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Review

PBDEs in environmental samples: Sampling and analysis

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ABSTRACT

The paper reviews the subject literature concerning analytical procedures routinely sed for monitoring polybrominated diphenyl ethers (PBDE) in environmental samples.

It describes and summarizes subsequent stages of analytical procedure including sample collection and preparation, extraction, clean-up and final determination. Different approaches with their advantages and limitations are presented. Special attention is drawn to the newly developed, promising extraction techniques, especially: liquid–liquid-microextraction (LLME) with its modifications, cloud point extraction (CPE) and hollow fiber microextraction. The review compares available detection techniques taking into account their usefulness for determining different PBDEs in complex matrix as well as discussing possible limitations that may occur during the analysis. The quality assurance and quality control aspect of analytical procedure is described. Finally special attention is paid to the determination of highly brominated PBDE compounds (e.g. BDE209), which requires implementation of different analytical approach.

Contents

Abbreviations: APCI, atmospheric pressure chemical ionization; APPI, atmospheric pressure photoionization; ASE, accelerated solvent extraction; ASTM, American Society for Testing and Materials; BFR, brominated flame retardants; CPE, cloud point extraction; DCM, dichloromethane; DLLME, dispersive-liquid–liquid-microextraction; ECD, electron capture detector; ECNI, electron capture negative ionization; EIMS, electron impact mass spectrometry; GC, gas chromatography; GFF, glass fiber filter; GPC, gel permeation chromatography; HF-LPM, hollow fiber microporous membrane liquid–liquid extraction; HF-LPME, hollow fiber liquid phase microextraction; HF-MMLLE, hollow fiber micro-porous membrane liquid–liquid extraction; HPLC, high pressurized liquid chromatography; HRMS, high resolution mass spectrometry; ICP-MS, plasma coupled mass spectrometry; IUAPC, The International Union of Pure and Applied Chemistry; IM, ion mobility; LC, liquid chromatography; LLE, liquid–liquid extraction; LLME, liquid–liquid microextraction; LRMS, low resolution mass spectrometry; MAE, microwave assisted extraction; MSD, mass selective detector; MS, mass spectrometry; MWCNTs-SPME, multi walled carbon nanotubes-solid phase microextraction; PBB, polybrominated biphenyls; PBDEs, polybrominated diphenyl ethers; PCBs, polybrominated biphenyls; PCDD/F, polychlorinated dibenzodioxines; POPs, persistent organic pollutants; QA/QC, quality assurance/quality control; PTV, programmed temperature vaporizing injector; PTV-LV, programmed temperature vaporizing large volume injector; QFF, quarto fiber filter; QISTMS, quadrupole ion storage mass spectrometry; QuEChERS, quick easy cheap effective rugged safe; SBSE, stir bar sorptive extraction; SFE, supercrtical fluid extraction; SPE, solid phase extraction; SPE-DLLME, solid phase liquid–liquid-microextraction; SPLE, selective pressurized liquid extraction; SPME, solid phase microextraction; SVOC, semivolatile organic compounds; TOF, time of flight (analyzer); UPLC, ultra performance liquid chromatography; USAE, ultrasound assisted extraction; USAL-DPSE-DLLME, ultrasound-assisted leaching-dispersive solid-phase extraction followed by dispersive liquid–liquid microextraction.

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1. Introduction

1.1. Polybrominated diphenyl ethers; characteristics and distribution

Polybrominated diphenyl ethers (PBDEs) belong to the group of brominated flame retardants (BFRs), introduced in middle of 70s of XX century, in response to the ban of previously used flame retardants, such as polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs) [1]. Since then, the interest in behavior of PBDEs and their distribution into different compartments of environment has systematically increased. This can be reflected in the increasing number of articles published on the issue of chemical analysis of PBDEs during the last 10 years (Fig. 1). According to the ISI Web of Knowledge^{SM}, there have been more than 30 review articles published on the issue of BFRs so far. The most frequently citied review articles, together with their main scientific scopes are listed in Table 1.

According to the scientific papers, 209 congeners are classified as PBDEs, among which all contain diphenyl ether skeleton and all are named according to the number and position of bromine atoms by the IUPAC system [10]. Chemical structure of polybrominated diphenyl ethers (PBDEs) is presented in Fig. 2.

Polybrominated diphenyl ethers are applied as additives to numerous polymers; plastics, textiles, and other materials to prevent or retard the spread of fire. Thus they are present in the wide range of consumer products, such as, furniture electrical or electronic devices and automobile parts [11]. Examples of materials in which different mixtures of PBDEs are present are listed in Table 2. Despite wide range of applications, not all of PBDEs are employed in commercially available mixtures: penta-, octa- and decaBDE. The pentaBDE mixture is mostly applied in furniture, while the two other remaining higher-brominated mixtures (octa- and decaBDE) are employed in hard plastics, house electrical equipment, such as TV sets and computers. PBDEs are easily integrated into polymers during manufacture process, however, due to the lack of binding sites on polymers surface are not chemically bonded to the material. Therefore PBDEs are classified as additive flame retardants and can be easily released into environment by volatilization or dust formation during the use of treated products. According to the reviews published on this issue, PBDEs are distributed into all compartments of environment (Fig. 3) [12,13]. The environmental fate of different congeners depends to a large extent on their chemical properties, such as partitioning coefficients. Therefore pentaBDE is reported to be present mainly in the atmosphere and aqueous media, while higher brominated compounds (e.g. BDE209) tend to accumulate in soil and sediments [6].

Polybrominated diphenyl ethers tend to bioaccumulate, especially in aqueous organisms. Swedes Andersson and Blomkvist were first who in 1981 detected PBDEs congeners in freshwater species collected along the Viskan River in southern Sweden. Then, few years later Jansson confirmed the presence of PBDE in tissues of fish-eating birds and marine mammals living in Baltic

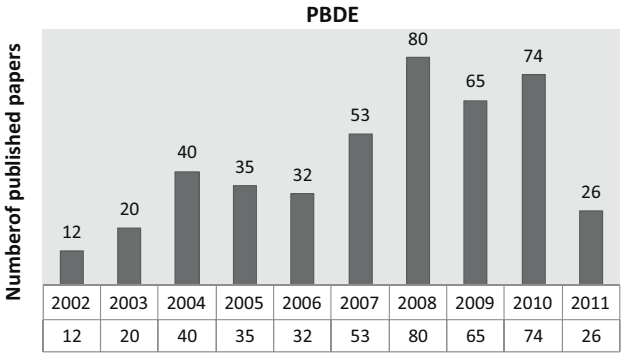

Fig. 1. Number of papers published on PBDEs issue since 2002.

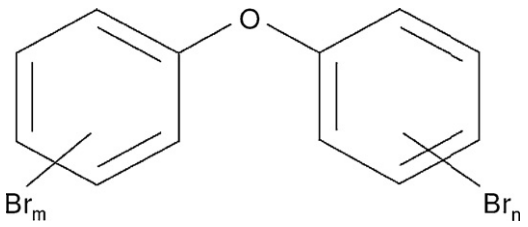

Fig. 2. Chemical structure of polybrominated diphenyl ethers (PBDEs).

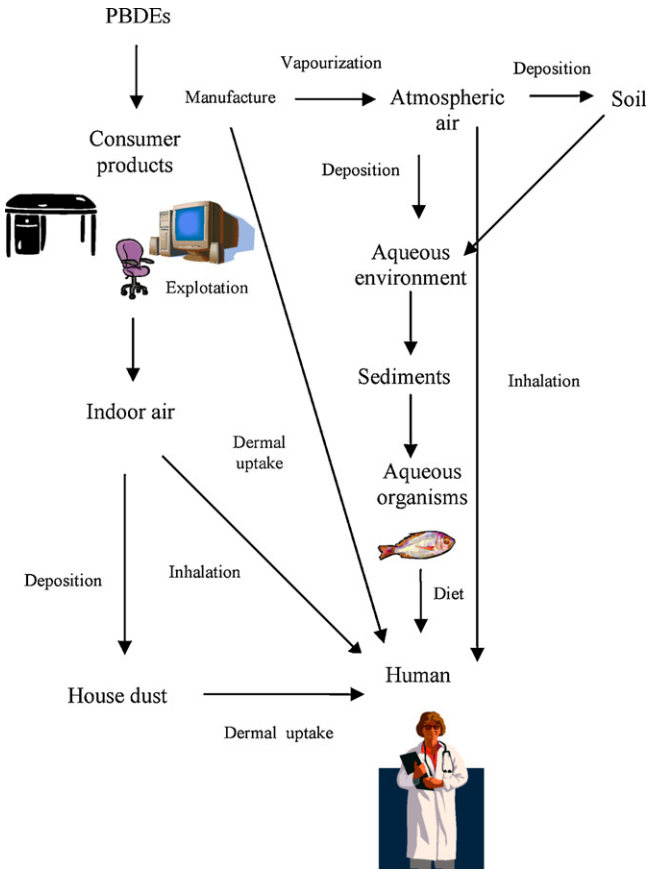

Fig. 3. The scheme of PBDEs circulation and environmental fate.