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Hollow fiber liquid–liquid–liquid microextraction followed by solid-phase microextraction and in situ derivatization for the determination of chlorophenols by gas chromatography-electron capture detection

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ABSTRACT

A method based on the combination of hollow fiber liquid–liquid–liquid microextraction and solid-phase microextraction (SPME) followed by gas chromatography-electron capture detection was developed for the determination of chlorophenols in water and wastewater samples. Silica microstructures fabricated on the surface of a stainless steel wire were coated by an organic solvent and used as a SPME fiber. The analytes were extracted through a hollow fiber membrane containing *n*-decane from sample solution to an alkaline aqueous acceptor phase. They were then extracted and in situ derivatized on the SPME fiber using acetic anhydride. Experimental parameters such as the type of extraction solvent, acceptor phase NaOH concentration, donor phase HCl concentration, the amount of derivatizing reagent, salt concentration, stirring rate and extraction time were investigated and optimized. The precision of the method for the analytes at 0.02–30 $\mu g\,L^{-1}$ concentration level ranged from 7.1 to 10.2% (as intra-day relative standard deviation) and 6.4 to 9.8% (as inter-day relative standard deviation). The linear dynamic ranges were in the interval of 5–500 $\mu g\,L^{-1}$, 0.05–5 $\mu g\,L^{-1}$, 0.02–1 $\mu g\,L^{-1}$ and 0.001–0.5 $\mu g\,L^{-1}$ for 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol, respectively. The enrichment factors were between 432 and 785. The limits of detection were in the range of 0.0004–1.2 $\mu g\,L^{-1}$. Tap water, well water and wastewater samples were also analyzed to evaluate the method capability for real sample analysis.

1. Introduction

In the past two decades, the determination of chlorophenols (CPs) in different environmental samples has received great attention because of their toxicity and the potential of carcinogenicity [1]. CPs are usually found in the environment due to their use as wood preservatives, disinfectants, pesticides and herbicides [2]. They can also be formed during the chlorination of drinking water or pulp bleaching with chlorine [2]. Because of their toxicity, durability and unpleasant organoleptic properties [3,4], both the US Environmental Protection Agency and the European Union have categorized several phenols in the list of highly polluting materials [5–7]. Hence, there is no doubt that the trace analysis of CPs in environmental samples is of great importance.

Most analytical methods for the analysis of CPs are based on high performance liquid chromatography (HPLC) and gas chromatography (GC) detection. HPLC coupled to ultraviolet (UV) [8] and mass spectrometry (MS) detection [9] has been the most common methods used for the determination of phenols. HPLC-MS is very sensitive and selective; however, it is expensive. On the other hand, the determination of CPs by HPLC-UV is not sensitive for analysis at low concentration levels. GC with electron capture detection (ECD) is one of the most popular techniques employed for the analysis of CPs because of its high sensitivity and selectivity [10–12]. However, to obtain good resolution and avoid peak tailing in GC, an additional derivatization step is usually carried out before the analysis [13]. Among various derivatization methods, acetylation with acetic anhydride has been the most widely used technique [10]. Usually, acetylation is performed in aqueous samples before extraction.

Regardless of the sensitivity and selectivity of detection instrument, analyte enrichment step and sample clean-up are usually essential because of the low concentration of CPs and the

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complexity of environmental samples [14]. Among different sample pretreatment methods developed in recent years, liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) are the two attractive and efficient microextraction techniques used for the analysis of CPs [15].

Hollow-fiber (HF) LPME, as introduced in 1999, combines extraction, concentration and sample clean-up in one step [16]. HF-LPME is performed in two- and three-phase sampling modes. In the two-phase mode, analytes are extracted from sample into a hydrophobic organic solvent supported by the fiber [16]. In the three-phase sampling mode (hollow-fiber liquid–liquid–liquid microextraction, HF-LLLME), which is limited to the extraction of ionizable analytes (basic and acidic compounds), the analytes are extracted from a water sample into a solvent impregnated into the hollow fiber pores and finally, into an aqueous acceptor phase inside the lumen of the HF by means of pH gradient [17]. The small pore size of HF prevents large interfering molecules and particles from entering the extracting phase. Therefore, the technique, especially in the three-phase mode, may provide high analyte enrichment and excellent sample clean-up, even from samples with complex matrices. In spite of the advantages of HF-LLLME, since the final extract (acceptor phase) is aqueous, it cannot be combined with GC [18,19]. To remove the incompatibility of HF-LLLME with GC, three-phase LLLME using two immiscible solvents has been developed [18–21]. In these techniques, the final acceptor phase is an organic solvent which can be directly injected into GC [20,21].

To provide a very clean extract from samples with complex matrix, hollow-fiber membrane-protected solid-phase microextraction (HFM-SPME) has been developed [22–24]. The technique is suitable for the protection of SPME fiber in “very complex” samples. Actually, HFM-SPME is a combination of two-phase HF-LPME and SPME.

The aim of the present work was developing a method based on the combination of three-phase HF-LPME and SPME to improve the selectivity and clean-up capability of the extraction. The method was used for the extraction of chlorophenols (as model compounds) from samples with a complex matrix such as wastewater samples. The method also allowed overcoming the incompatibility of three-phase LPME (with aqueous acceptor phases) with GC.

In this study, silica microstructures fabricated on the surface of a stainless steel wire were coated by an organic solvent and used as a SPME fiber. Four chlorophenols (2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) were extracted from an aqueous sample into an organic HF membrane and a subsequent back extraction was followed from the organic membrane into an alkaline aqueous acceptor solution. The analytes were then extracted on the SPME fiber, which had already been placed inside the lumen of the HF. The analytes were in situ, derivatized by acetic anhydride loaded on the SPME fiber. The studied compounds were determined by GC-ECD. Various experimental parameters affecting the extraction efficiency such as the type of organic solvent, NaOH concentration of the acceptor phase, HCl concentration of the donor phase, the amount of derivatizing agent (acetic anhydride), salt concentration, sample stirring rate and extraction time, were studied and optimized. Finally, the method was applied for the analysis of chlorophenols in environmental water samples.

2. Experimental

2.1. Chemicals and standard solutions

HPLC grade methanol, sodium hydroxide, acetic anhydride, 2-chlorophenol (2-CP, 98%), 2,4-dichlorophenol (2,4-DCP, 98%) and 2,4,6-trichlorophenol (2,4,6-TCP, >97%) were purchased from Merck (Darmstadt, Germany). Pentachlorophenol (PCP, 97%) was obtained from Fluka (Buchs, Switzerland). Other reagents were also obtained from Merck.

Standard stock solution of each analyte was prepared by dissolving the selected chlorophenols at the concentration of 1000 mg L^{-1} in methanol and stored in the refrigerator. A mixed standard solution at concentration of 0.1–150 mg L^{-1} (2-CP, 150 mg L^{-1}; 2,4-DCP, 2 mg L^{-1}; 2,4,6,-TCP, 0.5 mg L^{-1}; PCP, 0.1 mg L^{-1}) was prepared by diluting the stock standard solutions in methanol. More diluted working solutions were prepared daily by diluting the mixture of the standard solution with pure water. Pure water was prepared by Overseas Equipment & Services water purification system (OK, USA).

Aqueous samples were prepared in pure water spiked with the analytes at known concentrations to investigate the extraction efficiency under different conditions.

The surgical grade stainless steel plunger (0.21 mm, o.d.) of a disposable spinal needle (27G, BARTAR Co., Tehran, Iran) was used as the substrate of silica layer for SPME fiber.

The Accurel Q3/2 polypropylene hollow fiber membrane was obtained from Membrana (Wuppertal, Germany). The inner diameter of the hollow fiber was 600 μm, the thickness of the wall was 200 μm, and the pore size was 0.2 μm. A digital magnetic stirrer (MR 3000D) from Heidolph (Kelheim, Germany) was used for the stirring of solutions.

2.2. Instrumentation

The analysis of the CPs was carried out using a SP-3420 gas chromatography equipped with a split/splitless injector and an electron-capture detector (BEIFEN, Beijing, China). The injector was equipped with a low volume insert designed for SPME fibers desorption (Restek Bellefonte, PA, USA). Nitrogen gas (99.999%) at a head pressure of 100 kPa was used as carrier gas. The components were separated on a 30 m × 0.25 mm I.D., 0.15 μm film thickness DB-35MS column (J&W Scientific, Folsom, CA, USA). The injector and detector temperature were set at 250 °C and 290 °C, respectively. The column temperature was held at 50 °C for 1 min and then programmed at 25 °C min^{-1} to a final temperature of 250 °C for 8 min.

2.3. Synthesis of silica microstructure SPME fiber

Microporous silica nanoflakes were created on the surface of stainless steel wire by a hydrothermal precipitation process inside a soda glass vial as precursor [25]. According to the method, the stainless steel wires were cut to 3 cm and used as the substrate for silica microstructures fibers. After washing with water and sonicated in methanol for 5 min, they dried at 50 °C. A screw-cap soda glass vial was used as the reaction vessel and the bulk glass source. The vial was filled with 1.5 mL of 50% (w/v) NaOH solution and purged with nitrogen gas (99.99%) for 5 min to remove oxygen. A 1 cm length of the wire was dipped in the solution. The vial was capped and heated at 140 °C for 20 h in an oven. The vial was then cooled at room temperature and the fibers were washed with water and methanol. After drying at 50 °C, the fibers were conditioned under N_2 atmosphere at 300 °C for 20 min.

2.4. Extraction procedure

The schematic diagram of the extraction device and extraction procedure was depicted in Fig. S1 (supplementary data). A polyethylene cap with a diameter equal to the inner diameter of the glass vial has been fixed at the top of the glass bottle to hold the HF during the extraction. The hollow fiber was cut into 1.5-cm