ANALYSIS OF TBBF-A (TETRABROMOBISPHENOL -A) IN FISH, MUSSLE AND COWS MILK SAMPLES

Malte Petersen, Matthias Opel and Olaf Paepke

Eurofins GfA GmbH, Neuländer Kamp 1, 21079 Hamburg, Germany

Abstract

Tetrabromobisphenol -A (TBBP-A) is currently the most widely used BFR and mainly used as a reactive flame retardant bonded to the polymer matrix in epoxy and polycarbonate resins used in electronic equipments and in printed circuit boards. Food can generally a source for the accumulation of BFRs
We analyzed a number of fish and mussel samples (10) and cows milk samples (15) collected in different countries of Northern (fish) and Western Europe (milk) between 2007 and 2008. All analyses were performed following the isotope dilution method. The samples were freeze dried and homogenized. After adding of internal standard, $^{13}C_{12}$-labeled TBBP-A, extraction was performed by Soxhlet with hexane: acetone (4:1). After dramatization with BSTFA, forming TMS-derivative, samples were measured by GC-MS.

Concentrations found were low, mostly below limit of quantification (LOQ) of 0.005 ng/g wet weight. Only for fish liver (1 sample) concentrations were found at 0.31 ng/g wet weight and and for mussle samples at 0.26 ng/g wet weight (mean). The values found are similar to results from other investigations performed in Europe.

Introduction

Tetrabromobisphenol A (TBBP A) is currently the most widely used BFR with an estimated global use of 170.000 tonnes in 2004. TBBP A is mainly used as a reactive flame retardant bonded to the polymer matrix in epoxy and polycarbonate resins used in electronic equipments and in printed circuit boards [1]). It can also be used as an additive, for instance in high impact Polystyrene (HIP). It has been identified as an endocrine disrupter due to its structural similarity to 17-β-estradiol and thyroxine (T4), and also displays a high potency to bind to human transthyretin and immunotoxicity . However, the potential toxicity of TBBP-A exposure is mitigated to some extent by its estimated human half-life of 2.2 days[5, 6])

Materials and Methods

We analyzed a number of fish and mussel samples (10) and cows milk samples (15) collected in different countries of Northern (fish) and Western Europe (milk).
All analyses were performed following the isotope dilution method. The native TBBPA standard and two $^{13}C_{12}$ labeled standards (TBBP-A, BDE-138) were obtained from Wellington Laboratories, Canada.

The biota samples were freeze dried and homogenized. The internal standard, $^{13}C_{12}$-labeled TBBP-A, was added to the homogenized fraction and the extraction was performed by Soxhlet with hexane:acetone (4:1). The lipid weight was determined gravimetrically after evaporation of the solvents.

The lipid extract was further purified with sulphuric acid, followed by silica gel clean-up. The final extract, containing $^{13}C_{12}$ labeled BDE 138 as recovery standard, was derivatized with BSTFA, forming TMS-derivative, prior to GC-MS analysis.
The measurements were performed using high-resolution gas chromatography /low resolution mass spectrometry (HRGC /LRMS) with negative chemical ionization (NCI) mode using a DB 5 (15 m, 0.25 mm ID, 0.1 µm film) column for gas chromatographic separation. The identification of TBBPA-TMS derivative was based on retention time and isotope ratio. Recoveries measured for the internal standards used range between 80 and 110 %.

Reduction of solvents and control of blank data is an important step in quality control when analyzing TBBPA at ultra trace levels. Solvents and reagents were tested before the laboratory procedures. All glassware was rinsed by solvents prior to use. No plastic equipment was used. The accuracy of the analytical method was verified by

analysing a fish reference material for TBBP-A and a laboratory blank was run with each batch of ten samples. Quantification was only done if sample data was at least twice the blank value.

Results and Discussion

Results of the investigation are given in Table 1. Concentrations were found to be very low, mostly below LOQ of 0.005 ng/g wet weight. Highest concentrations could be found in fish liver and in all 3 mussel samples.

Table 1: Tetrabromobisphenol-A (TBBP-A) in fish, mussel and milk samples. Values given in ng/g wet weight. Collection of samples in 2007 and 2008

Sample	n	Mean	Median	Min	Max
Haddok	2	<0.005	<0.005	<0.005	<0.005
Cod	2	<0.005	<0.005	<0.005	<0.005
Halibut, Greenland	1	<0.005			
Redfish	1	<0.005			
Fish liver	1	0.31			
Mussel	3	0.26	0.20	0.15	0.44
Cows milk	15	<0.005	<0.005	<0.005	0.006

< : <LOQ (Limit of quantification)

In general there are not many data on TBBP-A in biota samples available. Herzke et al. (2005) [2]) found in eggs of birds of prey from Norway values between <0.003 (LOQ) and 0.013 ng/g ww. On the other hand, Russel et al. (2008) [3]) did not find any TBBP-A in three deep water fish species (flesh and liver analyzed) collected off the west coast of Scotland at LOQ of 0.3 ng/g ww.

TBBP-A (including other brominated components like brominated dioxins, polybrominated biphenyls (PBBs) and brominated flame retardants) was analysed in composite samples of 48 fish and shellfish and 10 samples of fish oil dietary supplements, all consumed in the UK. These included farmed and wild oily fish and white fish, shellfish, canned fish and fish paste, and supplements based on cod liver, halibut liver, shark liver, salmon and tuna oils. TBBP-A was not found above the limit of detection in any samples.[4])

Based on the results of the UK survey, the independent expert Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) concluded that the estimated exposure to brominated compounds by consumers following the Food Standards Agency's advice on fish consumption was unlikely to represent a risk to health and there was no need for the Agency to amend its advice on fish consumption.

TBBP A is characterised by completely different physico-chemical properties compared to other BFRs like PBDEs, HBCS or PBB. Due to two hydroxy groups TBBP-A is a weak acid, resulting in a lower bioaccumulation rate.

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