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Determination of alkylphenols and bisphenol-A
A comparative investigation of functional polymer-coated membrane microextraction and solid-phase microextraction techniques

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Abstract

A functional polymer (hydroxylated polymethacrylate) coated on porous polysulfone hollow fiber membrane (PS-HFM) was used as an adsorbent for the extraction of alkylphenols and bisphenol-A from seawater samples. Analyses of the extracts were performed using gas chromatography–mass spectrometry (GC–MS) after injection-port derivatization using bis(trimethylsilyl)trifluoroacetamide (BSTFA). We term the procedure as polymer-coated hollow fiber microextraction (PC-HFME). Owing to high porosity PS-HFM coated with hydroxylated polymer showed high extraction efficiency. Compared with solid-phase microextraction (SPME), PC-HFME showed good selectivity and sensitivity. Detection limits of alkylphenols and bisphenol-A ranged between 0.07 and 2.34 ng l^{-1}. The linearity range was from 0.01 to 15 $\mu g\, l^{-1}$ and the correlation coefficient (*r*) up to 0.997. The sensitivity and selectivity of the coated HFM could be potentially tuned by changing the characteristics of the coated hydroxylated polymer. The PC-HFME procedure was applied to the detection of alkylphenols and bisphenol-A in the coastal waters of Singapore.

Keywords: Alkylphenols and bisphenol-A; Polymer-coated hollow fiber microextraction; Endocrine disruptors; Environmental analysis; Extraction methods; Solid-phase microextraction

1. Introduction

Alkylphenols (APs) and bisphenol-A (BPA) have been used for more than 40 years as detergents, emulsifiers, wetting agents and dispersing agents. They have been reported to cause a number of estrogenic effects in a variety of aquatic organisms [1].

Octylphenols and nonylphenols are used in plastic packing materials or as spermicides. The estrogenic properties of the nonylphenols and octylphenols are well documented [2]. Similarly, diethyl stilbestrol, bisphenol-A is capable of binding to DNA after metabolic activation and has estrogenic properties at low concentrations [2]. Low doses of bisphenol-A in mice could bring on early puberty in females [3]. Recently trace level contamination of alkylphenols and bisphenol-A in seafood and blood samples have been reported [4,5]. Healthy humans exposed to low level dosage of alkylphenols and bisphenol-A via daily activities may be associated with health risks [6]. Therefore, the detection and quantification of these endocrine disruptors in the aquatic environment is necessary to learn more about their biohazards.

The increased awareness of the presence of APs and BPA in the environment has led to an intensified interest in the trace

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Abbreviations: AP, alkylphenol; BPA, bisphenol-A; BSTFA, bis(trimethylsilyl)trifluoroacetamide; LLE, liquid–liquid extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; SBSE, stir bar sorptive extraction; PC-HFME, polymer-coated hollow fiber extraction; PDMS, polydimethoxysilane; PDMS–DVB, polydimethoxysilane–divinylbenzene; PA, polyacrylate; PS, polysulfone; HFM, hollow fiber membrane; RSD, relative standard deviation; GC–MS, gas chromatography–mass spectrometry; HPLC, high performance liquid chromatography; CE, capillary electrophoresis; LC–MS, liquid chromatography–mass spectrometry; UV, ultraviolet

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analysis of these compounds. Determination of APs and BPA from environmental samples at low concentrations is still a challenging task. Traditional techniques for the extraction and concentration of APs and BPA from aqueous samples are liquid–liquid extraction (LLE) [7] and solid-phase extraction (SPE) [8,9]. However, in both LLE and SPE, large amount of sample and solvents are need. In recent years, solventless and solvent minimized polymer sorption techniques such as solid-phase microextraction (SPME) [10] and stir bar sorptive extraction (SBSE) [11] techniques have been employed for the extraction of APs and BPA. In SPME, polymer fibers coated with relatively polar adsorbents such as polyacrylate (PA) and polydimethoxysilane–divinylbenzene (PDMS–DVB) have been used for the extraction of APs and BPA. In the SBSE, only PDMS coated stir bars are commercially available, although, strictly speaking, the non-polar PDMS is not suitable for the extraction of APs and BPA [12]. In SBSE, thermal desorption and solvent desorption are generally used for desorption of the analytes from the PDMS coating on the stir bar [13–15].

For quantitative determination of APs and BPA, GC–MS with electron impact ionization [16], and chemical ionization [17], HPLC with UV absorbance [18], or fluorescence detection [19], LC–MS [20] and CE [21] have been used. Analysis of APs and BPA using GC–MS is more common than others [22]. Due to the polarity of APs and BPA, GC–MS requires derivatization of the analytes before analysis. A wide range of derivatization procedures have been reported in the literature, e.g. methylation [23], acetylation [24], and silylation [25]. Silylation using bis(trimethylsilyl)trifluoroacetamide (BSTFA) is a rapid and commonly used derivatization technique, even though excessive amount of BSTFA and moisture content could affect the derivatization process [22]. Three different BSTFA derivatization approaches after microextraction have been reported, which include (i) headspace derivatization [26], (ii) injection-port derivatization [27–29] and (iii) direct derivatization (extract and BSTFA were mixed and then analysed) [30].

In this study, we introduce polymer-coated hollow fiber extraction (PC-HFME) of AP and BPA in which hydroxylated polymethacrylate is coated on porous polysulfone (PS) hollow fiber membrane (HFM) and used as adsorbent. Compared with SPME sorbent coating materials, our novel polymer has high number of functional groups and increased swelling tendency in water. Such features are expected to enhance the extraction efficiency. Results from PC-HFME are compared with SPME experiment to evaluate the procedure.

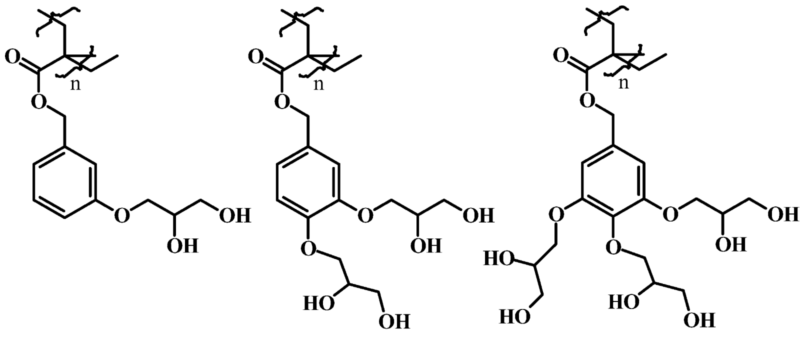
2. Experimental

2.1. Chemicals and reagents

The following chemical standards (purity ≥97%) were obtained from Wako Chemicals (Tokyo, Japan): 4-*n*-butylphenol, 4-*tert*-butylphenol, 4-*n*-pentylphenol, 4-*n*-hexylphenol, 4-*n*-octylphenol, 4-*tert*-octylphenol, 4-*n*-heptylphenol, 4-nonylphenol, and bisphenol-A. The derivatization agent bis(trimethylsilyl)trifluoroacetamide (BSTFA) (purity >98%) and all HPLC-grade organic solvents, hydrochloric acid, sodium hydroxide and sodium chloride were purchased from Merck (Darmstadt, Germany). Ultrapure water was prepared on a Milli-Q (Milford, MA, USA) system. A standard stock solution of 50 $\mu g\,ml^{-1}$ of each analyte was prepared in acetone. A working standard solution (1 $\mu g\,ml^{-1}$ of each analyte) was used for low concentration spiking (<1000 $ng\,l^{-1}$) and for higher concentrations the 50 $\mu g\,ml^{-1}$ stock solution was used.

2.2. Materials

MicroPES® 0.3/2 polysulfone hollow fiber membrane (PS-HFM) was purchased from Membrana (Wuppertal, Germany). The HFM with an inner diameter of 300 μm and a pore size of 0.2 μm was used for polymer-coating. The SPME fiber holder and fibers (PDMS 7 μm, 100 μm, PDMS–DVB and polyacrylate (PA) 85 μm) and extraction vials, septa and aluminium caps were purchased from Supelco (Bellefonte, PA, USA) and used without modification. Before extraction the fibers were conditioned in the GC injection port based on the manufacturer's recommended procedure. Ultrasonicator was purchased from Midmark (Versailles, Ohio, USA) and



1 **2** **3**

Fig. 1. Molecular structure of the polymers (**1**–**3**) used in our investigation.