

POLYBROMINATED FLAME RETARDANTS - POSTERS

AN INVESTIGATION OF REFERENCE MATERIALS FOR BROMINATED FLAME RETARDANTS

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Introduction

Cumulative global production of Brominated Flame Retardants (BFRs) is estimated at 150,000 tons. BFRs account for the majority of halogenated flame retardants currently in use. There are two groups of BFRs: reactive and additive. Reactive flame retardants (i.e. tetrabromobisphenol, -TBBPA), are chemically bonded into the plastics. Additive flame retardant compounds (i.e. Brominated Diphenyl Ethers-BDEs) are mixed directly with polymers. Environmental occurrence of BFRs is highly dependant on their rates of decomposition. TBBPA's break down with exposure to UV light as do some BDE congeners¹. Larsen et al.² demonstrated that the reactive BFRs are readily metabolized in rats. Hakk et al.³ found that the metabolism rates of some additive BFRs, e.g. BDE-47 and BDE-99 congeners, to be low resulting in their presence and persistence in the environment.

BFRs have been detected in a variety of organisms throughout the food chain. As well, BFRs have been detected in human serum, adipose tissue and more significantly, Noren & Meironyte⁴ showed that the concentrations of BDEs in breast milk has doubled every 5 years over the last 25 years. The need to analyze and assess potential risks of BFRs to humans and the environment is urgent due to their ubiquitous environmental occurrence and the tendencies of some congeners to bioaccumulate.

Within any one class of compounds individual congeners exhibit different physico-chemical properties and biological activity which cause different environmental distributions and toxicity profiles (e.g. only 17 of the possible 210 dioxin/furan congeners are considered toxic). This complicates the derivation of scientifically based regulations for risk assessment. Toxicological tests have shown BDEs can act as both inhibitors and inducers of the Ah receptor⁵. The World Health Organization (WHO) identified TEFs for 12 Polychlorinated Biphenyls (Dioxin-like PCBs or DLPCB) congeners that demonstrated dioxin-like toxicity (AhR-mediated responses)⁶.

This study reports a survey of potential reference material extracts to identify the major BDE congeners present.

Currently there are no certified reference materials for BDEs. It is expected that BDEs will be present in the mono-ortho fraction of a dioxin/furan/DLPCB sample analysis. Analysis of these extracts for BDEs using external standard methods will enable semi-quantitative determination of BDEs present in the sample.

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A Reference Material containing BDEs can be used to monitor a laboratory's performance (precision and bias and assess data quality of a specific sample set analyzed along with the CRM. This is particularly important during the early stages of analyses of emerging classes of compounds.

Method and Materials

Approximately 5g of sample were used for biota and soil/sediment samples. The samples were fortified with the $12\text{ }^{13}\text{C}_{12}$ DLPCB surrogates prior to extraction. Soil samples were Soxhlet extracted using toluene for approximately 16 hours. Tissue samples were acid digested overnight in concentrated HCl. The digested tissue samples were then extracted with hexane via liquid-liquid extraction.

All samples analyzed in this study were cleaned using a classical 3 column (silica/alumina/carbon) dioxin/furan cleanup method. Mono-ortho PCBs (MO-DLPCBs) were isolated in one fraction and the coplanar PCB congeners were isolated in a second fraction with the dioxins and furans. The MO-DLPCB portion of the extract contains the majority of PCBs, organochlorines, and halogenated Diphenyl Ethers (DPEs). The method was developed to force halogenated Diphenyl Ethers into the mono-ortho PCB fraction, away from the dioxin/furan fraction, where they interfere.

Instrumentation

All analyses were performed on a Micromass Ultima NT GC-HRMS, operated at 10,000+ resolving power. An HP6890 *Plus* gas chromatograph was interfaced to the mass spectrometer. Chromatographic separations were carried out on a 40m DB-5 column with an internal diameter of 0.18mm and a stationary phase film thickness of 0.18 μm . Ultrahigh purity helium was used as the carrier gas. The splitless injector temperature was set at 280°C with a column flow rate of 1.5mL/min. The GC oven temperature program was: Initial temperature 100°C, ramp @ 10°C/min to 110°C held for 0.64 min., ramp @ 33.38°C/min to 180°C no hold time, followed by a final ramp of 3.12°C/min to 280°C, hold for 15 minutes.

A 4-function Selected Ion Monitoring (SIM) experiment was used to monitor tri- to hepta-BDEs. Six BFR congeners were monitored (see Table I) and quantitated. Congener identification was performed using isotopically-labelled BDE standards from Wellington Laboratories, Guelph, ON.

Calibration standards were made using the 6 native and $^{13}\text{C}_{12}$ -labelled BDPEs and $^{13}\text{C}_{12}$ -labelled DLPCBs. Samples were quantified using an external standard method. Response factors were determined from the calibration standards.

Results and Discussion

Data listed in Table I show the presence of BFRs in the Ministry of Environment sediment reference material (LSBRM9801) and a potential freeze-dried fish reference material. Concentrations of all congeners in the sediment reference material appear to be approximately one tenth of those values in CIL EDF-2525, while the freeze-dried fish values are ten times

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higher. Congener profiles differ slightly between matrices. Although BDE-47 is the predominant congener in all matrices, the contribution of BDE-99 relative to BDE-47 in the sediment is twice that found in the fish.

Table I – Survey results for potential BFR reference materials

| Compound | MOE LSBRM9801 (pg/g) N=2 | MOE FISH (pg/g) N=1 | CIL EDF-2525 (pg/g) N=1 |
|----------|-----------------------------------|---------------------------|-------------------------------|
| BDE 28 | 2 | 3000 | 200 |
| BDE 47 | 500 | 100000 | 10000 |
| BDE 99 | 200 | 10000 | 1000 |
| BDE 153 | 1 | 5000 | 2000 |
| BDE 154 | 2 | 3000 | 2000 |
| BDE 183 | 2 | 30 | 70 |

In conclusion DBES were identified in the MO-DLPCB fractions. Analysis of these fractions can be used to estimate BDE concentrations. Furthermore historic surveys of older extracts are therefore possible.

Quantification using isotope dilution MS will be pursued to ensure more accurate quantitation of the all congeners identified.

References:

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