



A simple method for the enrichment of bisphenols using boron nitride



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ABSTRACT

A simple solid-phase extraction method for the enrichment of 5 bisphenol derivatives using hexagonal boron nitride (BN) was developed. BN was applied to concentrate bisphenol derivatives in spiked water samples and the compounds were analyzed using HPLC coupled to fluorescence detection. The effect of pH and organic solvents on the extraction efficiency was investigated. An enrichment factor up to 100 was achieved without evaporation and reconstitution. The developed method was applied for the determination of bisphenol A migrated from some polycarbonate plastic products. Furthermore, bisphenol derivatives were analyzed in spiked and non-spiked canned food and beverages. None of the analyzed samples exceeded the migration limit set by the European Union of 0.6 mg/kg food. The method showed good recovery rates ranging from 80% to 110%. Validation of the method was performed in terms of accuracy and precision. The applied method is robust, fast, efficient and easily adaptable to different analytical problems.

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1. Introduction

Bisphenol A [BPA] is one of the first synthetic substances, having an estrogenic effect as recognized by the early studies of the British biochemists Edward Charles Dodds and Wilfrid Lawson (Dodds & Lawson, 1938). BPA and its derivatives possess high potential as endocrine disruptor in humans and wildlife. Exposure to BPA may result in harmful effects, including reproductive, developmental and metabolic disorders (Rubin, 2011).

BPA is used as a raw material for the production of epoxy resins, polycarbonate, polyester, and polyacrylates (International Food Safety Authorities Network (INFOSAN), 2009). In addition, BPA is the precursor of bisphenol A diglycidylether (BADGE), which is the most common monomer in the epoxy resin industry (Sabu & Visakh, 2011). BADGE and its hydrolyzed products BADGE·2H₂O or BADGE·H₂O are suspected for mutagenic, genotoxic and anti-androgenic effects (Hyoung et al., 2007; Vanhoutte et al., 1995). Nowadays tins and glass jar metal lids have an epoxy resin as an internal coating to prevent the contact and the reaction between food and beverage with the metallic surface (Li et al., 2014). During production, most canned food are sterilized at 121 °C for 20 min under 2 bar pressure (Heldman & Hartel, 1997). Therefore, non-cross linked BADGE or BPA are migrated from coatings into food and beverage during the heating process.

(Goodson, Robin, Summerfield, & Cooper, 2004). Furthermore, the composition of food matrix can accelerate the migration of BPA and its derivatives. Migration is enhanced significantly with the increase in glucose and NaCl content, acidity, storage temperature and shelf lives (Errico et al., 2014; Sungur, Koroglu, & Ozkan, 2014). The European commission has fixed a specific migration limit for BPA at a maximum level of 0.6 mg/kg food (European Union, 2004) and 9 mg/kg for BADGE and its hydrolytic derivatives (European Union, 2005).

On the other hand, BPA leaches from polycarbonate plastic products which are commonly used in food product packages, water bottles, bottles for infant food, kitchen utensils and medical consumables.

For the protection of human health, the European Commission (EC) has set a tolerable daily intake (TDI) of 0.05 mg/kg body weight (EFSA, 2006). Furthermore the European Union banned the manufacture of polycarbonate feeding bottles containing BPA in March 2011 and their import and sale in June 2011 (European Union, 2011). In January 2015, the European Food Safety Authority (EFSA) presented its latest comprehensive re-evaluation of BPA exposure and toxicity and reduced the safe level of tolerable daily intake (TDI) to 0.004 mg/kg/bw/day (EFSA, 2015).

Analysis of BPA and its derivatives is a great challenge due to their low concentrations as well as the complex and diverse matrices. Therefore, various methods such as liquid–liquid microextraction (Cunha, Cunha, Ferreira, & Fernandes, 2012) or different

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solid-phase extraction methods (SPE) were developed. SPE can be divided into either non selective or selective methods. The non-selective methods are based on reversed phase materials such as bonded silica derivatized with C18 (Cao et al., 2011) (Kim, Do, Yeh, & Cunningham, 2014) or polymeric sorbents as vinylpyrrolidone/divinylbenzene (OASIS[®]) (Sajiki et al., 2007). The selective method includes molecular imprinted polymers (MIP) (Li et al., 2014), restricted access materials (RAMs) (Ballesteros-Gomez, Rubio, & Perez-Bendito, 2009) or immunoaffinity based sorbents (Maiolini et al., 2014). The sample pre-treatment methods were developed to clean up and to enrich the sample prior to analysis, usually by HPLC followed by fluorescence or mass spectrometric (MS) detection (Lu, Yang, Zhang, & Shao, 2014). Besides, gas chromatographic separation coupled with MS (GC-MS) was applied for the analysis after derivatization of BPA and its derivatives (Cunha & Fernandes, 2013).

In previous study, hexagonal boron nitride (BN) was successfully applied as an efficient SPE material for the enrichment and desalting of peptides and phosphopeptides (Fischnaller, Köck, Bakry, & Bonn, 2014). The choice of BN is based on its extraordinary chemical and physical properties e.g. resistance to oxidation, good thermal stability and conductivity. It is chemically inert, non-toxic, environmentally compatible, and it has a wide range of applications e.g. in cosmetics, electronics and ceramics industries (Haubner, Wilhelm, Weissenbacher, & Lux, 2002). In addition, BN displays enhanced physisorption properties due to the dipolar fields near its surface (Lei, Portehault, Liu, Qin, & Chen, 2013). In comparison to other reversed phase materials such as graphite or C18, BN possess higher hydrophilicity (Li & Zeng, 2012) and therefore, no activation or equilibration is necessary.

This work describes the development of a fast, simple, efficient and validated dispersive SPE method utilizing BN for the determination of BPA and its derivatives (BPF, BPZ, BADGE and BADGE-2H₂O). The developed method permits trace analysis of bisphenols without evaporation and reconstitution. The recovery rates of the analyzed compounds in aqueous solutions ranging from 0.5 to 100 ng/mL were evaluated by HPLC and fluorescence detection and the results were compared with the commercially available silica C18 sorbents.

The influence of different pH values ranging from 1.5 to 12.6 and the presence of organic solvents (e.g. ethanol, acetonitrile) on the extraction efficiency of BN was investigated. In addition, the local river and tap water were analyzed. Through the enrichment with BN, it was possible to determine the leached BPA from selected polycarbonate plastic containers, including baby bottle, bbq cup, muffin form and syringe. Furthermore, the contamination of BPA and its derivatives into canned food and beverages was determined. The potential of the proposed method was investigated by determination of the recoveries of the 5 bisphenol derivatives from spiked urine.

2. Experimental

2.1. Reagents and chemicals

Combat[®] hexagonal BN powder (BN) with 60 m²/g surface area and 6 μm particle size was a gift from Saint-Gobain Ceramic Materials (Amherst, New York, USA). Acetonitrile (ACN) (G Chromasolv for HPLC), methanol (Chromasolv for HPLC), isopropanol (LC-MS Chromasolv), tetrahydrofuran (THF) (inhibitor-free, Chromasolv Plus), bisphenol A (BPA) (≥99%), bis(4-hydroxyphenyl)methane (BPF) (98%), bisphenol A diglycidyl ether (BADGE), bisphenol A bis(2,3-dihydroxypropyl) ether (BADGE-2H₂O) (≥97.0%), 4,4'-cyclohexylidenebisphenol (BPZ) (98%), orthophosphoric acid (85.0%) and sodium hydroxide (ACS

reagent ≥ 97.0%) were provided by Sigma-Aldrich. Ethanol (LiChrosolv) and potassium dihydrogen phosphate (KH₂PO₄) were purchased from Merck KGaA (Darmstadt, Germany). A stock solution of each bisphenol (100 μg/mL) was prepared in ACN and stored at 4 °C. Intermediate solutions were prepared weekly with a concentration of 1 μg/mL and the aqueous working solutions were prepared daily (0.5–100 ng/mL). Water was purified by a Milli-Q unit (Merck Millipore, Darmstadt, Germany) and used for all experiments.

2.2. Solid-phase extraction

The SPE was carried out in 2 mL Eppendorf tubes and 10 mL glass centrifuge tubes with a polyethylene septum. About 5–20 mg of BN were placed into the tubes and filled up with the maximum sample volume (2 and 10 mL, respectively). In contrast, the C18 material (Hypersil ODS) was activated with ACN, equilibrated with 2% ACN and incubated with sample solution containing 1% ACN. Graphite was activated with ACN and equilibrated with water before sample loading.

The tubes were vortexed for 1 min and ultrasonicated for 10 min to achieve an optimal distribution and interaction between the sample and the BN particles. Afterwards, KH₂PO₄ (3 or 14 mg, respectively) was added, ultrasonicated for 5 min, centrifuged for 3 min and the supernatant was removed. The sample was washed with 400 μl 50 mM KH₂PO₄, centrifuged for 2 min and the supernatant was removed carefully. The remaining amount of water was calculated from the mass difference. Finally, the bisphenols were eluted by adding 100 μl of organic solvent, ultrasonicated for 10 min and centrifuged for 3 min.

The effect of pH on the adsorption of bisphenols to BN was carried out using 50 mM KH₂PO₄ titrated to the desired pH values with either phosphoric acid or 1 M sodium hydroxide and shortly before SPE the samples were spiked with bisphenol derivatives (2 ng/mL).

The influence of the presence of organic solvent, e.g. ACN and ethanol on the extraction efficiency of BN was carried out. Loading solutions containing ACN or ethanol with concentrations ranging from 0 to 35 vol%, spiked with bisphenol derivatives (2 ng/mL) were incubated with BN.

For the study of the effect of incubation time on the extraction efficiency of BN, 5 mg BN was mixed with 2 mL bisphenols standard solution (0.2 μg/mL and 10 μg/mL in 50 mM KH₂PO₄, pH 5) ultrasonicated for a defined time (0.5–10 min) and followed by centrifugation for 1 min. the supernatant was collected and analyzed with HPLC.

The binding capacity of BN was measured by equilibrating 10 mg BN with different amounts of BPA ranging from 0.076 to 25 μg per mg BN in 50 mM KH₂PO₄ (pH 5.0). The mixture was suspended by ultrasonication for 10 min, then centrifuged for 1 min and the aqueous supernatants were analyzed with HPLC.

A calibration curve and a linear regression equation were determined for each bisphenol standard using dilutions ranging from 75 to 800 ng/mL (Fig. S1). Standard solution at each concentration level was analyzed in triplicate. Limits of detection (LODs) and limits of quantification (LOQs) were estimated based on the residual standard deviation of the response (SD) and the slope (S) of a specific calibration curve containing standard solutions in the range of LOD according to the formula: LOD = 3.3 (SD/S) and LOQ = 10 (SD/S), respectively. The obtained LODs and LOQs were verified experimentally by analysis of standards with concentrations close to LOQs and LODs.

The repeatability of the extraction procedure was evaluated by using the standard deviation (SD) of triplicate measurements of standard solutions on 1 day or 3 days.

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