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Determining leaching of bisphenol A from plastic containers by solid-phase microextraction and gas chromatography–mass spectrometry☆

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Abstract

This study evaluates solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) to determine trace levels of bisphenol A in water and leached from plastic containers. The extraction using headspace post-derivatization with bis(trimethylsilyl) trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS) vapor, following SPME was compared with extraction without derivatization. The SPME experimental procedures to extract bisphenol A in water were optimized with a relatively polar polyacrylate (PA)-coated fiber, an extraction time of 50 min and desorption at 300 °C for 2 min. Headspace derivatization following SPME was performed using 7 μL of BSTFA with 1% TMCS at 65 °C for 30 s. The precision was 5.2% without derivatization and 9.0% headspace derivatization. The detection limit was determined to be at the ng/L level. When SPME was used following headspace derivatization, the detection limit was one order of magnitude better than that achieved without derivatization. The results of this study reveal the adequacy of SPME–GC–MS method for analyzing bisphenol A leached from plastic containers. The concentrations of bisphenol A leached from plastic containers into water ranged from 0.7 to 78.5 μg/L.

Keywords: Bisphenol A; Solid-phase microextraction; Plastic containers; GC–MS

1. Introduction

Bisphenol A, 4,4′-(1-methylethylidene) bisphenol or 2,2-(4,4-dihydroxydiphenyl) propane is used as stabilizing material or antioxidant for numerous types of plastics including polyvinyl chloride [1]. It is also used by manufacturers as an intermediate in producing epoxy resins, polycarbonate, flame retardants and other specialty products [2,3]. The final products include protective coating, powder paints, automotive lenses, protective window glassing, building materials, adhesives, compact disks, optical lenses, paper coating and products for encapsulating electrical and electronic parts. The amount of bisphenol A used increases with the production of plastics. It has been discharged directly or indirectly into the environment, contaminating the atmosphere, water and soil. It has also been shown that bisphenol A leached from lacquer-coated cans [4] and baby feeding bottles [5] due to the hydrolysis of the polymer during thermal treatment. Bisphenol A is slightly to moderately toxic and has a low potential for bioaccumulation in aquatic organisms. Bisphenol A, which is leached from polycarbonate flasks during autoclaving, has been demonstrated to exhibit estrogenic activity [6–8]. Most countries have classified it as an endocrine disrupter. Yasuhara et al. [9] examined the concentration of bisphenol A in the most polluted leachate, and found that it was lower than the reported toxic concentrations for invertebrates or fish. The leaching of bisphenol A is likely to become an important problem because much of it is produced and this compound is widely used. Therefore, a rapid, accurate and sensitive analytical method is acquired to identify and determine the amount of

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bisphenol A in water or the amount leached from various plastics.

Numerous methods have been developed to identify trace bisphenol A in various matrices, although they are based primarily on chromatographic methods, including gas chromatography (GC) and liquid chromatography (LC) [10–15]. Many species of plastic additives, such as phthalates, with the potential to interfere in the detection of bisphenol A may leach from the plastics to the water. A gas chromatography–mass spectrometry (GC–MS) method is typically applied because it has high selectivity and sensitivity, preventing such interference. However, the validity of an analytical sample for trace bisphenol A analysis depends on suitable sampling and preconcentration. Earlier investigations have set forth various means of extracting bisphenol A from water, including liquid–liquid extraction [16,17] and solid-phase extraction [18–20] with reversed-phase materials. Conventional extraction methods, while efficient and precise, are relatively time-consuming, hazardous to human health since they use organic solvents, and extremely expensive because of the disposal of solvents. Hence, a relatively simple, rapid and solvent-free extraction method must be developed. Solid-phase microextraction (SPME) can solve many of the above problems. Zhang et al. detailed the underlying principles and merits of trace organic analysis and applying SPME to extract trace organic compounds from a complex matrix [21]. Some of the applications of SPME in environmental trace analysis have been evaluated in our laboratory [22–24].

Gas chromatographic analysis reveals that low-volatility polar compounds such as phenolic and acidic compounds exhibit low sensitivity and tailing. Derivatization methods have been extensively applied to improve various gas chromatographic parameters including accuracy, reproducibility, sensitivity and resolution, by suppressing tailing and enhancing thermal stability. The derivatization approaches such as methylation [25], acetylation [26–29] and silylation [20,30–34] have been used for analyzing trace bisphenol A. The goal of this work was to evaluate SPME coupled with GC–MS to determine trace levels of bisphenol A in water. In this study, bisphenol A adsorbed on the fiber coating of the SPME is derivatized after it is extracted from water with a mixture of bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1) vapor in a headspace device. The optimum conditions for extracting bisphenol A from water are also systematically studied. To confirm the proposed method's effectiveness, the optimized procedure combined with GC–MS to determine the amount of bisphenol A leached from plastic materials was performed.

2. Experimental

2.1. Reagents and materials

Bisphenol A (>99%) was purchased from Sigma–Aldrich Inc. (Milwaukee, WI, USA). Bis(trimethylsilyl)trifluoroacetamide (BSTFA) that contained 1% trimethylchlorosilane (TMCS) were also obtained from Sigma–Aldrich Inc. Stock standard solution of bisphenol A was prepared at a concentration of 100 mg/L in acetone and diluted with water to yield the required concentration. The standard solutions were stored at 4 °C in a refrigerator. All chemicals and reagents used in this work were analytical or research grade without further purification. The purified water was obtained using an “Ultra Clear” purification system (SG Water, France). All glassware was silanized before it was used by soaking the glassware overnight in toluene solution with 10% dichlorodimethylsilane. The glassware was rinsed in toluene and methanol and then thoroughly dried for 4 h. The leached samples were collected from water at 100 °C in baby feeding bottles, and containers of polycarbonate and polyvinyl chloride.

2.2. Apparatus

Chromatographic analysis was undertaken on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with an MS Engine mass spectrometer and a split/splitless injection port. The column was a 30 m × 0.25 mm i.d. fused-silica capillary column DB-5MS and a stationary phase thickness of 0.5 μm (J&W Scientic, Folsom, CA, USA). Helium carrier gas was at a rate of 1 mL/min using an electronic pressure control. During fiber injection, the injector was used at 300 °C. The transfer line was held at 250 °C. The oven was initially set at 80 °C, for 2 min, a linear temperature gradient of 20 °C/min to 280 °C and held for 1 min.

Bisphenol A was quantified in the selected ion monitoring (SIM) mode, and its characteristic masses were selected from their full spectra. The ion, m/z 213 was selected for quantification, and that ion, m/z 228 was used as confirmed ion for bisphenol A analysis without derivatization. Following derivatization, the masses of the quantification and confirmed ions were changed to m/z 357 and m/z 372, respectively.

2.3. Sampling

SPME was performed using commercially available fibers and housed in the manual holder (Supelco, Bellefonte, PA, USA). The microextraction fibers tested herein were coated with poly(dimethylsiloxane) (PDMS) of 100 and 7 μm thickness; 85 μm thickness of polyacrylate (PA); 75 μm thickness of carboxen/poly(dimethylsiloxane) (CAR/PDMS); 65 μm thickness of polydimethylsiloxane/divinylbenzene (PDMS/DVB) and 65 μm thickness of carbowax/divinylbenzene (CW/DVB). All of them were purchased from Supelco. The fibers were conditioned before their first use according to the manufacturer's specifications. All analyses were undertaken using 40 mL sample vials that contained 30 mL of solution and closed using a PFTE-coated septum. During extraction, the aqueous samples were con-