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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.

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: penta-BDE, 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

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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.

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, BDE-153, 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, Fluka AG, 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