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QUANTIFICATION OF BROMINATED FLAME RETARDANTS IN FOOD BY UPLC-MS/MS: CHALLENGES, ANALYTICAL METHOD DEVELOPMENT AND VALIDATION IN FOOD

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The study was undertaken in order to respond to the Commission Recommendation 2014/118/EU on the monitoring of brominated flame retardants (BFRs) in food in Europe (1). BFRs are anthropogenic chemicals that are added to a wide variety of consumer products in order to improve their fire resistance. BFRs may slowly leak from the products into the environment. Due to their persistence and potential to bioaccumulation in the food chain, BFRs may cause adverse effects in humans and animals. There is a lack of information on the occurrence data of BFRs in food which has hampered accurate completion of intake assessment. The main objective of the work was to provide a sensitive analytical method for quantification of brominated phenols (BrPh) and hexabromocyclododecanes (HBCDs) in foodstuffs. Measurements of BFRs were performed using ultra-high performance – tandem mass spectrometry (UPLC–MS/MS) technique on ACQUITY UPLC system (Waters) coupled to Xevo-TQ-S mass spectrometer (Waters). The MS was operated in electrospray ionization mode in negative polarity. In addition to its selectivity and superior sensitivity, the LC–MS technique was chosen over gas chromatography-mass spectrometry (GC–MS) because of applicability for compounds susceptible to thermal decomposition (derivative of tetrabromobisphenol A) and isomeric interconversion (HBCD isomers). The optimisation of sample preparation procedure was performed using lyophilized salmon as matrix. Spiking experiments demonstrated good results applying acetonitrile as extraction solvent. The extract was defatted using consequent addition of hexane. To enhance phase separation between hexane and acetonitrile, addition of water was required. The organic phase containing hexane was brought onto a multi-layer silica column (including layers of acidified silica) for lipid elimination. For solvent exchange, the aqueous phase was cleanedup by solid-phase extraction using Oasis® HLB cartridges. After the clean-up, the extracts were evaporated, reconstituted in acetonitrile/water (50/50) and combined before injection into the UPLC–MS/MS system. In this work, challenges encountered in the mass spectrometric detection of BFRs, as well as considerations in extraction and quantification of these compounds will be discussed. Validation of the developed UPLC–MS/MS method will be presented for a variety of food groups, including fish, meat, eggs, milk and vegetable oils.

[1] Commission Recommendation of 3 March 2014 on the monitoring of brominated flame retardants in food (2014). Official Journal of the European Union, L65: 39-40.

Keywords: *brominated flame retardants, food, monitoring, UPLC–MS/MS*

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IDENTIFICATION AND DETERMINATION OF TOXIC SUBSTANCES (PESTICIDES AND MYCOTOXINS) AND THEIR TRANSFORMATION PRODUCTS IN NUTRACEUTICALS BY UHPLC–ORBITRAP–MS

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Nutraceuticals can be considered an alternative to pharmaceutical products by society, and they have been acquiring importance in the last decade. Such products may range from isolated nutrients, dietary supplements and specific diets to genetically engineered foods, herbal products, and processed foods such as cereals, soups and beverages. Keeping in mind that a nutraceutical product is a concentrated form of a food or plant, it can be contaminated from the raw material with toxic substances, such as pesticides or mycotoxins. In the European Union, there exist legislation involving maximum residue limits for pesticides [1] and mycotoxins [2] in food and feed, although they only consider their presence in the raw material and not in the nutraceutical presentation (capsules, tablets, extracts, etc.). Another problem is that these contaminants can be degraded to other substances, which in some cases could be more toxic than the original ones. These are considered transformation products (TPs). Most of these TPs are unknown and few studies have been performed to analyze them. Therefore, analytical methodologies that ensure food safety in this kind of commodities are needed, monitoring toxic substances as well as their respective TPs. In this work, different nutraceuticals, such as green tea, royal jelly, soy isoflavones and ginkgo biloba, have been studied looking for more than 350 toxic substances (including pesticides and mycotoxins) using ultra high pressure liquid chromatography coupled to high resolution mass spectrometry (UHPLC–Orbitrap-MS). A “dilute and shoot” extraction procedure was applied for all the matrices studied, followed by a clean-up step using different sorbents, such as primary secondary amine (PSA), graphitized carbon black (GCB), C18, Florisil and zirconium oxide (Z-Sep+). The methodologies were validated, obtaining recoveries between 70 and 120% and precision values below 20%. The limits of detection and quantification were below 10 and 20 μg kg-1, respectively. After validation, the methods were applied to different commercial nutraceutical products (36 in total), finding 28 pesticides and 4 mycotoxins. TPs were defined for each toxic substance found in the real samples, building a list of 31 TPs. From this list, 5 TPs were putatively identified by Orbitrap-MS in the commercial nutraceutical products analyzed, performing retrospective analysis.

[1] REGULATION (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC.
[2] REGULATION (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants and foodstuffs.

Keywords: *nutraceuticals, pesticides, mycotoxins, transformation products, high resolution mass spectrometry*

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