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An etched stainless steel wire/ionic liquid-solid phase microextraction technique for the determination of alkylphenols in river water

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ABSTRACT

In this study, a stainless steel wire/ionic liquid-solid phase microextraction technique was developed for the direct extraction of APs from water samples. Some parameters were optimised, such as selection of the substrate and ILs, extraction time, extraction temperature, stirring rate and sample pH, etc. The experimental data demonstrated that the etched stainless steel wire was a suitable substrate for IL-coated SPME. The coating was prepared by directly depositing the ILs onto the surface of the etched stainless steel wire, which exhibited a porous structure and a high surface area. The $[C_8MIM][PF_6]$ IL exhibited maximum efficiency with an extraction time of 30 min, and the aqueous sample was maintained at 40 °C and adjusted to pH 2 under stirring conditions. The enrichment factor of the IL coating for the four APs ranged from 1382 to 4779, the detection limits (LOD, S/N=3) of the four APs ranged from 0.01 to 0.04 ng mL^{-1} and the RSD values for purified water spiked with APs ranged from 4.0 to 11.8% (n=3). The calibration graphs were linear in the concentration range from 0.5 to 200 ng mL^{-1} ($R^2 > 0.9569$). The optimised method was successfully applied for the analysis of real water samples, and the method was suitable for the extraction of APs from water samples.

1. Introduction

Alkylphenols (APs) are ubiquitous environmental contaminants resulting from the degradation of alkylphenol polyethoxylates (APnEOs). APnEOs are surface-active agents that are commonly used in household cleaning products, agricultural applications and the chemical industry [1]. The residual surfactants and their degradation products are directly discharged to plants or surface water without any treatment, and the residuals can disperse into different environmental compartments. APs possess lipophilic properties, are stable in the environment and exhibit a tendency to accumulate in living organisms. The European Union (EU) listed APs as endocrine-disrupting chemicals (EDCs) in 1996. Emerging research suggests that APs are widely distributed in various environmental matrices, and an increased awareness of the presence of APs in the environment has led to an intensified interest in the trace analysis of these compounds [2,3].

The determination of APs from environmental samples at low concentrations remains a challenging task, and major studies on APs have focused on the development of rapid and simple extraction methods. The conventional methods for extracting APs from an environmental sample are liquid–liquid extraction (LLE) [4] and solid-phase extraction (SPE) [5,6]. However, these methods are tedious, time-consuming and require large amounts of high-purity organic solvents, which are expensive, toxic and cause additional environmental problems. Over the past decade, special attention has been focused on sample preparation methods that ensure a reduction in the amount of organic solvents required or even eliminate them completely and limit the number of operations and processes to a minimum.

Solid-phase microextraction (SPME) is a sample preparation technique that integrates sampling, isolation, enrichment and injection into one step [7–9]. SPME has sparked great interest in the scientific community because it is solvent-free, sensitive, fast, simple to operate and easily incorporated into chromatographic analysis. A polymer-coated microfibre plays the key role in the SPME procedure; the fibre can adsorb certain organic analytes and concentrate them from the various phases of a sample [10].

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The fibre has a crucial effect on the accuracy and selectivity of the SPME procedure. Certain commercial fibres of this have been developed; however, these fibres are expensive, fragile and unstable under extreme thermal and chemical conditions, which limit the applications of SPME for real samples. To meet the requirements of complex analysis, new SPME coatings with remarkable properties, such as enhanced sensitivity [11], high thermal stability [12], mechanical and chemical stability and low cost, have been continually developed using new preparation methods [13] or new materials [14,15]. Moreover, fused silica has the disadvantages of being fragile and expensive. Therefore, recent studies have focused primarily on the development and further extension of supports with a long lifetime [16]. Other materials have been explored to replace silica rods as the SPME substrate [17–20]. Stainless steel, which is flexible and durable and exhibits good mechanical properties, is a suitable SPME substrate [21–23]. Stainless steel is resistant to corrosion in various environments, such as in acidic solutions and under alkaline conditions.

Room-temperature ionic liquids (ILs) are ionic compounds that are liquid over a temperature range near or below room temperature. ILs are non-molecular solvents consisting of a heterocyclic cation and an anion. ILs exhibit good thermal stability, negligible vapour pressure and convenient use. Because the cations and the anions can be integrated in different combinations, we can also obtain ILs with specific functions by specially designing the structure thereof. ILs exhibit good extractability for various organic compounds and metal ions [24–26]. Considering the above mentioned characteristics and advantages, ILs may be potential adsorbents for SPME. Jiang [27] and Amini [28] demonstrated that [C_8MIM][PF_6] can be physically adsorbed on the surface of fused silica tubing or stainless steel wire as the coating for SPME.

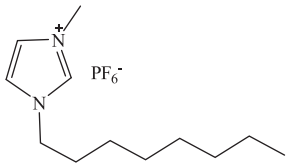
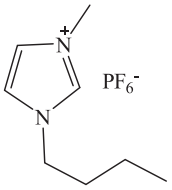
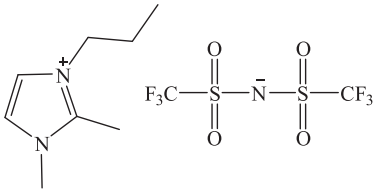
In this study, we prepared a SPME fibre based on the deposition of an ionic liquid on an etched stainless steel wire, instead of a commercial polyacrylate (PA) fibre, to analyse APs in water samples. Four oestrogenic APs (4-*n*-pentylphenol, 4-*n*-hexylphenol, *p*-*tert*-octylphenol and nonylphenols) were used as the target compounds. The goal of this study was to develop a sensitive, robust and inexpensive SPME method that can be used for the analysis of APs in water samples. Therefore, we also investigated the effects of the various experimental parameters that affected the extraction efficiency. Under the optimised conditions, we compared the enrichment factor with that obtained from a commercial PA fibre. Finally, the fibres were applied to extract APs from actual river-water samples to evaluate their applicability in real sample analysis.

2. Experimental

2.1. Chemicals and materials

The alkylphenol standards (4-*n*-pentylphenol, 4-*n*-hexylphenol, *p*-*tert*-octylphenol and nonylphenols), the silylation reagent BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) and the internal standard (phenanthelene-d_{10}) used in this study, whose purities were higher than 99%, were purchased from Chem. Service (Hatfield, PA, USA). Standard solutions (1000 mg L^{-1}) of each compound were prepared in HPLC-grade methanol and stored in a refrigerator. A mixture of these alkylphenol compounds was prepared by diluting the standard solution with methanol, and additional diluted working solutions were prepared daily by diluting the standard solution with purified water or river water. The ILs used in this study were 1,2-dimethyl-3-propylimidazolium bis (trifluoromethylsulphonyl)imide [C_3MIM][NTf_2], 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]), which were purchased from Sigma-Aldrich (Bellefonte, PA, USA). The structures and densities of the three ILs are shown in Table 1. The organic solvents used (dichloromethane, acetonitrile, methanol and acetone) were of HPLC grade and obtained from Caledon (Georgetown, Ont., Canada). Trifluoroacetic acid was of HPLC grade and purchased from Sigma-Aldrich (Bellefonte, PA, USA). Purified water was provided by a Milli-Q water purification system. Hydrofluoric acid (40.0%) was purchased from a local chemical reagent agent.

Table 1
Property of the three ILs selected in our experiment.

Abbreviation	ILs structure	Mw	Density (g cm^{-3})
[C_8MIM][PF_6]		340.29	1.24
[C_4MIM][PF_6]		284.18	1.38
[C_3MIM][NTf_2]		419.36	1.47

Solid-phase microextraction fibres composed of polyacrylate with a film thickness of 85 μm (PA, 85 μm) were purchased from Sigma-Aldrich (Bellefonte, PA, USA). The PA fibres were conditioned before every use in the hot injector of a gas chromatography system for 30 min at 230 °C according to the instructions provided by the supplier. A fibre holder for manual use was purchased from Sigma-Aldrich (Bellefonte, PA, USA). The needle core of a 1-μL microsyringe (Zhenhai, Zhejiang, Jiangsu) was used. PTFE stir bars (5 mm × 1 mm × 1 mm) were obtained from Sigma-Aldrich (Bellefonte, PA, USA). All glassware and other equipment were thoroughly washed with methanol and dried in an oven at 400 °C for 12 h after use.

2.2. Instrumentations

The chromatographic conditions of APs analysis were similar to those reported by Yang et al. [29,30]. Specific as follows:

HPLC analysis was performed using an Agilent 1100 series (Palo Alto, CA, USA) HPLC system. The HPLC system consisted of a quaternary pump, a vacuum degasser, a high-performance autosampler and a temperature-controlled column compartment. An Agilent G1315A diode array detector (Palo Alto, CA, USA) was employed. A ZORBAX Eclipse XDB-C_8 analytical column (150 mm × 4.6 mm, 5 μm) was used for chromatographic separation, and the constant flow of the mobile phase was maintained at 1 mL min^{-1}. A 4.6 mm × 12.5 mm Eclipse XDB-C_8 column (4.6 mm × 12.5 mm, 5 μm) drop-in guard cartridge (Agilent, CA, USA) was attached in line after the sample injector port and before the analysis column to trap residual contaminants that may have been contained in the mobile phase and/or the HPLC system. The solvent composition used as the mobile phase