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Quick and simple sample treatment for multiresidue analysis of bisphenols, bisphenol diglycidyl ethers and their derivatives in canned food prior to liquid chromatography and fluorescence detection

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ABSTRACT

We report herein a multiresidue method for canned food determination of 12 bisphenols [bisphenol A (BPA), bisphenol B (BPB), bisphenol F (BPF), bisphenol E (BPE)], bisphenol diglycidyl ethers [bisphenol F diglycidyl ether (BFDGE), bisphenol A diglycidyl ether (BADGE)] and their derivatives [BADGE·2H_2O, BADGE·H_2O, BADGE·HCl·H_2O, BADGE·HCl, BADGE·2HCl and BFDGE·2HCl]. The method was based on the microextraction of the target contaminants in 200 mg food sample with 600 μL of a supramolecular solvent made up of inverse aggregates of tetradecanol, followed by analysis of the extract by liquid chromatography/fluorescence detection using external calibration. Chromatographic separation of all target compounds, including the *ortho–ortho, ortho–para and para–para* isomers of BFDGE and BFDGE·2HCl, was achieved with baseline separation (Resolution ≥ 1.52). No concentration of the extracts was required, the microextraction took about 30 min and several samples could be simultaneous treated. Method validation was carried out according to the recommendations of the European Commission Decision 2002/657/EC. Quantitation limits for the different analytes ranged between 0.9 and 3.5 μg kg^{-1}. Repeatability and reproducibility, expressed as relative standard deviation, were in the ranges 1.8–6.8% and 4.4–8.1%. The method was applied to the analysis of the target compounds in different food categories including vegetables, legumes, fruits, fish and seafood, meat product and grain. Recoveries in samples were within the range 80–110%. Only BPF and BPE were undetected in the canned food analyzed. The concentration found for the rest of bisphenols, diglycidyl ethers and derivatives was in the range 7.1–959 μg kg^{-1}. The study of the isomeric distribution of BFDGE and BFDGE·2HCl in food showed that they are preferentially present as one of the isomeric forms, that highlighting for further studies. The analytical and operational characteristics of this multiresidue method make it suitable for monitoring programs intended for the assessment of human exposure to bisphenols, diglycidyl ethers and derivatives from diet.

1. Introduction

Epoxy phenolic resins are widely used as protective linings for food and beverage cans. Bisphenol A (BPA) is the core substrate to produce bisphenol A diglycidyl ether (BADGE), the main monomer used in the epoxy resin industry [1]. Both BPA and BADGE can migrate from the protective lining into food and the latter can generate different derivatives during food storage by hydrolysis of epoxy groups (e.g. BADGE·2HCl, BADGE·HCl, BADGE·H_2O, BADGE·2H_2O and BADGE·HCl·H_2O) [2]. Table 1 shows the structure and some physicochemical properties of these compounds.

Occurrence of BPA in food has been widely documented in scientific literature and an interesting analysis of the data published from 2006 onwards has been included in the European Food Safety Authority (EFSA) draft scientific opinion on the risks to public health related to the presence of BPA in foodstuffs, which is scheduled for completion in mid-2014 [3]. Minimal and maximal average concentrations for BPA in the 17 canned food categories considered by EFSA were 0.2 μg kg^{-1} and 52 μg kg^{-1} for sugar and confectionary and snack and desserts, respectively. Data were extracted from a total of 2521 samples and BPA concentrations varied in a wide interval (i.e. 0.1–395 μg kg^{-1}). Occurrence of BADGE and derivatives in canned food has been also well documented, the concentrations ranging from undetected to 860 μg kg^{-1} [4–7]. To protect human health, a tolerable day intake (TDI) of 0.05 mg kg^{-1} of body weight for BPA was set by the European Commission (EC) in 2006 [8]

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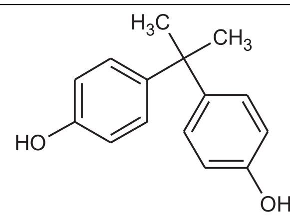
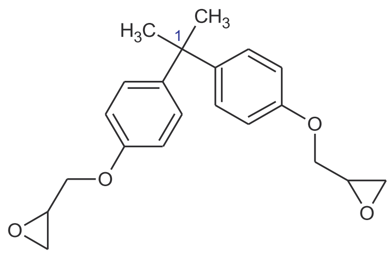
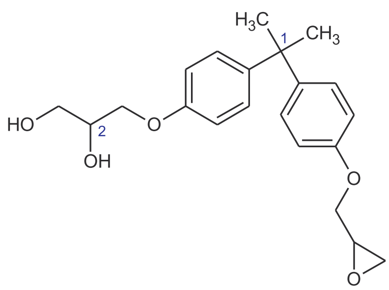
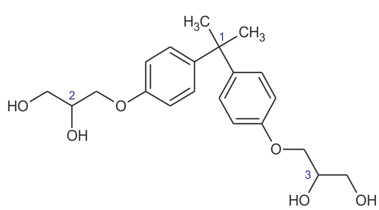
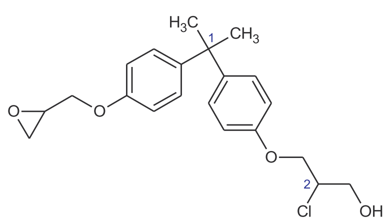
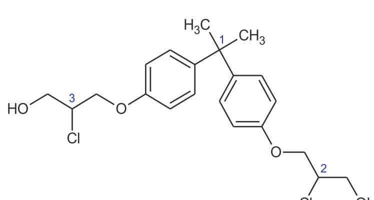
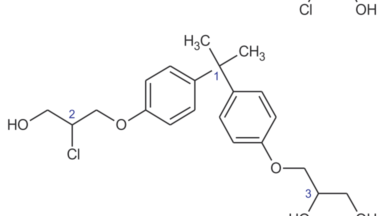
Table 1
Chemical structure, ionization constants, octanol–water partition coefficients and number of proton donors and acceptors for the target bisphenols.

Compound name	Structure	pKa_1 [a]	pKa_2 [a]	Log K_{ow} [a]	Sum of hydrogen donors and acceptors [a]
2,2-Bis(4-hydroxyphenyl)propane (BPA)		10.29	10.93	3.46	4
2,2-Bis(4-glycidyloxyphenyl)propane (BADGE)		–	–	3.59	4
2-[4-(2,3-Dihydroxypropyloxy)phenyl]-2-[4-(glycidyloxy)phenyl]propane (BADGE·H2O)		13.53	15.02	2.47	7
2,2-Bis[4-(2,3-dihydroxypropoxy)phenyl]propane (BADGE·2H_2O)		14.72	15.32	2.05	10
2-[4-(3-Chloro-2-hydroxypropyloxy)pheny]-2-[4-(glycidyloxy)phenyl]propane (BADGE·HCl)		13.13	–	4.27	5
2,2-Bis[4-(3-chloro-2-hydroxypropoxy)phenyl]propane (BADGE·2HCl)		12.83	13.48	4.34	6
2-[4-(3-Chloro-2-hydroxypropyloxy)phenyl]-2-[4-(2,3-dihydroxypropyloxy)phenyl]propane (BADGE·HCl·H_2O)		13.53	15.02	2.89	8