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Simultaneous determination of tetrabromobisphenol A, tetrachlorobisphenol A, bisphenol A and other halogenated analogues in sediment and sludge by high performance liquid chromatography-electrospray tandem mass spectrometry

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Abstract

A high performance liquid chromatography–electrospray (negative) ionization-tandem mass spectrometry (HPLC–ESI(−)-MS–MS) based method has been developed for simultaneous determination of bisphenol A (BPA), tetrachlorobisphenol A (TCBPA), and tetrabromobisphenol A (TBBPA), as well as lower brominated BPA analogues in sediment and sludge samples. Samples were extracted with MTBE, target compounds were partitioned by aqueous solution of sodium hydroxide. The solution was subsequently acidified, and the enrichment and desalting were performed via solid phase extraction (SPE). After cleanup the target compounds were determined by HPLC–ESI(−)-MS–MS. The method limits of quantification (MLOQs) from sediment and sludge for BPA, monobromo-bisphenol A (mono-BBPA), dibromo-bisphenol A (di-BBPA), tribromo-bisphenol A (tri-BBPA), TBBPA and TCBPA were 0.15, 0.02, 0.02, 0.04, 0.05, and 0.03 ng/g (dry weight), respectively. Mean recovery of the analytes from spiked samples ranged from 70 to 105%, and the relative standard deviation ranged from 4.9 to 13.1%. The method was successfully applied to sediment and sludge samples analysis.

Keywords: Liquid chromatography tandem mass spectrometry; BPA; TCBPA; TBBPA; Sludge; Sediment

1. Introduction

Tetrabromobisphenol A (4,4′-isopropylidenebis(2,6-dibromophenol), TBBPA) is one of the primary components in a high volume, commercially-used flame retardant know as TBBPA. TBBPA is used as a reactive or additive flame retardant in polymers, such as ABS, epoxy and polycarbonate resins, high impact polystyrene, phenolic resins, adhesives, and others. In printed circuit boards TBBPA content may be as high as 34% by weight [1]. Despite the reactive properties of TBBPA, environmental release has been shown to occur for TBBPA and degradation products from both additive- and reactive-treated products [1]. TBBPA has been found in samples of air, soil, sediment and sludge, wildlife and human serum [2–10].

Similar to TBBPA, tetrachlorobisphenol A (4,4′-isopropylidenebis(2,6-dichlorophenol), TCBPA) is also used commercially as a flame retardant, but to a lesser extent than TBBPA. Recently investigation showed that chlorination of BPA in aqueous media may also result in the formation of TCBPA [11]. Regardless, there are very few published reports on TCBPA as an environmental residue in the literature [10,12].

Bisphenol A (BPA) is a major industry product and widely used in the production of epoxy resins and polycarbonate

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plastics, which are used as food-contact surface coatings for cans, metal jar lids, coatings, finishes, automobile parts, high-impact windows and others [13]. BPA is commonly found in sediment, sludge and environmental water samples, as well as drinking water, juice, milk and other food product [14,15].

Biodegradation studies have shown that TBBPA can be partly degraded to lesser brominated analogues under both aerobic and anaerobic conditions, in soil, and in river sediment [16]. This degradation is dependent on soil type, temperature, humidity, and the composition of the soil. It was reported that anaerobic incubation of the sediment with TBBPA and peptane–tryptone–glucose–yeast extract medium resulted in an 80% decrease in the TBBPA concentration and transformation to a non-brominated bisphenol A (BPA) metabolite [17]. TBBPA was reductively debrominated to BPA, and thus it is possible that degradation to other lesser brominated BPAs might occur [18].

The acute oral toxicity of BPA and its halogenated analogues for laboratory animals is low, but recent research indicates that these chemicals have high potential as endocrine disruptors in human and wildlife [19]. Although as much as 10,000 times less potent than the estrogen 17β-estradiol, BPA has been recognized as a relatively potent xenoestrogen in human and wildlife in vivo and in vitro studies [20]. TBBPA and lesser brominated analogues share structural similarities to thyroxine (T4), the major circulating form of thyroid hormone. With respect to T4, TBBPA competitively binds with human transthyretin (TTR) which is the major thyroid hormone transport protein in mammals and avian species [21]. It has also been reported that with a decreasing number of bromine atoms, polybrominated BPAs become poorer TTR binding competitors, but become increasingly potent agonists for estrogen receptor (ER)-mediated gene expression in, e.g. human breast and embroyonic kidney cell transfected with estrogen-responsive luciferase reporter gene construct (pEREtata-Luc) [22]. Like TBBPA, TCBPA has been shown to possess thyroid hormone disrupting potential [23].

Concern continues to rise with respect to the environmental presence and fate of TBBPA, TCBPA and BPA, due to high volume production, widespread commercial use and ubiquitous occurrence in aquatic environments. BPA, TCBPA, and TBBPA and its halogenated analogues are expected to associate with solid matrices such as sediments and suspended particulate matter [5]. Because of its partition coefficient ($\log K_{ow} = 4.5$) and low water solubility (0.72 mg/L), TBBPA in generally adsorbed to organic matter and is frequently not detectable in water samples. BPA has a lower $\log K_{ow}$ of 3.4, but it has been predicated that about 50% of BPA in the environment is bound to sediments or soils [24].

Few analytical methods have been reported for determination of BPA in sediment and soil [14,15]. BPA can be spectroscopically determined using HPLC with ultraviolet (UV) detection, although it is often not an adequately sensitive technique for BPA determination in environmental samples [17]. With four bromine atoms, TBBPA can be determined at very low levels in sample fractions by gas chromatography-electron capture detection (GC-ECD) or mass spectrometry with electron capture negative ionization detection (GC–MS(ECNI)) [4,5,10,25]. However, derivatization is necessary for GC separation, and GC-ECD or GC–MS(ECNI) is generally insensitive for lower brominated BPAs unless an effective electron-capturing functional group is introduced into the molecule by derivatization.

High performance liquid chromatography (HPLC) with mass spectrometric detection, e.g. single quadrupole MS, tandem quadrupole MS–MS, ion trap MS–MS and TOF-MS, has been successfully employed in the determination of TBBPA in sediment, sludge and biological tissue samples [6–8]. To our knowledge, simultaneous determination of BPA, TCBPA and TBBPA and its lower brominated analogues by HPLC–MS has not yet been reported. We presently report on a high performance liquid chromatography–electrospray (negative) ionization-tandem mass spectrometry (HPLC–ESI(−)-MS–MS) based method for the sensitive, precise and simultaneous determination of BPA, TCBPA, TBBPA, tribromo-bisphenol A (tri-BBPA), dibromo-bisphenol A (di-BBPA) and monobromo-bisphenol A (mono-BBPA) for sediment and sewage sludge samples.

2. Experimental

2.1. Chemicals and materials

The molecular structures of target compounds studied in this work are shown in Fig. 1 Tetrabromobisphenol A, tetrachlorobisphenol A and bisphenol A were obtained from Aldrich Chemical Co. (WI, USA) and were of minimum 97% purity. Ring-$^{13}C_{12}$ labeled TBBPA was obtained from Cambridge Isotope Laboratories Inc. (MA, USA) and was of minimum 99% purity. mono-BBPA and tri-BBPA were a kind gift from Drs. Göran Marsh and Åke Bergman (Department of Environmental Chemistry, Stockholm University, Sweden). 4,4′-Isopropylidenebis(2-bromophenol) (di-BBPA) was synthesized in our lab according to the method reported by Eriksson et al. [18]. Briefly, 0.5 g of BPA was dissolved in acetic acid (200 mL) and 0.24 mL bromine solution was added. The reaction mixture was stirred at room temperature for 4 h. The solution was neutralized with sodium hydrogen carbonate after 100 mL water was added. The product was liquid–liquid extracted using dichloromethane, and was subsequently purified by three successive column chromatography steps using silica gel. HPLC–ESI(−)-MS–MS and GC–MS(ECNI) analysis demonstrated that the final di-BBPA purity was >97%.

Individual standard stock solutions of BPA, TCBPA, TBBPA, tri-BBPA, di-BBPA and mono-BBPA of 1 mg/mL of each were prepared by dissolving in methanol accurate amounts of pure standard compounds. Working solutions (10 μg/mL of BPA and 2 μg/mL of other compounds) were prepared by mixing individual stock solutions, followed by necessary serial dilution with methanol. The internal standard, $^{13}C_{12}$-labeled TBBPA, working solution concentra-