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Determination of polybrominated diphenyl ethers in domestic dust by microwave-assisted solvent extraction and gas chromatography–tandem mass spectrometry

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Abstract

In this paper, a rapid and simple method for the analysis of polybrominated diphenyl ethers (PBDEs) in house dust samples based on microwave-assisted solvent extraction (MASE) and gas chromatography–tandem mass spectrometry (GC–MS/MS) is presented. Extraction conditions were optimized using a multifactorial experimental design approach. The use of an aqueous NaOH phase in combination with a non-polar organic phase (hexane) to extract the target analytes from dust allowed an efficient extraction and reduced chromatographic background. The final hexane extracts could be analyzed after a simple one-step cleanup procedure using Florisil. The validation of the method was performed in terms of accuracy, linearity, and repeatability. The limits of detection (LODs) ranged from 0.29 to 0.55 ng/g for all compounds. The target PBDEs were found in several real dust samples collected in urban and rural houses of Northwestern Spain.

Keywords: Polybrominated diphenyl ethers; Flame retardants; Microwave-assisted solvent extraction; Factorial design; Gas chromatography–tandem mass spectrometry; Home dust

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of brominated compounds widely used as additive flame retardants in many common domestic products such as furniture, carpeting, mattresses, and electrical and electronic equipment. As additives, they are physically combined with the polymeric material being treated and they have the potential to diffuse out of the material into the environment when conditions are favourable. Once in the environment, PBDEs can be very persistent or break down into other forms, depending on surrounding conditions [1].

These compounds are manufactured as three main technical mixtures, pentaBDE, octaBDE, and decaBDE, accounting for 11, 6, and 83% of the global market, respectively [2]. The pentaBDE has been mainly used in polyurethane foam for soft furnishings, mattresses, car seating and insulation; the octaBDE is mainly used in acrylonitrile-butadiene-styrene (ABS) polymer for equipment casings; and the decaBDE mixture is used in hard plastics for electronic equipment components and casings, plus flame retarded rubbers and textile back coatings [3].

In contrast to the decreasing levels of most of persistent organic pollutants over the last 20 years, PBDEs levels in the environment are increasing [4]. In spite of decaBDE mixture having the major market share, BDE-47 and BDE-99, the main congeners of the pentaBDE mix, are generally those detected at the highest levels in biota and the environment [5]. Due to their persistent and bioaccumulative nature, penta- and octabrominated commercial mixtures have been banned in the European Union and phasing out of their use has recently begun in North America. However, PBDEs will be still present in consumer products for decades to come [6].

Sources of human exposure to PBDEs remain poorly characterised and, although intake through food consumption is undoubtedly important, the potential for exposure to PBDEs in the indoor environments, is also real. In this way, inhalation and inadvertent ingestion of house dust have been recently reported to be the largest contributor of PBDEs exposure of toddlers through to adults [7].

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Sample preparation procedures for the analysis of PBDEs generally consist of the extraction of the analytes from the sample matrix, followed by cleanup and extract fractionation to remove interfering compounds [8,9] and finally, analytical determination by GC with electron-capture detection (ECD) [10–12] or GC–MS [13–15]. The determination of these compounds in dust is a difficult task due to the high content of organic matter (from 20 to 40% of total organic carbon) in this kind of matrix. This makes necessary an exhaustive cleanup of the extract to obtain a chromatographic suitable solution.

PBDEs have been mainly extracted from dust by Soxhlet [16–20], although other extraction techniques such as pressurized solvent extraction [6,21] and ultrasounds assisted extraction [22] have recently been applied. Regarding extract cleanup, in most cases interfering compounds were removed using multistep procedures generally including, normal phase sorbents and gel permeation chromatography [9,21]. As known, multi-step procedures induce several inherent problems such as time-consumption, risk of analyte loss and contamination.

The present study constitutes the first application of microwave-assisted solvent extraction (MASE) for the determination of PBDEs in house dust. The final analysis was carried out by gas chromatography coupled to tandem mass spectrometry (GC–MS/MS). Extraction conditions were optimized by means of a multifactorial experimental design approach. The selectivity of the extraction procedure enabled to perform a simple and rapid on-batch extract cleanup step as an alternative to multistep procedures, in an attempt to reduce time-consumption and to overcome some of the above commented problems. Method performance was evaluated in terms of recovery, precision, accuracy and limits of detection (LODs). Finally, several real samples collected in urban and rural houses of Northwestern Spain were analyzed.

2. Experimental

2.1. Reagents, standards and materials

Sulphuric acid, sodium hydroxide, organic solvents for trace analysis (acetone, *n*-hexane and isooctane), anhydrous sodium sulphate, and neutral silica (40–63 μm) were purchased to Merck (Darmstadt, Germany). Florisil (150–250 μm) was obtained from Sigma–Aldrich (Milwaukee, WI, USA). Silica and Florisil were activated at 130 °C overnight before use. Sep-Pak cartridges (3 mL, 500 mg) were supplied by Waters (Milford, MA, USA).

PentaBDE mixture in cyclohexane with a total PBDE concentration of 10 μg/mL was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The composition of this commercial solution is: 4.1 μg/mL of BDE-47, 0.10 μg/mL of BDE-85, 4.1 μg/mL of BDE-99, 1.2 μg/mL of BDE-100, 0.23 μg/mL of BDE-153 and 0.34 μg/mL of BDE-154 [15]. Individual solutions of BDE-47, BDE-100, BDE-99, BDE-154, BDE-153 and ^{13}C-labeled BDE-99 (50 μg/mL in nonane) were obtained from Wellington Labs (Ontario, Canada). BDE-85, (50 μg/mL in isooctane) was purchased to Accustandard (New Haven, CT, USA). Working standard solutions, at different concentrations, were prepared by subsequent dilutions in *n*-hexane. Both stock and working solutions were stored at −20 °C.

Dust samples were obtained from vacuum cleaner bags collected in homes of the North West of Spain. Samples were passed through a 60 μm stainless steel sieve to remove fibrous material and other large pieces and to obtain a suitable degree of homogeneity. They were then stored at room temperature until analysis. One additional sample was kindly supplied by the RIVO Institute (IJmuiden, The Netherlands) in the frame of an interlaboratory comparison study. A standard reference material for organic contaminants in house dust (SRM 2585) was purchased to the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

2.2. Experimental set-up

Microwave-assisted extractions were performed using an Ethos E Microwave Solvent Extraction Labstation (Milestone, Bergamo, Italy), equipped with 12 pressurized 100 mL vessels. Numerical analysis of the data resulting from the experimental design was made with the statistical package Statgraphics-Plus 5.1 (Manugistics, Rockville, MD, USA).

Prior to extraction, 20 ng of ^{13}C-labeled BDE-99 (in hexane) were added to each sample as surrogate standard. Under final optimized conditions, dust samples (0.8 g) were extracted using 8 mL of *n*-hexane and 4 mL of a 10% sodium hydroxide aqueous solution at 80 °C for 15 min. The organic phase was taken and dried with anhydrous sodium sulphate. After a simple cleanup step (see below), 2 mL of extract were evaporated to approximately 0.5 mL using the Turbo Vap system (Zymark, Hopkinton, MA, USA) and then transferred to GC autosampler vials and additionally concentrated to 0.2 mL under a gentle stream of nitrogen. Final extracts were stored at −20 °C until analysis.

Factorial design optimization was performed using 0.8 g portions from a pooled dust sample spiked with the technical pentaBDE mixture in a total concentration of 200 ng/g. For the recovery study, real samples (0.8 g) were spiked at 50 and 200 ng/g with the pentaBDE mixture. Extractions were carried out once the solvent was evaporated, after at least 6 h.

2.3. Instrumental analysis

PBDE determination was carried out using a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA) coupled to an ion trap mass detector Varian Saturn 2000 with a wave-board for MS/MS analyses and operated with a Saturn GC–MS workstation 5.4 software-based data handling. The column used was a CP-Sil8 CB low bleed (30 m × 0.25 mm I.D., 0.25 μm film thickness). The GC oven temperature was programmed from 60 °C (2 min) to 250 °C at 30 °C/min and then until 280 °C (hold for 8 min) at 5 °C/min (total analysis time: 22.33 min). The injector temperature was held at 280 °C, and the injection was performed in the splitless mode (2 min). The split flow was set at 50 mL/min. Helium (purity 99.999%) was employed as carrier gas at constant column flow (1.2 mL/min). The mass spectrometer was operated in