



Simultaneous analysis of historical, emerging and novel brominated flame retardants in food and feed using a common extraction and purification method

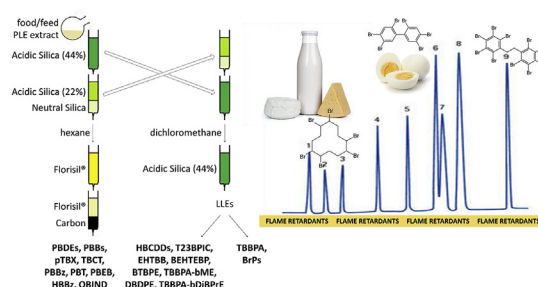
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HIGHLIGHTS

- Determination of multi- BFRs in a single method.
- LOQ and uncertainty determination for quantitative results in food and feed.
- Full detailed sample operating procedure fit for purpose.

GRAPHICAL ABSTRACT



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ABSTRACT

Brominated Flame Retardants (BFRs) are still widely used for industrial purposes. These contaminants may enter the food chain where they mainly occur in food of animal origin. The aim of our work was to provide a unique method able to quantify the widest range of BFRs in feed and food items. After freeze-drying and grinding, a pressurized liquid extraction was carried out. The extract was purified on acidified silica, Florisil[®] and carbon columns, the four separated fractions were analyzed by gas and liquid chromatography coupled to high resolution and tandem mass spectrometry. Isotopic dilution was preferentially used when commercial labelled compounds were available. Analytical sensitivity was in accordance with the expectations of Recommendation 2014/118/EU for PBDEs, HBCDDs, TBBPA, TBBPA-bME, EHTBB, BEHTEBP and TBBPA-bME. Additional BFRs were included in this analytical method with the same level of performances (LOQs below $0.01 \text{ ng g}^{-1} \text{ ww}$). These are PBBs, pTBX, TBCT, PBBz, PBT, PBEB, HBBz, BTBPE, OBIND and T23BPIC. However, some of the BFRs listed in Recommendation 2014/118/EU are not yet covered by our analytical method, i.e. TBBPA-boHEE, TBBPA-bAE, TBBPA-bGE, TBBPA-bDiBPrE, TBBPS, TBBPS-bME, TDBPP, EBTEBP, HBCYD and DBNPG. The uncertainty measurement was fully calculated for 21 of the 31 analytes monitored in the method. Reproducibility uncertainty was below 23% in isotopic dilution. Certified reference materials are now required to better characterize the true-ness of this method, which was applied in the French National Control Plans.

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1. Introduction

Brominated Flame Retardants (BFRs) have been used since the 1970s in the industry to prevent fire breaking outs and spreads. Polybromodiphenylethers (PBDEs), which are BFRs, have contaminated the environment and the food chain over time. According to the risk assessment performed by the European Food Safety Authority (CONTAM, 2012), the European Commission has recommended in 2014 the monitoring of selected classes of BFRs (2014/118/EU, 2014) to better characterize the contamination level of food items. In parallel, this recommendation has encouraged their determination in feed, in order to understand their related concentrations in food of animal origin.

The literature has reported several quantitative methods in food for the historical BFRs, i.e. PBDEs (Alaee et al., 2001; USEPA, 2007; Antignac et al., 2008; Kalachova et al., 2013; Baron et al., 2014; Portoles et al., 2015; Bichon et al., 2016; Aznar-Alemany et al., 2017), hexabromocyclododecane (HBCDDs) (Antignac et al., 2008; Munschy et al., 2013; Aznar-Alemany et al., 2017) and tetrabromobisphenol A (TBBPA) (Antignac et al., 2008; Aznar-Alemany et al., 2017). Some of these analytical strategies have already included novel and emerging BFRs. The analytical measurement of Bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl-ethane (DBDPE), Hexabromobenzene (HBBz), hexabromocyclopentenyldibromocyclooctane (HCBDCO), octabromo-1-phenyl-1,3,3-trimethylindane (OBIND), pentabromobenzene (PBBz), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), tetrabromo-*o*-chlorotoluene (TBCT), 2,3,5,6-tetrabromo-*p*-xylene (pTBX) and 2,4,6-Tribromophenol (2,4,6-TBP) are described in previously published works (Kalachova et al., 2013; Baron et al., 2014; Aznar-Alemany et al., 2017). Nevertheless, the complete list recommended by the European Commission (2014/118/EU, 2014) is not fully covered by any of the published literature. Indeed, the derivatives of TBBPA, the class of bromophenols and the additional emerging and novel brominated flame retardants such as tris(2,3-dibromopropyl) phosphate (TDBPP); *N,N'*-ethyl-enebis(tetrabromophthalimide) (EBTEBP); hexabromocyclodecane (HBCYD); bis(2-ethylhexyl) tetra-bromophthalate (BEHTBP); 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and dibromoneopentylglycol (DBNPG) are rarely included in the multi-analyte methods related to BFRs. Currently, some of these last compounds are not even measured independently.

As other halogenated contaminants monitored in food and feed, BFRs require a dedicated sample preparation. Fresh samples (Kalachova et al., 2013) often combined with sodium sulfate (Alaee et al., 2001; USEPA, 2007; Baron et al., 2014; Aznar-Alemany et al., 2017) or freeze-dried samples (Munschy et al., 2013) are generally used before fat extraction. For that purpose, Soxhlet and Pressurized Liquid Extraction are mainly reported with hexane as extracting solvent or hexane/dichloromethane, hexane/acetone or toluene/acetone mixtures. Lipids are generally hydrolyzed by sulfuric acid directly added in the extract or mixed with silica gel. The clean-up usually consists of SPE cartridges or home-made columns containing neutral alumina (Baron et al., 2014; Aznar-Alemany et al., 2017) or silica gel (Kalachova et al., 2013) before further purification on Florisil® and carbon columns (USEPA, 2007; Munschy et al., 2013). Gel permeation chromatography is also reported (Alaee et al., 2001; USEPA, 2007). The quantification strategy relies upon isotopic dilution in most cases (when the corresponding labelled compounds are commercially available).

The analysis of BFRs in food and feed can be done either by gas chromatography or liquid chromatography coupled to mass spectrometry. The BFRs which are sufficiently volatile and apolar (historical, emerging and novel) are classically separated by gas

chromatography. This concerns PBDEs but also PBEB, HBBz, PBBz, DBDPE, HCBDCO, EHTBB, BEHTBP, TBBPA-*b*DiBrPE, pTBX, TBCT, OBIND and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE). An equivalent of a 5%-phenyl-methylpolysiloxane stationary phase is classically used, with a column of 15 m length, 0.25 mm internal diameter and 0.1 µm film thickness to prevent any degradation of the heaviest compounds (Ali et al., 2011; Gao et al., 2016; Aznar-Alemany et al., 2017). Ionization techniques are historically based on an electron ionization at 70 eV (USEPA, 2007; Aznar-Alemany et al., 2017). The comparison with electron capture negative ionization using methane as a reagent gas is well described; it provides excellent sensitivity, but limited selectivity (bromine ion monitoring) (Alaee et al., 2001; Ali et al., 2011; Kalachova et al., 2013; Baron et al., 2014; Gao et al., 2016). More recently, atmospheric pressure chemical ionization was presented as an alternative, allowing selectivity and sensitivity simultaneously (Portoles et al., 2015; Bichon et al., 2016). Robust measurement of BFRs at the lowest levels in food (around the fg injected on-column) is provided by high resolution mass spectrometers (double sector) (USEPA, 2007; Antignac et al., 2008). The last generation of triple quadrupole instruments demonstrated comparable performances (Portoles et al., 2015; Bichon et al., 2016). The thermolabile, less volatile and/or most polar BFRs, such as bromophenols, TBBPA and HBCDD, are monitored by LC/MS/MS using electrospray in the negative ionization mode (Antignac et al., 2008; Aznar-Alemany et al., 2017). Separation is achieved on a C18 functionalized silica column, with conventional dimensions of 100 × 2.1 mm and from 2.6 to 3.5 µm particle diameters.

In this context, the aim of our work was to develop an analytical strategy allowing a large number of historical, emerging and novel BFRs to be monitored, starting from a single feed or food sample while respecting the criteria set in the European Recommendation (2014/118/EU, 2014). Particular attention has been paid to method validation focusing on sensitivity, selectivity and accuracy as well as contamination handling for all BFRs individually.

2. Materials and methods

2.1. Material

2.1.1. Standards solutions

Standard solutions are listed in Table 1 with their associated abbreviations and providers. All calibration standards and spiking solutions have been prepared by successive dilutions in toluene or methanol and stored at 4 °C until use. Two internal standard solutions have been prepared, i.e. IS1 containing the historical labelled BFRs ¹³C₁₂-BDE 28/47/99/100/153/154/183 at 0.5 ng mL⁻¹, ¹³C₁₂-BDE 209 at 2.5 ng mL⁻¹, ¹³C₁₂-TBBPA at 2 ng mL⁻¹, <alpha>, <beta> and <gamma>-¹³C₁₂-HBCDD at 5 ng mL⁻¹ and ¹³C₁₂-PBB-153 at 0.5 ng mL⁻¹ and IS2 including the nBFRs amongst which ¹³C₁₂-DBDPE and ¹³C₆-BTBPE at 20 ng mL⁻¹ and ¹³C₆-HBBz, ¹³C₆-PBBz, ¹³C₆-BEHTBP, ¹³C₆-EHTBB and ¹³C₆-BRPS at 8 ng mL⁻¹. Four external standard solutions were also prepared; ES1 with ¹³C₁₂-PBDE 77/138 at 1 ng mL⁻¹, ES2 with d₁₈-β-HBCDD at 500 ng mL⁻¹, ES3 with ¹³C₁₂-TCBPA at 100 ng mL⁻¹ and ES4 with ¹³C₁₂-PBDE 77/138 at 25 ng mL⁻¹.

2.1.2. Samples

Thirty feed samples (fish oil and meal) and 577 food samples (including fish, crustaceans, milk, eggs, muscle and sheep liver) collected in France during 2014–2016 official monitoring plans were used to determine the limits of quantification (LOQ) of the developed analytical method. Two types of quality control (QC) samples were used for reproducibility and trueness assessment. QC1 was a fish oil sample naturally contaminated with PBDEs and

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