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Short communication

Use of fluorinated polybrominated diphenyl ethers and simplified cleanup for the analysis of polybrominated diphenyl ethers in house dust

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ABSTRACT

A simple, cost-effective method is described for the analysis of polybrominated diphenyl ethers (PBDEs) in house dust using pressurized fluid extraction, cleanup with modified silica solid phase extraction tubes, and fluorinated internal standards. There are 14 PBDE congeners included in the method, some typically contained in the commercial mixtures used as flame retardants, and some which are not routinely reported in the peer-reviewed literature. A gas chromatographic–mass spectrometry instrumental method provides baseline separation in <20 min, detection limits <20 ng/g, and quantitation limits <60 ng/g for most congeners. Method blanks contained an average concentration < 9 ng/g for all congeners except BDE209 which had an average around 40 ng/g. Spiked samples showed good accuracy with relative percent difference (RPD) <7%, and good precision with relative standard deviation <22% for all congeners except BDE209. The method was applied to the analysis of a standard dust (NIST Standard Reference Material 2585) and showed good accuracy with RPD <25% except for BDE154. Overall, this method exhibited good performance characteristics in all categories including simplicity, cost, sensitivity, selectivity, accuracy, and precision.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are among a class of brominated flame retardants (BFRs) that have widely been used in consumer products. In a typical home, PBDEs can be found in electronic products, textiles such as mattresses and carpets, and furniture. PBDEs are typically additive flame retardants, meaning that they are physically bound to the substrate. Since they are not chemically bound, PBDEs tend to migrate from the product into the indoor environment [1], particularly to dust which is a substantial source of exposure [2–5]. PBDEs are of concern because of potential health impacts including disruption of thyroid hormones [6], neurodevelopmental consequences [7–9] and endocrine disruption [10,11]. While the PBDEs have been or will be removed from U.S. products due to growing concerns about potential health risks [12,13], products containing these chemicals will remain in household use for the foreseeable future. Thus it is important to continue adding and improving the methods for assessing the presence of these chemicals.

There are several important issues that complicate the study of PBDEs in house dust (e.g., matrix complexity, range of physical chemical properties). To facilitate the analysis of PBDEs, sample extracts are cleaned up to isolate analytes from the other components of the dust. These procedures tend to be time consuming and use complex cleanup columns. Therefore, this work developed simple yet effective methods for the cleanup using commercial SPE tubes modified to improve their performance.

Alternatives to the ^{13}C-labeled PBDE internal standards are needed because the labeled PBDEs are relatively expensive and have analytical challenges, particularly ion selection issues and breakdown during analysis [14]. Gas chromatographic mass spectrometry (GC/MS) with negative chemical ionization (NCI) is the method of choice for the analysis of PBDEs in environmental samples. However, labeled PBDEs cannot be used in the NCI analysis because for most congeners, the 79/81 bromide ions are used for quantitation for sensitivity reasons and no differentiation can be made between the labeled and unlabeled congeners. If different analytical instrumentation, ionization modes, or NCI ion selections were made to allow the use of isotopically labeled standards, it is very likely the sensitivity would be diminished and/or the cost

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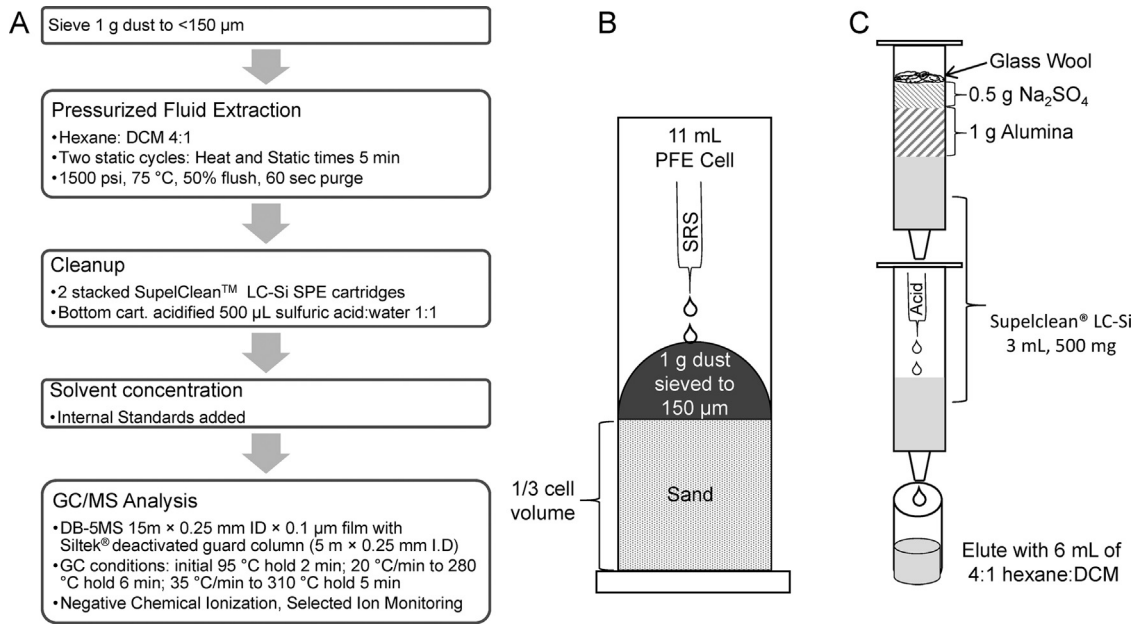

Fig. 1. Analytical procedure flow diagram (A) and drawings of extraction (B) and cleanup (C) steps.

of analysis would increase. In the case of higher brominated congeners where alternate ion selection can differentiate between labeled and unlabeled molecules, we have found that there is not a significant methodological advantage over less expensive alternative internal standards. The use of fluorinated PBDEs reduces or eliminates degradation of highly brominated internal standards to lower brominated BDEs generated during analysis. In this work we demonstrate the analysis of 14 PBDEs using three fluorinated PBDEs (F-PBDEs) as internal standards. Fluorinated PBDEs have a different retention time than the parent PBDE from which it was derived, and are less costly than labeled PBDEs.

2. Materials and methods

A variety of methods have been recently published for the extraction (Soxhlet [15], PFE [16], sonication [17]), cleanup (manually packed columns [18], SPE [19], on-line [20], in-cell [21]), and surrogate/internal standards (^{13}C-BDE(s) [22], native BDEs [23], F-BDEs [24], non-BFR compounds [25]), and instrumental analysis (GC-EI [18], GC-ECNI [26], GC-ECD [27], GC–MS/MS [28], LC–MS/MS [29]) for different combinations of PBDE congeners in dust. The method presented here is similar to that described by Stapleton, Dodder, Offenberg, Schantz and Wise [30] in that both use pressurized fluid extraction (PFE; ASE 200; Dionex Corp., Sunnyvale, CA), commercially available solid phase extraction (SPE) cartridges, analysis by GC/MS with NCI, and MCDE 86L as a surrogate (recovery) standard. In contrast, this method decreases the volume of dichloromethane, pressure and temperature used for extraction; uses modified SPE cleanup cartridges, a thinner film in the GC column with Guard column and heated injection; adds both surrogate recovery and internal standards; and quantitates different congeners and monitors different ions in the mass spectrometer. The exact conditions for this method are described below and are displayed in Fig. 1A–C.

2.1. Extraction

Fig. 1B shows the assembly of the PFE cells to extract house dust mixed with Ottawa sand (Fisher Scientific, Fair Lawn, NJ). 200 ng of MCDE 86L (Wellington Laboratories, Ontario, Canada) and PBDE 181 (Cambridge Isotope Laboratories, Andover, MA) surrogate recovery standards (SRS) were added to the dust prior to extraction. Table 1 details which SRS was used for each measured congener. Each sample was extracted twice and collected in separate 60 mL vials that were later combined. Additional extraction details are included in Fig. 1A.

2.2. Cleanup

Sample cleanup was accomplished using two modified 3-mL, SPE cartridges (Sigma–Aldrich, St. Louis, MO) in tandem. The bottom SPE cartridge was modified by adding 500 µL 95–98% sulfuric acid:water (1:1) and was used without drying. The top SPE cartridge was modified as shown in Fig. 1C. The SPE cartridges were flushed three times with 2 mL of hexane:dichloromethane (4:1). The concentrated sample extract was loaded onto the top cartridge, and eluted as shown in Fig. 1C. After concentration to 1 mL, 500 ng of F-BDEs 69 and 160 and 1000 ng of F-BDE 208 internal standards (Cambridge Isotope Laboratories or Chiron AS, Trondheim, Norway) were added to the extract. Table 1 details which internal standard was used for each measured congener.

2.3. GC/MS analysis

GC/MS analyses were performed on an Agilent Technologies (Santa Clara, CA) 6890N GC equipped with a model 5973 inert MS. The GC column specifications (Agilent Technologies and Restek, Bellefonte, PA), GC temperature program and select MS conditions are shown in Fig. 1A. Helium carrier gas was used at a constant flow rate of 3.2 mL/min. Injections were made in the splitless mode with the inlet temperature set at 260 °C. The ion source and quadrupole temperatures were 150 °C and methane reagent gas was used. Table 1 shows the retention time and ions monitored for each congener.

2.4. Detection/quantitation limit determination and calibration

To determine the detection and quantitation limits for the target congeners, eight PFE cells containing 0.5 g each of diatomaceous earth were spiked with 0 (blank), 1, 5, 10, 25, 50, 250, and 500 ng