Optimization of automated pressurized liquid extraction and cleanup of PBDE in animal feed

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Introduction

Polybrominated diphenyl ethers (PBDEs) are massively used as flame retardants in thermoplastics (e.g. computer and TV housing), textiles, foams, interiors of cars, buses and airplanes due to strict fire regulations. Concurrent with their increasing use, environmental levels of PBDEs have risen because of spillage and emission during production and use, as well as release from the consumer products during their usage and following their disposal at the end-of-life. These compounds are chemically and biologically persistent, lipophilic, able to bioaccumulate in fatty tissues and biomagnify throughout food chains. In 2009, the constituents of Penta-BDE and Octa-BDE technical mixtures (mainly consisting of tetra- to hepta-BDE congeners) have been added as persistent organic pollutants (POPs) candidates since they embody all characteristics of the Stockholm convention definition of POPs: bioaccumulation, toxicity, persistency and long-range transport potential. Penta-BDE mixtures have been banned in 2004 in the European Union [1-3].

Similarly to dioxins, PBDEs present in the animal feed may be transferred to lipid-containing food such as milk and eggs. Therefore, there is a need for developing efficient methods of PBDE determination in animal food matrices.

There are several approaches for sample preparation for PBDE analysis. Sample treatment procedures have typically been based on extraction, purification and fractionation. With animal feed matrices, an automated Power Prep system (Fluid Management System (FMS), USA) has previously been used for PBDE clean-up following manual column extraction and shaking with concentrated sulphuric acid [4].

Our goal was to optimize PBDE extraction and clean-up from a typical feed matrix (fish meal) using a more advanced Total-Rapid-Prep system (FMS, USA) which includes a pressurized liquid extraction module (PLE), multi-column sample cleanup module (Power-Prep) and evaporation/solvent exchange module (SuperVap).
Materials and method

Mixtures of mass-labeled PBDE congeners (BDE-3, -15, -28, -47, -99, -100, -126, -153, -154, -183) and mass-labeled PBDE internal standard solution (BDE-79, -138) were used.

About 10g of feed were mixed with diatomaceous earth, then spiked with 100 µl mixture of mass-labeled PBDE congeners and 100 µl mass-labeled PBDE internal standard solution to monitor recoveries. Extraction was performed on PLE (pressurized liquid extraction module) with n-hexane at 120 °C and 15 MPa (two static cycles of 20 min each, the purge time 120 s). The extracts were evaporated on SuperVap to 10 ml and subjected to automated cleanup on silica and alumina columns. Elution parameters such as solvent mixture composition were optimized (Fig. 1). Elution by 40 ml 20 % DCM/Hex followed by 120 ml 50% DCM/Hex gave the best recovery values for all congeners including di-brominated BDE-15 (Fig. 2). The purified extracts were concentrated on SuperVap and analysed on a TSQ 8000 Evo GC-MS/MS (Thermo, USA) [5].

Result and discussion

We optimized automated extraction and clean-up parameters for di- to hepta-PBDEs in fish meal using Total-Rapid-Prep system (FMS). Compared to the semi-automated method described in [4], we obtained better recoveries for di- to tetra-brominated congeners (Fig. 2) in a fully automated setup which saves time and solvents.

Figure 1. PBDE recoveries after single-run elution with either 20% DCM/Hex or 50% DCM/Hex solvent systems
Figure 2. PBDE recoveries after consecutive elution with 20% DCM/Hex and 50% DCM/Hex solvent systems

References

1. Adrian Covaci, Stefan Voorspoels, Laurence Roosens, Werner Jacobs, Ronny Blust, Hugo Neels. Polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in human liver and adipose tissue samples from Belgium. *Chemosphere* 2008, 73: 170-175.


