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Simultaneous liquid chromatography–tandem mass spectrometry analysis of brominated flame retardants (tetrabromobisphenol A and hexabromocyclododecane diastereoisomers) in French breast milk

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HIGHLIGHTS

- The study deals with endocrine disruptors TBBPA and HBCD in mother milk.
- A one-shot LC-ESI-MS/MS method for TBPPA and HBCD in mother milk is proposed.
- Substantial traces of TBBPA and HBCD were found in a series of 106 mother milk.
- The validated method is adapted for monitoring plans in the aim of risk evaluation.

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ABSTRACT

TBBPA and HBCDs are the two classes of flame retardants that are still allowed for use by the European Commission. In May 2013, HBCDs were listed as Persistent Organic Pollutants under the Stockholm Convention, and they were banned with an exemption on EPS/XPS for cavity wall insulation. This study describes the development and optimisation of a rapid LC-ESI-MS/MS method using isotopic dilution quantification including a simplified extraction step using a mixture of solvents and sulphuric acid hydrolysis followed by the one-shot analysis of TBBPA and each of the α-, β- and γ-HBCD diastereoisomers. The limits of detection and quantification (LOD and LOQ) were 0.5 and 2.5 ng g^{-1} (lipid weight, lw) for TBBPA and HBCD diastereoisomers, respectively. The method was applied to analyse 106 samples of individual mature breast milk. TBBPA was quantified in 42% of these samples within a range of <LOQ to 15.1 ng g^{-1} lw. HBCD diastereoisomers were quantified in 8%, 3% and 3% of the collected samples for α-, β- and γ-HBCDs, respectively. The α-form was predominant in each quantifiable breast milk sample. The rapid newly developed LC-MS/MS method appears to be suitable for simultaneously analysing and quantifying TBBPA and HBCDs (three isomers) in human breast milk with the aim of establishing BFR multi-contamination profiles of breast milk samples.

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1. Introduction

Brominated flame retardants (BFRs) are chemicals that, when added to materials, inhibit their ignition and slow down their rate of combustion. They are commonly used in the textile and furniture industries and in the fabrication of electronic components and in building materials (Alaee et al., 2003). The European Commission has estimated that the incorporation of flame retardants in a wide range of materials and goods has led to a 20% reduction in deaths in Europe during the last 10 years. However, brominated molecules released into the environment by the bromine industry or by the recycling of plastics or other components containing flame retardants is a major concern for human health because of their potential toxic effects as endocrine disruptors. The persistence of BFRs in the environment and their ability to contaminate the food chain also matters because each year, hundreds of thousands of tons of flame retardants are produced worldwide.

BFRs are classified into several groups (Alaee et al., 2003): (i) polybrominated diphenyl ethers (PBDEs) found in plastics, textiles

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and electronics; (ii) hexabromocyclododecanes (HBCDs) mainly used in the building industry as thermal insulators; (iii) phenols, and particularly tetrabromobisphenol A (TBBPA), used in printed electronic circuits and (iv) polybromobiphenyls (PBBs) mainly integrated in household appliances, textiles and plastic foams. PBBs are banned in Europe and have not been produced since 2000. In June 2006, the European Commission Directive 2002 also banned the use of PBDEs; however, HBCDs and TBBPA are still allowed for use in the manufacture of plastics and electronics. Indeed, considering the low potential for bioaccumulation and weak biological persistence of TBBPA, it was approved as an acceptable alternative compound to the banned PBDE. However, TBBPA, which has a chemical formula close to that of bisphenol A, is also known as a potential endocrine disruptor and an oestrogen agonist. The EFSA 2011a report compiles studies demonstrating TBBPA toxicity and its neurotoxic effects. The likely transfer of TBBPA from the environment into the food chain should therefore be considered a potential hazard for consumers. HBCD is used as an additive chemical to molten plastic. As no covalent link occurs at the molecular level, HBCD can be easily released into the environment and is assumed to enter the food chain. HBCD is usually sold as a mixture of α-, β- and γ-diastereoisomers, with the γ form representing the major form (at least 70%), followed by β- and α-HBCD forms, respectively (de Wit, 2002). γ-HBCD diastereoisomer is the most widespread form in the environment, while the α-HBCD form is mainly found in biota samples. HBCD compounds persist in the environment. They are suspected to have toxicity and eco-toxicity effects, which explains the worldwide ban as reported at the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2013 (http://chm.pops.int).

Two main routes of human exposure to these chemicals are (i) ingestion of indoor dust, from hand to mouth contact or by inhalation and (ii) food consumption. However, the relative importance of each exposure pathway is not accurately known (Roosens et al., 2009; Covaci et al., 2011). The fate of BFRs all along the food chain is considered comparable to that of POPs such as polychlorobiphenyls (PCBs). Recently, the European Commission (Official Journal of the European Union, 2014) has recommended that several kinds of food products (animal-derived products and infant food) be monitored. The persistent lipophilic molecules ingested through food tend to accumulate in the body (mainly as fat) throughout a person's lifetime. Some studies have shown that the body's impregnation, measured by BFR levels in body fluids (urine, blood and serum), is partly correlated with the consumption of animal foodstuffs such as meat and fishery products (Van Leeuwen and De Boer, 2008).

In humans, breast milk is known to be one of the excretion pathways for xenobiotic compounds and, in particular, the lipophilic and toxic substances to which the mother may be exposed. Lipophilic compounds accumulate and store in the body fat and can also enter breast milk by transfer from plasma. Breast milk can thus be used as a relevant indicator for infant exposure to many POPs such as dioxin, PCBs and pesticides. Indeed, as the detoxification pathway of newborns is immature, these compounds cannot be readily detoxified and eliminated.

Some studies have been published on the contamination of breast milk by TBBPA and HBCDs (Cariou et al., 2008; Abdallah and Harrad, 2011; Shi et al., 2013). Lankova et al., 2013 reported the presence of TBBPA and HBCDs in about one-third of the analysed breast milk samples in a wide range of 2–688 ng g^{-1}lw (lipid weight) for TBBPA and 1–76 ng g^{-1} lw for α-HBCDs. According to the chemical properties of TBBPA and HBCDs, these molecules are usually detected and quantified either by gas or liquid chromatography coupled to mass spectrometry (MS) (Cariou et al., 2005). GC–MS is not considered a suitable analytical tool for HBCDs, as the three α-, β- and γ-HBCD diastereoisomers are prone to thermal degradation in the injection port (Covaci et al., 2007). In addition, the GC–MS protocol does not separate the three diastereoisomer peaks. With regard to TBBPA, only low recovery rates were obtained after the acidification and chlorophormate derivatisation steps required by the GC–MS protocol (Covaci et al., 2008).

The aim of our work was, first, to develop a rapid LC-ESI-MS/MS method using isotopic dilution quantification including a simplified extraction step by a mixture of solvents and sulphuric acid hydrolysis followed by the one-shot analysis of TBBPA together with each of the α-, β- and γ-HBCD diastereoisomers. Second, the method was applied to the analysis of 106 individual breast milk samples. This analytical approach, which allows the simultaneous detection and quantification of TBBPA and HBCD isomers in a biological matrix, was found appropriate for the implementation of official monitoring studies on such POPs in food or biological fluids.

2. Materials and methods

2.1. Standards and chemicals

α-, β- and γ-HBCD diastereoisomers, TBBPA, $^{13}C_{12}$-labelled TBBPA and $^{13}C_{12}$-labelled α-HBCD, each at least 98% pure, were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) in a methanol solution of 50 μg mL^{-1} each. A mixture of all the native compounds was prepared gravimetrically to obtain 1 μg mL^{-1} in methanol and then stored at −18 °C. Further dilutions of this mixture were used as working standards to establish the calibration curve. $^{13}C_{12}$-labelled TBBPA and $^{13}C_{12}$-labelled α-HBCD to be used as internal standards were prepared to obtain 1 μg mL^{-1} in methanol.

Ultra-pure water (18.2 MΩ cm) was obtained using the Milli-Q system (Millipore S.A., St Quentin-en-Yvelines, France). Methanol, dichloromethane, acetonitrile, hexane, sulphuric acid and formic acid, all of HPLC grade, were provided by Fisher Scientific (Illkirch, France).

2.2. Sample collection

A total of 106 samples of mature breast milk were collected in 2010 by the Institut de Puériculture et de Périnatalogie de Paris (Paris, France). The protocol, including the informed consent of each mother, was approved by the local ethical committee in full compliance with the procedures of CNIL, France's National Commission for Information Technology and Civil Liberties. Breast milk samples were obtained at random from the milk bank, which regularly collects milk samples from volunteer mothers from 2 weeks postpartum. Each 50 mL sample of breast milk represents an aliquot of an individual specimen. The milk bank routinely checks the lipid content of breast milk samples through a fast method previously validated in-house using a Milkoscan FT 120 infrared spectrophotometer. Samples were then frozen for storage at around −20 °C. Before analysis, the samples were kept at room temperature for at least 4 h. Spiked samples were prepared 24 h in advance and stored in a fridge at approximately 4 °C before analysis. To study the specificity and reproducibility of the LC–MS/MS method, a larger sample of breast milk was prepared by pooling five individual milk samples taken at random among the available series. This pooled milk, which was also used as a blank matrix for spiking experiments, was checked for TBBPA and HBCD contents, which were found to be below the limit of detection (LOD).

2.3. Extraction and clean-up procedure

A Universal 1610/32R Centrifuge by Fisher Scientific (Illkirch,

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