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Multi-analyte method for the analysis of various organohalogen compounds in house dust

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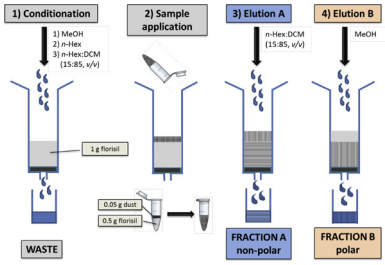
HIGHLIGHTS

- A novel approach for analysis of 27 BFRs and 18 PFASs in indoor dust is presented.
- A miniaturized method based on MSPD was used for the fractionation/isolation of analytes.
- Good performance characteristics were obtained for all target contaminants.
- A method was successfully applied for the analysis of BFRs and PFASs in dust samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, a novel analytical approach for the simultaneous determination of 27 brominated flame retardants (BFRs), namely polybrominated diphenyl ethers (PBDEs), isomers of hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and several novel BFRs (NBFRs), together with 18 perfluoroalkyl substances (PFASs) in indoor dust was developed and validated. To achieve integrated isolation of analytes from the sample and their fractionation, a miniaturized method based on matrix solid phase dispersion (MSPD) was employed. Principally, after mixing the dust (<0.1 g) with the Florisil®, the mixture was applied on the top of a sorbent (Florisil®) placed in glass column and then analytes were eluted using solvents with different polarities. For the identification/quantification of target compounds largely differing in polarity, complementary techniques represented by gas and liquid chromatography coupled to tandem mass spectrometry (GC–MS/MS and LC–MS/MS) were used. The results of validation experiments, which were performed on the SRM 2585 material (for PBDEs, HBCDs and TBBPA), were in accordance with the certified/reference values. For other analytes (NBFRs and PFASs), the analysis of an artificially contaminated blank dust sample was realized. The method recoveries for all target compounds ranged from 81 to 122% with relative standard deviations lower than 21%. The quantification limits were in the range of 1–25 ng g^{-1} for BFRs and 0.25–1 ng g^{-1} for PFASs. Finally, 18 samples (6 households × 3 sampling sites) were analyzed. The high variability between concentrations of PFASs and BFRs in the dust samples from various households as well as collecting sites in a respective house was observed. The total amounts of PFASs and BFRs were in the range of 1.58–236 ng g^{-1} (median 10.6 ng g^{-1}) and 39.2–2320 ng g^{-1} (median 325 ng g^{-1}), respectively. It was clearly shown that dust from the indoor environment might be a significant source of human exposure to various organohalogen pollutants.

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1. Introduction

House dust originates from a number of sources and is a sink for different organic compounds, varies substantially in its chemical and biological compositions and is a heterogeneous material. Therefore, the analysis of chemicals in this matrix is a good indicator of contamination occurring over a long period of time [1]. Indoor contamination by organohalogen pollutants, which may occur as a result of their migration from consumer products, has been recognized as an issue of concern. The indoor air and dust, in addition to food, are the major sources of exposure for general population [2–4]. Of particular concern is the high body burden in infants/children due to the "hand to mouth" contact with dust and the evidence, provided so far by animal studies, that these compounds may induce various adverse health effects related to hepatotoxicity, carcinogenicity, developmental neurotoxicity or endocrine disrupting effects [5,6].

High production volume chemicals such as perfluoroalkyl substances (PFASs) and brominated flame retardants (BFRs), the latter group represented mainly by polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA), are obviously present in the indoor environment. Due to their unique characteristics, such as chemical inertness, stability, hydrophobicity and lipophobicity of PFASs and an inhibitory effect of BFRs on the ignition of combustible organic materials, they are used in a variety of industrial and consumer applications [7,8]. As a result of the restrictions on the technical mixtures of PBDEs and HBCDs [9,10,11], one of them is their inclusion in the Stockholm Convention list in 2009 and 2013, respectively [12,13], it might be thought likely that there has been an increased demand for alternative (or novel/non-PBDE) flame retardants to meet flammability standards. Indeed, many researches have established the presence of these novel BFRs (NBFRs) both in indoor and outdoor environments as summarized by de Wit et al. [14]. In spite of the fact, that PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOS-F) have been added to the Stockholm Convention list of the new persistent organic pollutants since 2009 [15], the production of other fluoropolymers still continues [16].

Despite the growing number of studies dealing with the occurrence of BFRs and/or PFASs in dust, none of them considered integration of sample preparation steps into a common protocol. Regarding BFRs, several analytical protocols combining the determination of various brominated representatives, such as PBDEs, HBCD, TBBPA and/or NBFRs, have been recently published. In general, the most common isolation techniques for various BFR classes are Soxhlet extraction [17–20], pressurized liquid extraction (PLE) [21–24] and ultrasonic extraction with non-polar or slightly polar solvents and their mixtures: toluene, *n*-hexane (*n*-Hex), dichloromethane (DCM), acetone (Ac) [24–30]. Individual BFR groups can be subsequently fractionated/purified on the Florisil® [18,20,22,24,26], acidified (H_2SO_4)/deactivated (H_2O) silica [17,18,23,24,26,27,30] or deactivated Alumina [28]. In the case of PFASs, isolation strategies are mainly based on extraction by polar solvents (methanol (MeOH) and acetonitrile (MeCN)) [2,31–38]. Purification of crude extracts is often done by dispersive solid phase extraction (d-SPE) with an EnviCarb sorbent [2,36,38], or by a SPE column employing various sorbents, such as weak-anion exchange (WAX) and C18 [31,32,35,37].

Regarding to a typical co-occurrence of BFRs and PFASs in dust samples, we decided to integrate analysis of these two groups of halogenated contaminants into a single analytical protocol through combining the advantageous aspects of existing sample preparation approaches until now dedicated to individual groups. It was presumed that in this way, not only a lower sample amount would be required (a dust amount available for analysis is often very limited) and reduction of extraction solvent would be possible, but above all, increased sample throughput would be achieved. As discussed below, matrix solid phase dispersion (MSPD) was found to be a feasible sample processing strategy prior to the instrumental analysis. Within the preliminary investigation of the occurrence of BFRs and PFASs in Czech households the novel multi-analyte method was used for the examination of 18 house dust samples.

2. Materials and methods

2.1. Standards

Certified standards of target BFRs represented by PBDE congeners (No. 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207 and 209), hexabromobenzene (HBB), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), bis(2,4,6-tribromophenoxy) ethane (BTBPE), octabromo-1-phenyl-1,3,3-trimethylindan (OBIND), decabromodiphenyl ethane (DBDPE) and HBCD isomers (α-, β- and γ-) as well as isotopically labeled internal standards ($^{13}C_{12}$-α-HBCD, $^{13}C_{12}$-β-HBCD, $^{13}C_{12}$-γ-HBCD, $^{13}C_{12}$-BDE 47, $^{13}C_{12}$-BDE 99, $^{13}C_{12}$-BDE 153 and $^{13}C_{12}$-BDE 209) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). The standard of TBBPA together with $^{13}C_{12}$-TBBPA was obtained from Cambridge Isotope Laboratories (Andover, Massachusetts, USA). The individual standards of PFASs as well as their isotopically labeled analogues ($^{13}C_4$-PFBA, $^{13}C_5$-PFPeA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_8$-PFOA, $^{13}C_6$-PFDA, $^{13}C_2$-PFDoDA, $^{13}C_3$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_8$-FOSA, d_5-EtFOSA) were purchased from Wellington Laboratories. The purity of all individual standards was at least 98%. Calibration solutions prepared in MeOH containing HBCD isomers and TBBPA at concentrations 0.25, 0.5, 2.5, 5, 25 and 50 ng mL^{-1} and PFASs at 0.05, 0.1, 0.5, 1, 5 and 10 ng mL^{-1} were stored at 5 °C. Each calibration standard contained internal standard $^{13}C_{12}$-α-HBCD, $^{13}C_{12}$-β-HBCD, $^{13}C_{12}$-γ-HBCD and $^{13}C_{12}$-TBBPA at 5 ng mL^{-1} and ^{13}C-PFASs at 1 ng mL^{-1}. Similarly, calibration solutions with BDE 28–203, HBB, PBT, PBEB and BTBPE at concentration levels 0.05, 0.1, 0.5, 1, 5, 10, 50, 100 and 500 ng mL^{-1} and BDE 206, 207, 209, OBIND and DBDPE at 0.25, 0.5, 1, 5, 10, 50, 100, 500 and 1000 ng mL^{-1} were prepared in isooctane and stored at 5 °C in the refrigerator. Each calibration level contained internal standard $^{13}C_{12}$-BDE 47, $^{13}C_{12}$-BDE 99 and $^{13}C_{12}$-BDE 153 at 5 ng mL^{-1} and $^{13}C_{12}$-BDE 209 at 50 ng mL^{-1}.

The standard reference material of dust SRM 2585 used for the method development and validation experiments was supplied by the US National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, USA).

2.2. Chemicals, reagents and other materials

MeOH for LC–MS, *n*-Hex, isooctane and DCM were supplied by Merck (Darmstadt, Germany). HPLC grade ammonium acetate (99.99%) was obtained from Sigma–Aldrich (Steinheim, Germany). Water purified by a Milli-Q® Integral system (no PFASs containing polymers) supplied by Merck was used throughout the study. Acetone was purchased from Penta (Chrudim, Czech Republic). Polypropylene (PP) centrifuge tube filters (nylon, pore size 0.22 μm) were supplied by Sigma–Aldrich. Florisil® for residual analysis (0.15–0.25 mm) obtained from Merck was activated by heating at 600 °C for 4 h, than at 130 °C for 5 h and finally stored in a desiccator. Silica (0.063–0.200 mm) supplied by Merck was activated by heating at 180 °C for 5 h than deactivated by adding 2% of deionised water, shook for 3 h and finally stored in a desiccator for 16 h before use. The SPE glass columns (i.d. 1 cm, volume 6 mL) and glass wool were supplied by Sigma–Aldrich and Merck, respectively.