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Determination of bisphenol-type endocrine disrupting compounds in food-contact recycled-paper materials by focused ultrasonic solid–liquid extraction and ultra performance liquid chromatography-high resolution mass spectrometry

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ABSTRACT

Focused ultrasonic solid–liquid extraction (FUSLE) and reverse-phase ultra performance liquid chromatography (UPLC) coupled to a quadrupole-time of flight mass spectrometer (Q-TOF-MS) was applied to the determination of bisphenol-type endocrine disrupting compounds (EDCs) in food-contact recycled-paper materials. Recycled paper is a potential source of EDCs. Bisphenol A (BPA), bisphenol F (BPF) and their derivatives bisphenol A diglycidyl ether (BADGE) and bisphenol F diglycidyl ether (BFDGE) are used for the production of epoxy resins employed in the formulation of printing inks. The FUSLE of bisphenol-type EDCs from packaging is reported for the first time. First, different extraction solvents were studied and methanol was selected. Then, the main FUSLE factors affecting the extraction efficiency (solvent volume, extraction time and ultrasonic irradiation power) were studied by means of a central composite design. The FUSLE conditions selected for further experiments were 20 ml of methanol at ultrasonic amplitude of 100% for 5 s. Finally, the number of extraction cycles necessary for complete extraction was established in two. The analysis of the FUSLE extracts was carried out by UPLC-Q-TOF-MS with electrospray ionization and the determination of the four analytes took place in only 4 min. The FUSLE and UPLC-ESI-QTOF-MS method was validated and applied to the analysis of different food-contact recycled-paper-based materials and packaging. The proposed method provided recoveries from 72% to 97%, repeatability and intermediate precision under 9% and 14%, respectively, and detection limits of 0.33, 0.16, 0.65 and 0.40 μg/g for BPA, BPF, BADGE and BFDGE, respectively. The analysis of paper and cardboard samples confirmed the presence of EDCs in these packaging.

1. Introduction

There are a number of chemical substances that disturb regular performance of the hormonal system. They are referred to as endocrine disrupters (EDCs) [1,2] and their undesirable effects are felt by both men and women. These substances, including organochlorine pesticides, alkylphenols, phthalates, polychlorinated biphenyls and dioxins, organic tin compounds and bisphenols among others, disturb the hormonal equilibrium of organisms, which is particularly dangerous at developmental age, when changes are in most cases irreversible.

Bisphenol A (BPA) is considered to have a oestrogenic activity and it has been recently related to thyroid hormone action disruption [3]. The toxicity of bisphenol F (BPF), which has also been proven, is mainly related to its oestrogenic and antiandrogenic effects [4]. Regarding bisphenol A diglycidyl ether (BADGE) and bisphenol F diglycidyl ether (BFDGE), they are related to their cytotoxic effects, which make them tumorigen and mutagen [5]. The chemical structures of these four bisphenol-type compounds are shown in Fig. 1.

BPA and BPF have been used as a raw substance for mass production of epoxy resin, polycarbonate, polyester and polyacrylate plastics. Epoxy resins are used in a great number of applications: as tank coatings, structural steel coatings, aircraft finishes, can and drum linings, furniture finishes, in printing inks, in dental surgical and prosthetic applications, etc., [6]. The most popular coating varnishes and lacquers used in drink and food cans are those based on vinyl organosols (novolacs), which include in their composition epoxy resins obtained from BADGE or from BFDGE [7]. BPA and BPF can be released from packaging material and migrate into beverages and foods, being the rate of migration enhanced by treatments such as heat processing.

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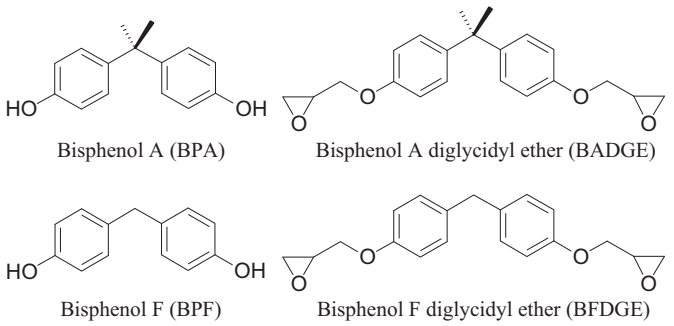

Fig. 1. Chemical structures of the four p–p bisphenol-type compounds.

Paper and cardboard are widely used as food packaging materials, directly in contact with food or more frequently protected by a barrier layer from direct contact with foodstuffs. It has, however, been demonstrated that these materials could contain pollutants of different origin, and these chemicals could be transferred to food in contact with the material [8–12]. BPA has been found in recycled paper and paperboard used for food packaging (pizza cardboard, paper bags) and in kitchen towels made from recycled paper, probably due to its use in printing inks [13]. For this reason, it is very important to establish the criteria to ensure that paper containing recycled pulp is safe enough to be used as food contact materials. Further data would be needed to quantify the impact of these sources in terms of BPA exposure in the population.

The use of plastic materials for food contact is regulated in many countries, but recycled paper and board is not regulated by law. However, the guidelines on paper and board materials and articles, made from recycled fibres, intended to come into contact with foodstuffs are established in the Proposal approved by the Council of Europe (Resolution RESAP (2002) 1, at www.coe.int/soc-sp).

Analytical methods for the determination of BPA in food have been recently reviewed [14]. The extraction of bisphenol-type compounds from liquid samples has been accomplished by different techniques including liquid–liquid extraction (LLE) [15–19], microliquid–liquid extraction (MLLE) [20], microliquid–liquid dispersive extraction (MLDE) [21], solid-phase extraction (SPE) [7,22–28], solid-phase microextraction (SPME) [29,30], and stir bar sorptive extraction (SBSE) [31]; while bisphenols have been extracted from solid samples by conventional lixiviation with solvents [32,33] for migration studies, matrix solid-phase dispersion (MSPD) [34], microwave-assisted extraction (MAE) [35–37], ultrasound-assisted extraction [38–41] with ultrasonic bath and pressurized liquid extraction [42–44]. However, to the best of our knowledge, only once BPA has been extracted by FUSLE (focused ultrasound solid–liquid extraction) [45] but from a different solid matrix (sewage sludge). Few methods have been proposed for the simultaneous determination of BPA, BPF and their corresponding diglycidyl ethers (BADGE and BFDGE) [7,14,16,24,46]. Besides, these have been developed for aqueous matrices using other extraction methods and this is the first time that FUSLE has been used for the extraction of bisphenol-type endocrine disrupters from packaging.

FUSLE is a relative new technique that has been successfully applied chiefly in the environmental field, for instance, for the determination of BPA, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalate esters, and nonylphenols in environmental samples [47–50], and it has also been applied for the determination of UV-filters in packaging [51].

FUSLE is a consequence of the cavitation phenomena. When a cavitating bubble collapses near the surface of a solid sample particle, micro-jets of solvent propagate towards the surface at high velocities, causing pitting and mechanical erosion of the solid surface, leading to particle rupture, and consequently, to smaller particle size [52]. Likewise, the cavitational bubbles implosion cause microscopically very high temperatures (up to 5000 K) and pressures (up to 2000 atm), which also favour an exhaustive extraction, without appreciable changing the extraction macroscopic conditions [53] because of the very small size of the bubbles. For this reason, it is an interesting technique for labile compounds. It is also worth mentioning that the microtip of the focused ultrasound, which emitted a high ultrasound power, is directly immersed in the slurry. This makes the power of FUSLE is 100 times higher than the traditional ultrasonic bath [47].

The determination of bisphenol-type EDCs has been usually developed through chromatographic techniques because of the complexity of the mixtures analysed, mainly high performance liquid chromatography (HPLC) coupled to mass detector (MS) [34,35–42] or fluorescence detection [54–57], and gas chromatography–mass spectrometry [46,56–58]. However, the gas chromatography method seems to be limited, for BADGE and BFDGE, due to their low volatility [7].

In this work, reverse-phase ultra performance liquid chromatography (UPLC) coupled to a quadrupole-time of flight mass spectrometer (Q-TOF-MS) was applied to the determination of BPA, BPF, BADGE and BFDGE. This UPLC–HRMS method is advantageous over conventional HPLC-MS methods in terms of shorter analysis time and improved selectivity. The FUSLE and UPLC–Q-TOF-MS detection of bisphenol-type EDCs from packaging is reported for the first time and has proved to be fast and efficient.

2. Experimental

2.1. Standards and material

Bisphenol A (99%), bisphenol F (98%), bisphenol A diglycidyl ether (97%) and bisphenol F diglycidyl ether (97%, a mixture of 3 isomers: ortho–ortho, ortho–para, para–para) were obtained from Fluka (Switzerland). The isotopically labelled BPA standard (BPA-d_{16}) used as internal standard for the GC–MS determination was purchased from Cambridge Isotope Laboratories (USA), and the derivatisation agent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTEFA) was obtained from Alfa Aesar GMbH (Karlsruhe, Germany).

Deionised water was obtained from a MilliQ water purification system (Millipore, USA). Acetonitrile, diclorometane, tetrahydrofuran, ethyl acetate and acetic acid, all LC-MS quality, were purchased from Scharlab (Barcelona, Spain). LC–MS-grade methanol and anhydrous sodium acetate (99%) were obtained from Panreac (Barcelona, Spain).

2.2. Samples and sample preparation

Standard solutions containing 1000 mg/l of the each compound were prepared in acetonitrile and subsequently diluted in methanol as necessary.

Different food-contact paper-based materials and packaging, including kitchen paper, tablecloth, food boxes and bags, were obtained from local supermarkets and fast-food outlets.

The samples were ground for 6 min using a cryogenic mill 6750 freezer/mill (SPEX CertiPrep, UK) before analysis.

Spiked cardboard was used for the study of variables and the method validation. It was spiked with 20 μg/g of each analyte by adding a standard solution to the milled cardboard. Solvent was let evaporate and then the spiked cardboard was triturated again to ensure proper homogenization of the sample. Before analysis,