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Determination of seven bisphenol analogues in reed and *Callitrichaceae* by ultra performance liquid chromatography–tandem mass spectrometry

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ABSTRACT

An analytical procedure was developed to simultaneously determine bisphenol S, bisphenol F, bisphenol B, bisphenol A, bisphenol AF, tetrachlorobisphenol A, and tetrabromobisphenol A in reed and *Callitrichaceae*. Homogenized samples were extracted with acetonitrile and purified using an ENVI™-Carb cartridge followed by an NH_2 cartridge. The analytes were separated and quantified by ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS). The recoveries at three fortified levels in reed and *Callitrichaceae* were 57–108% and 68–106%, respectively, with relative standard deviations of no more than 15% ($n = 6$). The method limits of quantification and detection for the seven bisphenol analogues were 0.005–0.500 μg/kg and 0.002–0.150 μg/kg, respectively. This method was used to analyze the seven compounds in ten reed and *Callitrichaceae* samples collected from Zhejiang, China.

1. Introduction

Bisphenol A (BPA, 2,2-bis (4-hydroxydiphenyl) propane) has been widely used as the primary intermediate in the production of polycarbonate plastics and epoxy resins for several decades [1–3]. BPA can trigger adverse health outcomes, particularly through endocrine disruption, even at doses of 10–100 ng/kg body weight [2–4]. The EU Commission, US Environmental Protection Agency, and Health Canada have set different limits on its application. BPA in commercial products is gradually being replaced with its analogues, such as bisphenol S (BPS, 4,4′-sulfonyldiphenol), bisphenol F (BPF, 4,4′-methylenebisphenol), bisphenol B (BPB, 2,2-bis (4-hydroxyphenyl) butane), and bisphenol AF (BPAF, hexafluorobisphenol A), to comply with these restrictions [5]. BPS is used as an alternative to BPA in the production of thermal paper [6], and BPF, BPAF, BPB, and BPS are used in the production of polycarbonate plastic and resins [7–11]. Another two widely used analogues are tetrachlorobisphenol A (TCBPA) and tetrabromobisphenol A (TBBPA), which are used as reactive flame retardants in resins and polycarbonate plastics.

Studies have shown that the toxicities (e.g., genotoxicity and estrogenic activity) of BPS, BPB, BPAF and BPF are similar to that of BPA [5,9,12]. The estrogenic effect of BPAF and BPB on gene and protein expression in MCF-7 breast cancer cells is greater than that of BPA [12], and BPAF binds to β-estrogen receptors more effectively than BPA [13]. BPAF may cause testosterone reduction by directly affecting testis function in adult male rats [14]. TBBPA and TCBPA could be ligands of peroxisome proliferator-activated receptors and inhibit the binding of T3 to TRα [15,16].

Among these bisphenol analogues mentioned above, BPA, TBBPA and TCBPA had been widely studied and found in different environmental matrices [3,17–19]. As emerging environmental contaminants, BPAF, BPS and BPF have been concerned recently on its occurrence in foodstuffs from the United States [20] and environmental matrices [21–23], mainly in water and sediment. Many methods have been developed for the analysis of BPA, TCBPA and TBBPA in environmental and food samples using high-performance liquid chromatography (HPLC), liquid chromatography–mass spectrometry (LC–MS/MS), gas chromatography–mass spectrometry (GC–MS/MS) and, to a limited extent, immunochemical methods [17–19,24–27]. A few analytical methods of the determination of bisphenol analogues in vegetables or fruits were recently reported. Kang et al. [28] developed an analytical method for determination of BPA in vegetables and fruits based on sample extraction with acetone and HPLC analysis with fluorescence detection. Lu et al. [29] reported the analysis of BPA in vegetables and fruits by GC–MS/MS.

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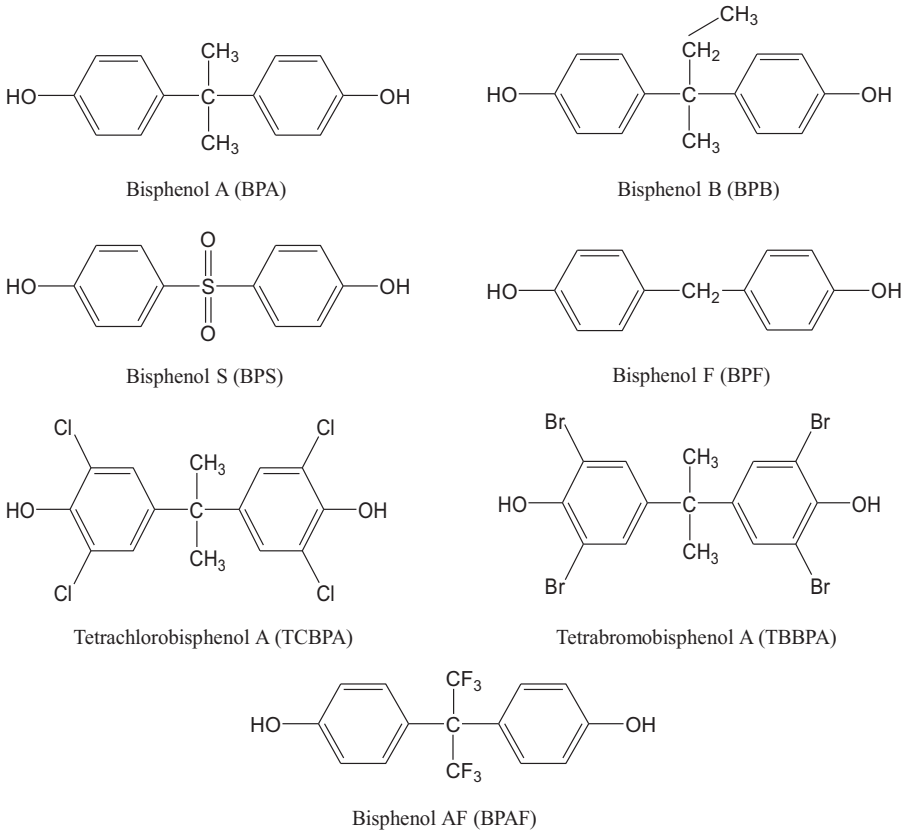

Fig. 1. Chemical structures of target compounds.

Li et al. [30] reported the analysis of TBBPA in cabbage and radish by LC–MS/MS based on Soxhlet extraction.

As important biological components of the environment, plants play a significant role in contaminant enrichment and removal. Reed and *Callitrichaceae* are two common aquatic plants in many regions. Reed and some other riparian buffer zone plants can remediate organic pollutants and decrease contamination of sludge [31,32]. An analytical method for determination of bisphenol analogues in aquatic plants was necessary to study the chemical's transformation in the whole aquatic ecosystems. Here, we developed a sensitive and precise method using solid-phase extraction (SPE) followed by ultra performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS) for the determination of BPS, BPF, BPB, BPA, BPAF, TCBPA, and TBBPA (chemical structures are shown in Fig. 1) in two common aquatic plants, reed and *Callitrichaceae*.

2. Materials and methods

2.1. Reagents and chemicals

BPS (>98.0%), BPF (>99.0%), BPF-d_{10} (>99.0%), BPA (98.5%), BPA-d_4 (>97.8%), BPB (>98.0%), and BPAF (98%) were purchased from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). TCBPA (>99.0%), TCBPA-$^{13}C_{12}$ (>99.0%), TBBPA (>99.0%), and TBBPA-$^{13}C_{12}$ (>99.0%) were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). HPLC-grade methanol, acetonitrile, ethyl acetate, and acetone were supplied by Dickma (Lake Forest, CA, USA). Ultrapure water was obtained from a Milli-Q Ultrapure water system (Millipore, Bedford, MA, USA). Formic acid (99%) was purchased from Acros Organics (Morris Plains, NJ, USA). Stock standard solutions (10 mg/mL) were individually prepared by dissolution in methanol and stored at −20 °C. Intermediate solutions were prepared from the stock solutions by appropriate dilution in methanol/water (50:50 v/v) and stored at −20 °C.

The Supelclean ENVI^{TM}-Carb cartridge (GCB, 500 mg, 6 mL) was purchased from Supelco (Bellefonte, PA, USA). Oasis HLB (500 mg, 6 mL) and Sep-Pak C18 (500 mg, 6 mL) cartridges were purchased from Waters (Milford, MA, USA). The Bond Elut LRC-NH_2 (100 mg) cartridge was from Agilent Technologies (Lake Forest, CA, USA).

2.2. Sample collection

The blank samples were collected from river and market of non-industrial pollution area in Beijing, both of which were ensured free of analytes and used for method development. After the analytical method was developed, some reed and *Callitrichaceae* were collected from different sampling sites in a region near a BPAF manufacturing plant in Zhejiang, China.

2.3. Sample pretreatment procedure

The collected samples were pre-rinsed with Milli-Q water. After removal of the surface water by air drying, the samples were homogenized with a BÜCHI B-400 mixer (BÜCHI Labortechnik AG, Switzerland) and stored at −20 °C until analysis. A total of 2.0 g *Callitrichaceae* or 1.0 g reed was spiked with 5.0 ng BPA-d_4, TCBPA-$^{13}C_{12}$, and TBBPA-$^{13}C_{12}$ as internal standards. The samples were extracted twice with 5 mL acetonitrile, sonicated at room temperature for 20 min, and centrifuged at 9000*g* for 10 min at 4 °C. The extract was diluted to 40 mL with water and then applied to GCB cartridge, which was conditioned and equilibrated with 18 mL of methanol followed by 6 mL of water. After washed by 6 mL of methanol/water (50:50 v/v), the GCB cartridge was eluted with 6 mL of methanol/acetone (40:60 v/v). Then, the eluate was applied to a NH_2 cartridge preconditioned by 6 mL methanol and