the latest extraction techniques, such as QuETChERS, stationary-phase microextraction (SPME), dispersive micro solid-phase extraction (DMSPE) or extraction using molecularly imprinted polymers (MIPs) [29,30,3–33]. Professional literature provides numerous procedures for determination of PBDEs in various samples of varying complexity of matrix composition. However, the procedures described in the literature are not universal and do not always lead to satisfactory results. Therefore, an attempt was made at documenting all the selection stages leading to the development of an optimum analytical procedure for the particular sample matrix composition. The objective of this study was to determine PBDEs contents in used car filters and dust samples collected from air conditioning filters. Main focus



was on the key element of the analytical procedure, i.e. the extraction and purification of extracts. The obtained results were used for estimation of human exposure to PBDEs.

Table 1 Advantages and disadvantages of techniques mainly used and proposed for PBDEs extraction from dust samples.

Extraction technique	Advantages	Disadvantages
PLE	<ul style="list-style-type: none"> - automation of the extraction process, - short extraction time, - moderate consumption of solvents, - the possibility of extraction of thermally unstable analytes, - possibility of extraction from samples with high humidity, - favorable extraction kinetics 	<ul style="list-style-type: none"> - high cost of equipment, - low selectivity of extraction
UAE	<ul style="list-style-type: none"> - allows for simultaneous extraction from several samples 	<ul style="list-style-type: none"> - the need to separate the extract from the sample, - in the case of PBDEs - relatively long extraction time
SE	<ul style="list-style-type: none"> - simplicity of implementation, - low cost, - the possibility of obtaining an extract separated from the residue 	<ul style="list-style-type: none"> - long extraction time, - the need to use significant amounts of solvent, - possibility of extraction only from a single sample, - moist samples require thorough drying before extraction begins
MAE	<ul style="list-style-type: none"> - easy to make, - allows for extraction from several samples at the same time, - short extraction time, - the consumption of small amounts of solvents 	<ul style="list-style-type: none"> - the need to separate the extract from the extraction residue, - the use of only solvents that have the ability to absorb and propagate microwaves (a dipole moment different from zero)
SPE	<ul style="list-style-type: none"> - allows for simultaneous extraction from several samples, - low cost, 	<ul style="list-style-type: none"> - usually it must precede the extraction of analytes with a solvent - time-consuming technique

<p style="text-align: center;">dSPE</p>	<ul style="list-style-type: none"> - allows for simultaneous extraction from several samples, - low cost, - easy to make 	<ul style="list-style-type: none"> - usually requires support, e.g. ultrasound or shaking, as well as additional purification using the classic SPE technique, - it can usually be used for pre-treatment of the extract, not as an independent and sufficient technique,
<p style="text-align: center;">MSPD</p>	<ul style="list-style-type: none"> - significantly shortening the sample preparation stage in comparison to the classic SPE technique, - combination of the extract purification stage with simultaneous purification of the extracts - reduced consumption of organic solvents, - low cost, - allows for simultaneous extraction from several samples, - no filtration requirement, 	<ul style="list-style-type: none"> - the possibility of problems with maintaining high and repeatable recovery of analytes, - a strong possibility of co-elution with some matrix components

2. Materials and methods

2.1. Materials and reagents

Reference standard solutions of eight individual PBDEs, namely isooctane solutions of BDE-28, BDE-47, BDE-99, BDE-100, BDE153, BDE-154, and BDE-183 and 2,2,4-isooctane:toluene (9:1 v/v) solution of BDE-209 were purchased from AccuStandard, USA. All standard solutions had the concentration of 50 µg/mL. The internal standard (IS) of decachlorobiphenyl (PCB-209) was purchased from Sigma Aldrich, Germany. All solvents (isooctane, n-hexane, dichloromethane, acetone, toluene) were HPLC grade and were purchased from Merck Co., Germany. The solid sorbents, including aluminium oxide (Alumina 60–325 mesh, Merck Co., Germany), silica gel (60–250 mesh, Merck Co., Germany) and magnesium silicate (Florisil 60–100 mesh, FlukaAG, Switzerland) were HPLC grade. Before analysis they were heated up and prepared as outlined in Table S1. Anhydrous sodium sulfate (Sigma Aldrich, Germany) was used to for water removal. Gaseous helium, nitrogen, air, and hydrogen (Linde Gaz, Poland) were used for chromatographic analyses. Vehicle filter samples were provided by volunteers. Cabin air filters and engine air filters were used in the study. Information on the duration of filter use and the age of the car were collected from all volunteers submitting the filters. Immediately after collection, the filters were wrapped in aluminium foil



or packed in the original packaging and then submitted to the analytical lab. The first step of sample preparation consisted in using forceps to remove any interfering objects such as insects or leaves. After elimination of visible contamination, filters were cut into fragments (squares ca 0.5 x 0.5 cm). Due to the very low quantity of dust being deposited on the filter surface (significant amounts of dust were clogged within the filter pores, and therefore the collection of “pure dust” samples was impossible), the analytes were extracted from samples consisting of filter material + the accumulated dust (for the sake of simplicity, these will be further referred to as “car filter samples”). In addition, it was very likely that PBDEs might have been adsorbed not only in dust, but in the filter material as well. Therefore, interference from a high number of compounds was expected due to the possibility of compounds contained in filter material being eluted upon extraction (i.e. the composition of matrix was more complex than in the case of dust alone). Three types of car filters were identified upon preliminary inspection: (i) paper filters, (ii) non-woven filters, (iii) filters consisting of two non-woven layers interspersed with activated charcoal. Activated charcoal is widely used as a sorbent for purification of air from chemical contaminants. The third category of filters was not included in the analyses due to the fact that the activated charcoal had been probably placed between the non-woven layers with the help of an adhesive or other substance preventing its spillage. As shown in laboratory tests conducted on this type of filters, the presence of such additive significantly worsens extraction and extract purification due to the formation of a thick gel upon solvent evaporation. Table S2 presents the descriptions and characteristics of samples. A total of 9 samples from each filter were subjected to the analyses. Dust samples were collected from air conditioning system pocket bag filters being replaced once a year according to internal procedures at one of the university buildings in Gdańsk. Filters subjected to the analyses were replaced in 2016 or 2017. Analyzed samples included those collected from inflow as well as exhaust filters. The building was located in the vicinity of a street with high motor vehicle traffic. A car park was also located nearby. Sample collection included sweeping off the dust being on the filter surface. Sampling was facilitated by the pocket filter’s design, because a large amount of dust was accumulated within the pockets. The dust was not sieved, and larger debris such as fragments of leaves or insects, were removed manually using forceps. All samples were stored at $-5\text{ }^{\circ}\text{C}$ in tightly closed containers without the access of light until being used for the analysis.

2.2. Analytes extraction

The extraction of PBDEs from the samples was achieved by means of ultrasound assisted extraction (UAE) in a ultrasonic bath from Bandelin Electronic Sonore (Germany). Before the



extraction, each sample was spiked with 1 μL of the internal standard (PCB209 at the concentration of 10 $\text{ng}/\mu\text{L}$). Extraction was carried out in 15 mL amber glass vessels. The mass of extracted samples was about 0.1 g for car filter samples and about 0.05 g for air conditioning filter dust samples. Table S3 presents the extraction variants taken into consideration. After extraction, samples were centrifuged (2500 rpm, 10 min, room temperature) so that the dust sedimented on the bottom of vials. The extract in amount of 9 mL was taken using a Pasteur pipette into a graduated test tubes. Caution was taken so as not to agitate the dust which had sedimented at the extraction vial bottoms. The collected extracts were evaporated under mild nitrogen stream to the volume of ca. 1 mL using the TurboVap® (Caliper LifeSciences, USA) device. In the case of dust samples, a decision was also made to test the feasibility of the MSPD technique (0.05 g of sample + 1.5 g of acidic silica gel + 0.5 g sodium sulfate) as a means for sample extraction that would ensure: 1) reduced consumption of organic solvents; 2) shorter sample preparation times (simultaneous extraction and purification from contaminants); 3) reduction of potential analyte loss at the stage of sample preparation.

The optimal conditions were: ultrasound-assisted dispersive solid phase extraction (UA-dSPE) for 1 h, with 1 g of acidic silica gel, 1 g of Na_2SO_4 and 10 mL of DCM:hexane (1:1 v/v) as extractant.

2.3. Extract purification

Solid phase extraction (SPE) was used at the extract purification stage. The extraction was carried out using SPE columns manually filled with various types of adsorption beds which had been conditioned by being washed once with 10 mL of DCM/n-hexane (1:1 v/v). The conditioning was aimed at elimination of any contaminants as well as at determination of the bed's solvent flow profile. The extracts were dried over a layer of sodium sulfate placed at the column head (if the drying process had not been performed previously). Fig. 1 presents information on the conditions of extraction and extract purification procedures. Quantities of solvents required for the elution of analytes (tri-deca-BDE) were determined by means of fractionation of the eluate obtained using a standard PBDEs mixture. The impact of variable conditions at each of the sample preparation stages was assessed using F1 car filter samples (cabin and engine air filters) as well as samples of dust collected from air conditioning filters being replaced in 2016. This facilitated set up the optimum conditions for each preparation stage. Purified extracts were evaporated to dryness under mild nitrogen stream. The residues were dissolved in 100 μL of isooctane and transferred to 2 mL amber glass vials with volume reduction inserts (200 μL). The exchange of the solvent prior to final determination was also

taken into account in the assessment of the analytical procedure. To this end, comparative tests were carried out using reference solutions (with DCM:n-hexane 1:1 v/v as the solvent), with 50 μL of isooctane being added to each sample before completion of evaporation. Evaporation was continued until the residual volume of ca. 50 μL . The entire volumes were transferred to amber glass vials using syringes and filled up to 100 μL .

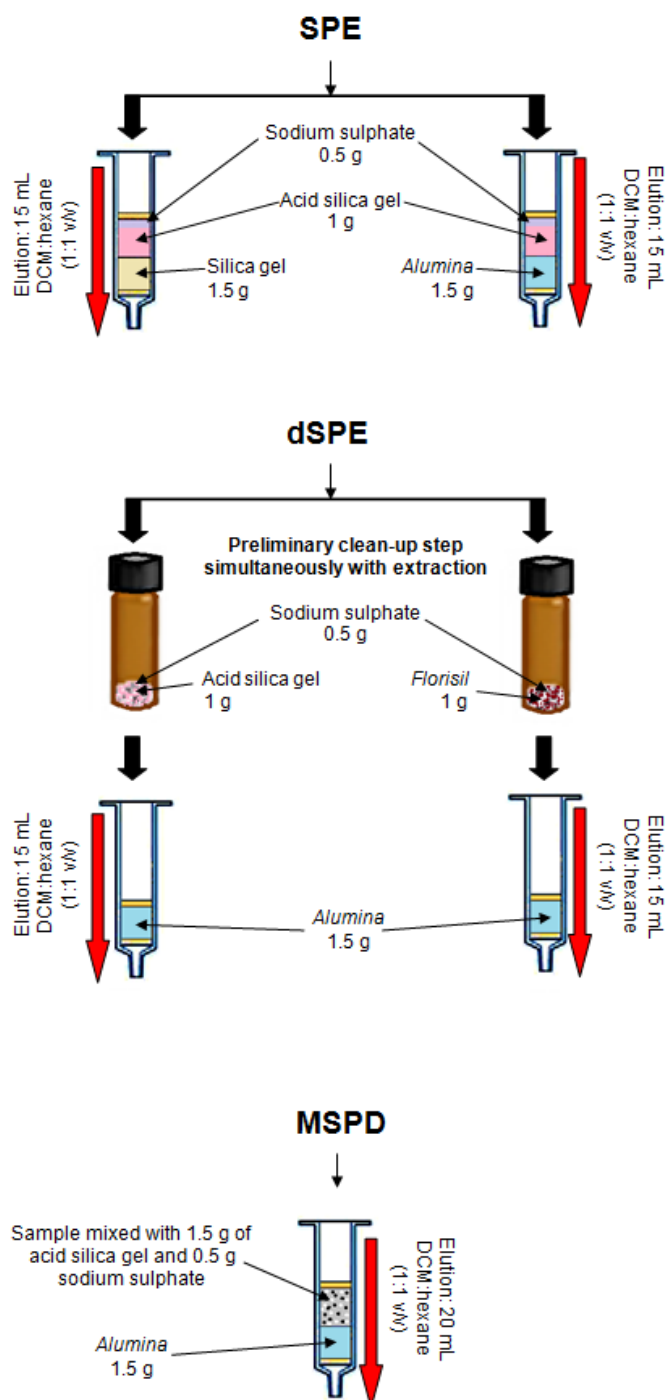


Fig. 1 Diagrams showing techniques of extraction / purification of extracts, used to isolate PBDEs compounds from car filter samples and dust samples from air conditioning filters

2.4. Chromatographic analysis

2.4.1. GC-EIMS

PBDEs separation, identification and determination was achieved using an Agilent 7890A gas chromatograph coupled with quadrupole Agilent 5977A mass spectrometer operating in electron ionization mode (GC-EIMS/SIM) and equipped with Agilent 7693 automatic liquid sampled (Agilent Technologies, USA). The injection sample volume was 1 μL . Chromatographic separation was achieved using a HP-5MS 30 m x 0.25 mm x 0.25 μm column (J&W, USA). Helium was used as the carrier gas. Detailed operating conditions of the chromatographic system are presented in Table S4. In order to increase the sensitivity of determination, the mass spectrometer was operated in the selected ion monitoring (SIM) mode. The m/z values of the monitored ions characteristic for the tested analytes are presented in Table S5. Quantitative analysis was carried out using the internal standard (IS) method. PCB-209 was selected as the IS based on similarity of its physicochemical properties, to those of the analytes as well as on its absence from the investigated samples. Before the analysis we checked the non-presence of PCB-209 in studied samples and also in the background (generally: this congener is absent in all environmental samples). Moreover, recent publication has shown that results obtained by using isotopically labelled internal standards do not render superior results compared to those obtained with other carefully selected suitable internal standards, such as PCB-209, other PBDE congeners, polychlorinated diphenyl ethers or F-PBDEs [33].

2.4.2. GC-ECD

A gas chromatograph equipped with an electron capture detector (ECD) was used to confirm the presence of higher-brominated PBDEs, particularly BDE-209. This was possible as our previous studies had shown that no other compounds were recorded at retention times corresponding to BDE-209 [14]. Detailed information on the operating parameters of the GC-ECD system are presented in Table S6.

2.5. Quality control/Quality assurance (QC/QA)

All procedures were carried out with due diligence to avoid contamination, including cross-contamination, of samples. Sample quality control involved the analyses of blank samples being performed after once in every 10 samples in the chromatographic sequence, as well as the analyses of procedural blank samples. In addition, 9 samples were taken from each tested material and each extract (of 9 samples) was analyzed in duplicate so to assess of the repeatability 18 results were taken into consideration. Retention time (RT) was read as the



average value of two measurements (after comparison with retention time of the standard). For identity confirmation for each compound, besides target ion, three ions (Q1 Q2 and Q3 qualifiers), which relative responses (in terms of the target ion 100%), determined based on the spectra from NIST library and the spectra obtained from analysis of standard solution at high concentration level, were established. To confirm analyte identity the relative responses of Q1, Q2 and Q3 ions were checked and compared to declared values for each single GC run. The measured values have to be in range of declared value $\pm 30\%$ uncertainty. The limit of detection (LOD) was determined for each PBDEs congeners from the following equation: (1) $LOD = 3.3 \cdot Sa/b$, where Sa - standard deviation of the detector response coefficient determined on the basis of the lowest concentration of the mixture of PBDE compounds, b - slope of the calibration curve. Following two conditions were verified as part of validating the limit of detection: (2) $10 \cdot LOD > C_{min}$, (3) $LOD < C_{min}$, where C_{min} - the lowest concentration of PBDE compounds in the calibration solution. The limit of quantification (LOQ) was determined from the following equation: (4) $LOQ = 3 \cdot LOD$ Linearity of calibration curves was verified by means of estimating the correlation coefficient (r). Additionally, intra-assay accuracy and precision were evaluated for each compound in five replicates at low, medium and high concentration levels with the lowest level being the LLOQ and the highest level being the HLOQ. The intra-assay accuracy was calculated as the error to the nominal concentrations (% of target), the intra-assay precision was calculated as the relative standard deviation (RSD%). The precision determined at each concentration should not exceed 20 % while the accuracy should be within 80–120%. The matrix effects were determining by assessment of the standardized detector responses for the analytes present in the studied samples. For this purpose, for the samples of car filters and dust samples from air conditioning filters of known mass, the same amount of each analyte (1 μ L of 1 ng/ μ L PBDEs solution) was added. Normalization was performed by dividing the mean value of the detector response for each analyte by the mean value of the detector response obtained by analyzing the PBDEs standard sample in isooctane (with the same concentration as was added to the dust and filter samples). The results are presented in the Table S7.

3. Results and discussion

3.1. Selection of extraction solvent

Polybrominated diphenyl ethers were extracted from car filter and dust samples by means of ultrasound-assisted solvent extraction. Extractability was tested for three solvents, including DCM/n-hexane (1:1 v/v), n-hexane/acetone (3:1 v/v), and toluene. The choice of solvents



resulted from the physical and chemical properties of PBDE. Because they are medium-polar compounds, a low or medium polarity solvent should be used to extract them. Based on a literature review, the solvents most commonly used for PBDE extraction from dust samples were selected [13,17–19]. In each case, the volume of extractant was 10 mL, the extraction temperature was 25 °C and the influence of extraction duration was additionally examined (Section 3.2.). Based on the analysis of the results obtained, it was decided to choose DCM:n-hexane (1:1 v/v) as an extractant. Large quantities of coextracted compounds were observed in the chromatograms of all extracts. In addition, significant baseline elevation was observed between elution minute 10 and minute 19, hindering the identification of BDE-28. This elevation was observed regardless of the solvent or the extract purification method. The largest quantities of coextracting compounds were measured for DCM/n-hexane (1:1 v/v) solvent mixture. Fig. S1 presents an example chromatogram with well-visible baseline elevation as compared to the blank sample chromatogram. As shown by the tests of real samples spiked with known amounts of reference PBDEs mixture, the efficiency of extraction using the n-hexane/acetone (3:1 v/v) solvent mixture was slightly lower than that obtained for the DCM/n-hexane (1:1 v/v) solvent mixture. This might be due to the n-hexane/acetone (3:1 v/v) mixture being evacuated to dryness before the solvent was switched to DCM/n-hexane (1:1 v/v). The solvent switch was required due to acetone mineralization being caused by acidic silica gel. The solvent switching requirement was also responsible for elongation of sample preparation times. Toluene did not come up to expectations and was ruled out as an extraction solvent at an early stage of the study. The yields of toluene extraction were low (ca. 10%), and the high boiling point of toluene was responsible for extension of solvent evaporation times. Therefore DCM/hexane (1:1 v/v) was selected as the extraction solvent. Fig. 2 presents the comparison of chromatograms of extracts obtained with different solvents at the solvent selection stage.



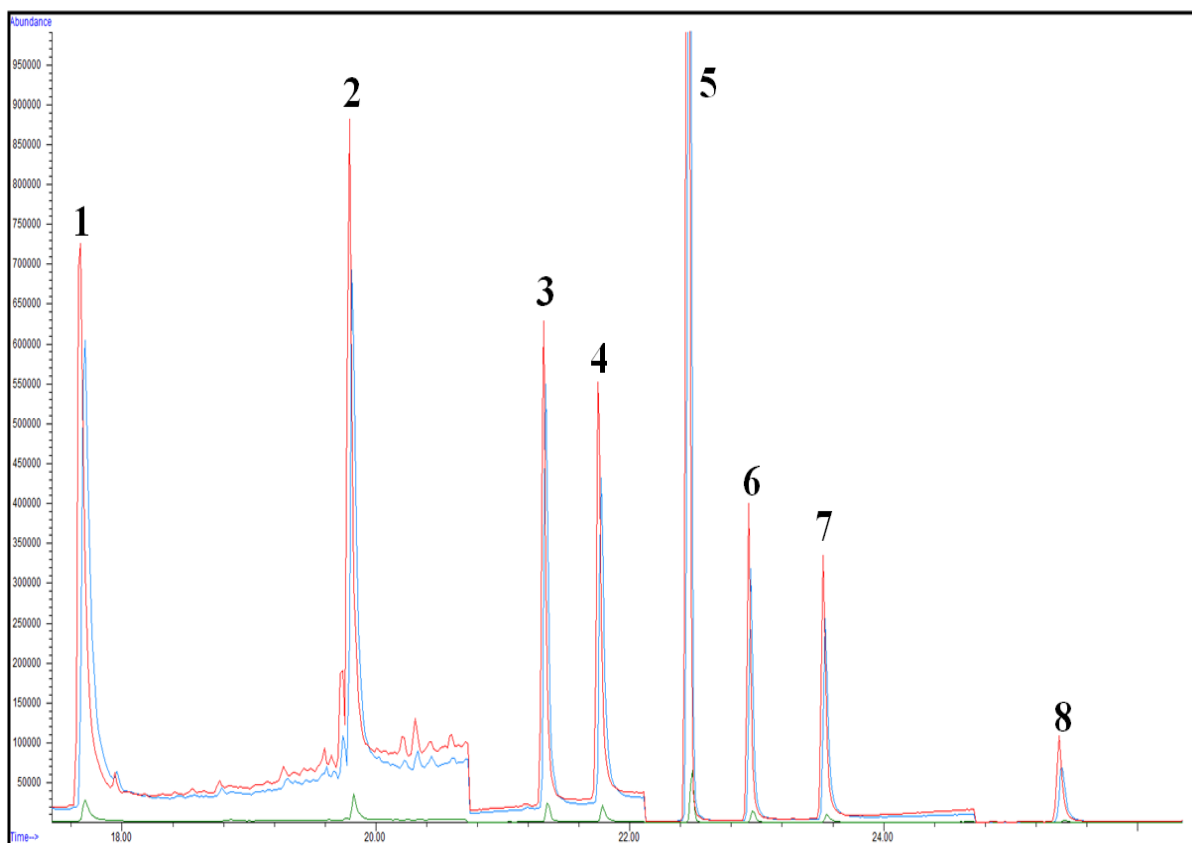


Fig. 2 Exemplary SIM chromatograms of real samples with addition of internal standard. The colour of line: green – extraction solvent was toluene, red – n-hexane:DCM (1:1 v/v) mixture and blue – n-hexane:acetone (3:1 v/v) mixture. The peaks: 1) BDE-28, 2) BDE-47, 3) BDE-100, 4) BDE-99, 5) internal standard PCB-209, 6) BDE-154, 7) BDE-153, 8)-BDE-183. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.2. Selection of extraction time

As part of the study, samples of car filters and air conditioning filter dust were submitted to ultrasound-assisted solvent extraction for 0.5 h, 1 h, and 2 h. Shorter extraction times (0.5 h) led to lower PBDEs extraction yields as determined by comparing the chromatograms of test samples with and without addition of PBDEs standard mixture. No significant differences were observed for extraction times of 1 and 2 h, and therefore the decision was made that the extraction procedure would last for 1 h.

3.3. Extracts clean-up

3.3.1. Solid-phase extraction (SPE)

Possibility of two different combinations of adsorption beds being used in extraction columns was examined. At the first stage, model studies were conducted to determine the optimum quantity of solvent ensuring elution of all tested analytes. One milliliter of the PBDEs reference mixture at the concentration of 1 $\mu\text{g/mL}$ was introduced onto the column and eluted with two 15 mL portions of DCM/n-hexane (1:1 v/v). Both fractions were collected separately and submitted to GC-EIMS and GC-ECD analyses. It was demonstrated that the first 15 mL portion of the solvent was sufficient for eluting all the tested analytes from the both adsorbents while simultaneously retaining some of the interfering compounds. Importantly, elution of the highest-substituted representative of the PBDEs class, i.e. BDE-209, was determined only by means of GC-ECD analysis. Similar results were obtained for real samples. As shown upon purification of real sample extracts, chromatograms obtained for samples purified on SPE columns filled with acidic silica gel-silica gel were characterized by higher baseline elevation for all groups of monitored ions. This is indicative of a higher quantity of interfering compounds and a lower efficiency of extract purification. Said elevation was most pronounced in the region of the peak corresponding to BDE-28 while around the BDE-183 elution times, the baseline was at similarly low levels for both acidic silica gel/silica gel and acidic silica gel/alumina beds. In addition, coelution of another compound was observed for a BDE-28 on both types of adsorption bed combinations used in the study. The obtained SIM MS spectrum was compared to a BDE-28 spectrum available in the spectral library. The comparison of relative intensities of the monitored ions revealed that the largest impact on the measurement was exerted by the ion of $m/z = 248$. Relative intensity of this ion's peak was incommensurably higher than that in the spectrum of BDE-28 available in the spectral library. This means that the compound which coeluted with BDE-28 was characterized by fragmentation involving formation of a $m/z = 248$ ion. This had the impact on the output information since the $m/z = 248$ ion was used as the target ion in quantitation of the BDE-28.

3.3.2. Ultrasound assisted dispersive solid-phase extraction (UA-dSPE)

Ultrasound assisted dispersive solid-phase extraction was carried out in two procedural variants: 1) with Florisil adsorption bed being added to the sample before extraction; 2) with acidic silica gel being added to the sample before extraction. Sodium sulfate was also added to each sample. Establishing the amount of sodium sulfate addition to the sample in the case of acidic silica gel being used as the adsorption bed, was impeded due to additional amounts of water being formed upon mineralization of sample components. It was impossible to precisely determine the quantity of water formed in the process, mainly due to the lack of information



regarding the sample components actually undergoing mineralization as well as to the lack of information regarding the repeatability of the mineralization process. Therefore the procedure uniformization was impossible and an additional sodium sulfate layer (0.5 g) was used preventively at the next stage: extracts purification using alumina filled SPE columns. Of note, extracts obtained using the UA-dSPE method were much clearer than those obtained using the ultrasound assisted extraction technique. In addition, collection of the sample supernatant was easier as the adsorption bed “retained” the fragments of car filters and dust particles. Based on the GC-EIMS chromatograms of the obtained extracts, dSPE with acidic silica gel was found to be better in terms of eliminating the interfering compounds than dSPE with Florisil adsorption bed (lower quantities of interfering compounds visualized on the chromatograms). In addition, Florisil was found not to ensure accurate separation of BDE-100 from interfering compounds. Acidic silica gel ensured good purification of extracts; chromatogram peaks were well differentiated, with no coelution being observed for any of the tested representatives of the PBDEs class. This pertained also to BDE-28 which had not been previously well separated from the interfering compounds using the conventional SPE technique at the extract purification step (Section 3.3.1.). Fig. S2 presents a comparison of chromatograms obtained following dSPE on Florisil and acidic silica gel beds. The large potential for removal of interfering compounds, the lowest baseline elevation were the decisive factors behind the choice of UA-dSPE on acidic silica gel as the method for preparation of all the remaining real-life samples (both car filter samples and air conditioning filter dust sampler).

3.4. Extracts enrichment

Evaporation of extracts under mild nitrogen stream was used to reduce the sample volume and thus to increase the concentration of analytes in the extracts. As shown by the comparative analysis of chromatograms, evaporation to dryness and subsequent reconstitution of the residue in isooctane does not affect the quality of results. No better analyte recovery rates were observed. Therefore, a decision was made to skip isooctane addition at the final stage of extract evaporation. The extracts were evaporated to dryness and then the residues were reconstituted in isooctane.

3.5. Matrix solid-phase dispersion (MSPD)

The feasibility of the MSPD technique with acid silica gel as a means of preparation of dust samples for PBDEs determination analyses was also tested. The chromatograms were characterized by higher numbers of peaks from interfering substances, indicating lower extract



purification efficacy. In the case of BDE-28, baseline elevation could be as much as two times higher than in the case of acidic silica gel dSPE. Higher baseline elevation and coelution were also observed within the region of collection of ions corresponding to the representatives of the penta-BDE class. Consequently, determination of BDE-99 and BDE-100 in the samples of dust collected from inflow air conditioning filters was impossible. Therefore, potential application of this technique at the stage of dust sample preparation requires further studies. The crucial element of these studies would consist in appropriate selection of adsorption bed and sample to sorbent weight ratios.

3.6. GC-EIMS and GC-ECD analysis

Using a ECD detector, we could determine the quantity of organic solvent required for elution of all PBDEs compounds from the SPE column beds. The use of GC-ECD system in all analyses was impossible due to the fact that the detector is sensitive towards all chloroorganic compounds thus interpretation of chromatograms would be more difficult. However, it is worthwhile to consider the use of this type of detector at the preliminary stage of a new method development, e.g. when assessing the extract purification efficacy of various adsorption beds. It should be highlighted that it is very difficult to obtain chromatograms characterized by a possibly low number of peaks originating from interfering substances, lack of coelution of interfering substances and analytes, and baselines free of characteristic elevations. This is an evidence of the complexity of composition of the car filter samples and the air conditioning filter dust samples which translates to difficulties in the selection of appropriate extract purification conditions. Further studies are required in this area. Fig. 3 presents example chromatograms obtained at selected extract purification conditions. The chosen analytical procedure consisting of the use of dSPE on acidic silica gel bed at the stage of extraction and extract purification, was a compromise between optimum analyte recovery rates and conditions ensuring efficient removal of interfering substances. In addition, Table 2 compares the main parameters of importance in the selection of the analytical procedure. In order to verify the correctness of the developed method, quality control of the tests was carried out. The parameters that characterize the quality of the tests are given in Table 3.



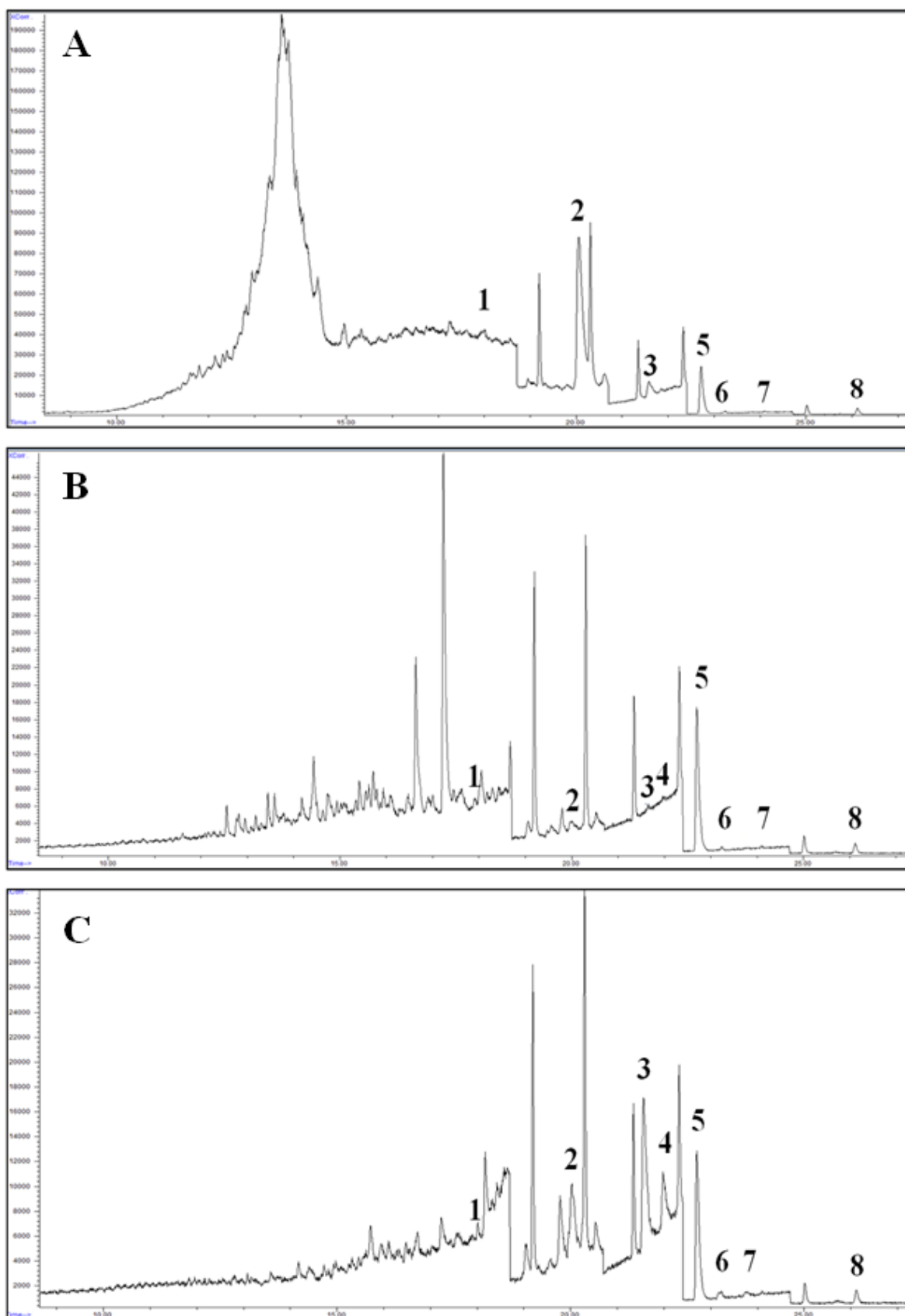


Fig. 3 Exemplary SIM chromatograms: a) cabin filter - at the stage of sample preparation, dSPE with acid silica gel was used; b) dust from the air-conditioning filter placed on the air inlet to

the building - at the stage of sample preparation, dSPE with acid silica gel was used; c) dust from an air-conditioning filter placed on the air outlet from the building - at the stage of sample preparation, MSPD with acid silica gel was used. The peaks: 1) BDE-28, 2) BDE-47, 3) BDE-100, 4) BDE-99, 5) PCB-209, 6) BDE-154, 7) BDE-153, 8)-BDE-183.

Table 2 Comparison of the parameters of the described analytical procedures.

Selected properties of analytical procedures	Tested analytical procedures		
	UAE-SPE-GC-EIMS	UA-dSPE-GC-EIMS	MSPD-GC-EIMS
Time spent on sample preparation	1 h 12 min	1 h 12 min	12 min
Solvent consumption for the sample preparation	35 mL per sample	30 mL per sample	20 mL per sample
Analytes recovery	37-65 %	53-82 %	57-89 %
Selectivity	+/-	++	+
Reproducibility	+	++	+/-
The number of sample preparation stages	5	5	3

Table 3 List of calibration parameters of the GC-EIMS system.

PBDEs congeners	Retention time [min]	R ² coefficient of the calibration curve*	LOD [ng/g]**		LOQ [ng/g]**	
			car filters	dust	car filters	dust
BDE-28	17.93	0.9995	1.4	2.9	4.2	8.7
BDE-47	20.06	0.9993	2.1	4.5	6.3	14
BDE-100	21.60	0.9995	4.2	6.9	13	21
BDE-99	22.02	0.9992	4.0	8.4	12	25
BDE-154	23.21	0.9994	6.3	13	19	39
BDE-153	23.78	0.9994	6.3	13	19	39
BDE-183	25.74	0.9998	2.7	5.8	8.1	17

* 5-point calibration curves (1-1000 µg/mL)

** obtained LOQ and LOD values refer to a 1 g sample

The highest-brominated representative of the class, deca-BDE, was not visible on chromatograms obtained using the GC-EIMS technique. This was probably due to thermal debromination of the compound in the operating conditions of the gas chromatography equipment. Quantitation of this compound was therefore impossible. However, deca-BDE is detected in chromatograms obtained using GC-ECD systems. No other compounds are detected at times corresponding to elution of this compound. Chromatograms obtained using the GC-ECD also featured peaks originating probably from products of thermal decomposition (debromination) of deca-BDE: nona-BDE, octa-BDE, and hepta-BDE. However, it was impossible to determine whether debromination occurred during extraction or during chromatographic analysis. Fig. S3 presents example chromatograms obtained in GC-ECD, with peaks from deca-BDE. The chromatographic image might be improved by using a shorter (e.g. 15 m) chromatography column which would reduce thermal decomposition of BDE-209.

3.7. Concentrations of selected PBDEs in studied samples

Table 4 and diagrams (Fig. S4) present the results of determination of selected PBDEs in car filter samples. Based on the results of analyses aimed at determination of PBDEs in car filter samples, one may observe that filters replaced after one year of exploitation are characterized by lower PBDEs concentrations. Filters from the car label F1 were the only filters to be replaced after two years of exploitation, and were therefore exposed to higher accumulation of PBDEs, particularly BDE-47. Filters from cars manufactured before the ban on the use of PBDEs in industrial production become effective (F1 and F4) were characterized by higher BDE-47 levels. BDE-47 was one of the main constituents of the penta-BDE technical mixture. In addition, compared to other PBDEs, BDE-47 is characterized by higher potential of migration from polymer materials into dust. This might be the cause of the high content of BDE-47 in the tested samples (assuming that the internal cabin air circulation was used by the car users) In most cases, the mean content of the tested representatives of the PBDEs class (except for BDE-47) was within the range of 6.4–12.3 ng/g regardless of whether car filters or air conditioning filter dust were used as the samples. This may suggest that the obtained values are representative for the atmospheric PBDEs content. Any deviations from the mean levels within the range specified above were observed only for lower-brominated BDEs which are characterized by higher potential for migration from the indoor equipment into air and subsequent deposition in dust. Therefore, all deviations from the aforementioned range may be interpreted as: 1) the effect of emission from cabin furnishing elements in cases when the range was exceeded for PBDEs levels in cabin air filters; 2) formation of lower-brominated PBDEs by means of



debromination of higher-brominated compounds at elevated engine operating temperatures in cases when the range was exceeded for PBDEs levels in engine air filters. Engine operating temperatures depend, among other factors, on proper operation of the cooling system. Radiator leaks are the most common causes of engine temperature elevation and possible overheating. In such conditions, the rate of debromination increases, possibly contributing to formation of higher quantities of lower-brominated PBDEs.

Table 4 Median and concentration ranges of selected PBDEs congeners determined in car filter samples (n = 9, each sample was analyzed twice).

			BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183
F 1	cabin	Median [ng/g]	9.7	424	30	15	9.6	9.8	7.4
		Range [ng/g]	9.3-10.4	137-537	27-33	13-18	9.2-10,8	9.2-10.1	7.1-9.1
	engine	Median [ng/g]	9.1	373	25	33	10	9.8	7.4
		Range [ng/g]	9.0-9.4	171-512	25-32	24-79	9-17	9.2-10.6	7.2-7.7
F 2	cabin	Median [ng/g]	9.7	177	9.1	<LOD	9.2	9.7	7.5
		Range [ng/g]	8.6-12.3	136-213	7.5-10.6	<LOD	8.0-10.5	8.9-10.6	6.3-7.8
	engine	Median [ng/g]	8.6	64.5	8.7	<LOD	8.8	9.6	7.5
		Range [ng/g]	8.9-9.4	46-96	8.6-10.0	<LOD	9.0-10.1	9.8-11.1	7.0-9.2
F 3	cabin	Median [ng/g]	9.7	51	9,0	<LOD	9.3	9.9	7.4
		Range [ng/g]	9.3-10.1	33-64	8.5-10.0	<LOD	9.1-9.6	9.7-10.6	7.1-8.2
	engine	Median [ng/g]	9.0	55	9.4	<LOD	9.1	9.9	7.1
		Range [ng/g]	8.9-9.3	31-96	9.1-10.3	<LOD	9.1-9.3	9.7-10.1	6.9-7.7
F 4	cabin	Median [ng/g]	9.4	533	9.7	<LOD	10	10	7.4
		Range [ng/g]	8.9-9.8	144-610	8.8-13.4	<LOD	9.1-10.8	9.7-10.5	7.2-7.9

	engine	Median [ng/g]	9.0	406	9.7	<LOD	9.8	10	8.0
		Range [ng/g]	8.9-9.3	370-688	9.0-11.3	<LOD	9.1-10.3	9.7-10.7	7.1-10.1
F	cabin	Median [ng/g]	9.5	334	10.1	<LOD	9.6	10	8.4
		Range [ng/g]	8.3-10.4	104-383	8.6-10.8	<LOD	9.2-10	9.2-10.6	7.3-9.2
5	engine	Median [ng/g]	9.0	274	9.6	<LOD	9.3	9.6	7.3
		Range [ng/g]	8.4-9.5	103-376	9.1-9.9	<LOD	9.1-9.3	9.1-9.9	7.1-9.9

Table 5 Mean value and standard deviation of PBDEs concentrations in dust samples taken from air conditioning filters placed at the air inlet and at the air outlet (n = 9).

			BDE28 [ng/g]	BDE47 [ng/g]	BDE100 [ng/g]	BDE99 [ng/g]	BDE154 [ng/g]	BDE153 [ng/g]	BDE183 [ng/g]
Changed in 2016	Outlet	dSPE	18.3±3.6	61.1±8.4	192±44	57±20	23.8±3.6	25.1±2.0	16.6±2.2
		MSPD	18.4±6.2	41±18	231±15	77±18	25.6±6.3	22.1±2.7	16.1±2.0
	Inlet	dSPE	18.7±8.9	21.7±2.2	17.2±9.3	<LOD	15.9±3.8	19.2±6.5	13.0±2.2
		MSPD	19.4±9.3	40±24	-	-	25.1±8.9	21.6±3.7	14.9±1.3
Changed in 2017	Outlet	dSPE	18.4±2.8	52±16	79±52	66±18	20.4±3.5	25.5±9.3	14.4±4.2
		MSPD	17.6±7.7	100±35	320±21	86±42	35±25	26.4±8.1	39±35
	Inlet	dSPE	19.2±1.6	20.2±3.2	16.9±2.5	<LOD	18.2±9.2	19.5±1.4	14.0±1.2
		MSPD	20.5±1.9	23.4±5.5	-	-	20.3±2.7	22.8±3.2	16.1±5.5

„-“, means occurrence of the co-elution and lack of the possibility of quantification

Further studies are required to confirm the aforementioned hypotheses. Table 5 lists the results of PBDEs determinations in dust samples collected from air conditioning filters. The results obtained using two sample preparation techniques, namely dSPE and MSPD are included. Histograms comparing the results of dSPE and MSPD were prepared to evaluate the efficiency of MSPD as the sample preparation technique (Fig. S5). This facilitated determination of the

statistical significance of the differences between the results obtained using different methods. The efficiency was assessed by verifying whether the uncertainty range of results obtained using the MSPD technique overlapped with the uncertainty range of results obtained using the dSPE technique. Most differences were found not to be statistically significant (the standard deviation ranges obtained for the procedures being compared had no common overlapping part only in the single case of BDE-100 in the sample of dust collected from an air conditioning exhaust filter exchanged in 2017). However, objections are raised by the unsatisfactory repeatability of results obtained using the MSPD technique as manifested by high standard deviation values of up to 90%.

3.8. Assessment of exposure to selected PBDEs

An attempt to estimate human exposure was made on the basis of the results of the determination of PBDEs content in car filter samples and air conditioning filter dust samples. The following equation was used for this purpose: (5) $E = C \cdot DIR \cdot IEF$, where E – size of the exposure [ng/day], C - concentration of PBDE compounds in the tested samples [ng/g], DIR - coefficients of dust particles absorption [g/day], IEF - part of the day during which the exhibition appeared.

Data on daily intake rates were obtained from the literature (DIR = 60 mg/day for children aged 12–24 months and 50 mg/day for adults). Since no data were available regarding daily intake of car filters, and since the amounts of dust deposited on the filter were small, surface the assumed value was that of 0.1 of the daily intake rate for dust. The IEF was assumed to have the value of 0.33 corresponding to 8 h being spent daily in the public institution from which the air conditioning filters were collected for dust sampling. In the case of passenger cars, the respective values were estimated at 0.06 for adults and 0.05 for children aged 12–24 months. The obtained exposure values should be adjusted for body weight, i.e. for the mean body weight of 75 kg for adults and the mean body weight of 15 kg for children aged 12–24 months. Presented in Tables S8 and S9 are the data on the exposure to PBDEs compounds calculated on the basis of PBDEs contents in car filter samples and air conditioning filter dust samples. In the literature there is lack of the knowledge about exposure assessment to the PBDEs occurring in the car filters. There are more information about research concern exposure to PBDEs after contact with the car dust [34–36]. Presented data can complement this information.

4. Conclusions



Samples of car filters and air conditioning filter dust are characterized by complex matrix composition. Therefore, much effort must be put into selection of optimum conditions for purification of extracts for determination of PBDEs. Since the concentrations of PBDEs are very low, conditions assuring high sensitivity of determinations are crucial. Ultrasound-assisted dispersive solid phase extraction (UA-dSPE) was found to perform better in terms of extract purification than the conventional SPE technique. Evidence to that was provided by the lower number of compounds coeluting with PBDEs and by lower elevation of chromatogram elevation). Determination of the highest-brominated representative, BDE209, was associated with significant problems. Model studies showed that the compound was eluted from individual SPE adsorption beds, as confirmed by quantitative GC-ECD analyses. Evaluation of PBDEs content in car filters may contribute to the knowledge on the quality of air within the vehicle cabins. In fact, determination of PBDEs in car filters collected from the cabin as well as the engine air purification systems, allowed for evaluation of the quality of inflowing air. However, vehicle age may have impact on the quantities of PBDEs deposited on car filters. This was indicated by the content of lower-brominated PBDEs being significantly higher in samples of filters which had been used for two years in a car manufactured before the ban was placed on the use of PBDEs in industrial production. This observation is valid on the condition that internal air circulation had been used in the car, as in this case, PBDEs emitted from cabin furnishing elements might have been deposited on dust and the filter material. In addition, differences were observed between the concentrations of analytes deposited on cabin filters and analytes deposited in engine air filters. Both filters are used for cleaning the air entering the vehicle from the outside, and therefore the higher concentration of lower-brominated PBDEs in cabin filter samples may be suggestive of emission from car interior equipment contributing to total PBDEs levels. On the other hand, when the levels of lower-brominated PBDEs are higher in engine air filter samples than in the cabin air filter samples, the finding may be explained by debromination of higher-brominated PBDEs occurring at elevated temperatures of engine operation. Verification of all these hypotheses requires further studies. As far as the air conditioning system filters were concerned, higher levels of PBDEs were observed in samples collected from filters responsible for purification of air being evacuated from the facilities. This was due mainly to the type of equipment present within the facilities (i.e. large quantities of electrical and electronic equipment) Tetra- penta-, and hexa-BDEs were predominant among the detected compounds; this may be due to the fact that these compounds are the main compounds of the commercial penta-BDE mix that had been widely used in the production of indoor furnishings. The higher concentrations of compounds containing 4 to 5



bromine atoms within their molecules is consistent with the order in which individual representatives of the PBDEs class are released from the surface of the indoor equipment: BDE47 > BDE99 > BDE100 > BDE153 > BDE154. Due to the presence of numerous electrical and electronic devices within the facility rooms, one should expect that the dust samples would contain BDE-209 since the deca-BDE commercial mix was dedicated to this type of products. Studies to verify this hypothesis will be carried out in near future. MSPD may provide an interesting alternative for SPE-based dust extract purification procedures. Of key importance is the selection of appropriate sorbents facilitating simultaneous extraction and purification of extracts. With no doubt, appropriate sample to sorbent mixing ratio is also important. The presented problem is worth further investigation as it may provide an interesting alternative for multistage analytical procedures and - on the other hand - for the PLE technique. The latter, despite allowing for significant shortening of the reaction times and solvent savings, may be unreliable when used with dust samples (as the particles may enter the system and clog it due to their small diameters). The presented attempt at estimating the exposure to PBDEs indicates the necessity of cabin filters and air conditioning filters being replaced in a regular fashion. In addition, the finding may be of importance for the assessment of occupational hazards to individuals responsible for regular filter replacements as well as provide a premise for the requirement of personal protection equipment (dust masks) being worn by such individuals.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: <https://doi.org/10.1016/j.chroma.2018.06.041>.

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