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Preconcentration of polar phenolic compounds from water samples and soil extract by liquid-phase microextraction and determination via liquid chromatography with ultraviolet detection

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ABSTRACT

This work proposes a liquid-phase microextraction (LPME) method to extract the highly polar compounds phenol (Ph), *o*-cresol (*o*-Cr), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr), and 2,4-dimethylphenol (2,4-DMP) from aqueous matrices. The first extraction step of the LPME method employed a common volumetric flask and *n*-octanol, and the second extraction step used NaOH as the acceptor phase. The optimized extraction conditions were 900 μL of *n*-octanol as the extraction solvent, NaOH at 0.60 mol L^{-1} as the acceptor phase, an extraction time of 5.0 min, HCl at 0.01 mol L^{-1} and NaCl at 20.0% as the donor phase, and an extraction temperature of 20.0 °C. The analysis of 50.0 mL of aqueous sample, pretreated under the optimized LPME conditions, afforded a limit of detection (LOD) between 0.3 and 3.5 μg L^{-1}, a limit of quantification (LOQ) between 1.2 and 11.6 μg L^{-1}, and a linear range from 2.50 to 50.0 μg L^{-1} for Ph, *o*-Cr, *m*-Cr and *p*-Cr and from 12.5 to 250 μg L^{-1} for 2,4-DMP. The proposed LPME method was a successful sample preparation strategy, and allowed for precise and accurate quantification of polar phenolic compounds in aqueous matrices such as tap water, river water, groundwater, and seawater, and also in a soil extract. The recovery values ranged from 72.5% to 126.0%, and the relative standard deviation was between 0.3 and 11.5%.

1. Introduction

Phenolic compounds are toxic substances that occur naturally in the environment, in plants and food [1]; they may also originate from decomposition of the lignin present in wood and humic substances [2]. This class of compounds has been employed as precursors and components of numerous chemicals in the industrial production of paper, detergents, polymers, pharmaceuticals, adhesives, explosives, phenolic resins, and petrochemical products [3]. However, several phenolic compounds present unpleasant organoleptic characteristics, toxicological effects or are highly persistent in the environment, which has placed them among the main contaminants in waters and soils. Indeed, the United States Environmental Protection Agency (US EPA) considers some of these compounds as priority pollutants and allows maximum total phenols concentrations of 1.0 μg L^{-1} and 100 μg kg^{-1} in drinking water and agricultural soils, respectively [4].

The toxicity and environmental issues associated with phenolic compounds have required the development of analytical techniques to quantify these substances. Gas chromatography (GC) [5–7] and liquid chromatography (LC) [8–11] are the main techniques employed in this scenario. The polar features and low volatility of phenolic compounds have favored the use of LC with ultraviolet detection (LC–UV) or coupled to mass spectrometry (LC–MS), because the use of LC avoids the need of derivatization processes [8,9,12]. Nonetheless, LC, especially LC–UV, usually presents higher limits of detection and requires sample enrichment before the determination of phenolic compounds in water samples [13].

Conventional methods like liquid–liquid extraction (LLE) and solid phase extraction (SPE) can aid in the preparation of aqueous samples for the determination of phenol content. However, these methods, particularly LLE, are time-consuming and tedious and they demand the use of large volumes of toxic solvents. To overcome these drawbacks, chemical analysts have turned to SPE-based miniaturized techniques such as solvent-free solid-phase

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microextraction (SPME) [14,15] and stir bar sorptive extraction (SBSE) [16,17] to extract and preconcentrate phenolic species in water samples. Nevertheless, SPME and SBSE are relatively expensive, their coupling to LC is difficult, and additional steps like desorption, evaporation, and reconstitution are necessary prior to analysis [11]. In addition, the sorbent phases are fragile, susceptible to carryover, and they have a limited lifetime [5].

The limitations inherent to LLE, SPE, and even SPME and SBSE have encouraged investigations into miniaturized LLE pretreatment approaches based on solvent microextraction, the so-called liquid phase microextraction (LPME) techniques. LPME generally employs between 1 and 1000 μL of an acceptor organic solvent, which is immiscible with water, to extract the analyte from the aqueous phase, that is, the donor phase. It is possible to use LPME with GC, LC, and capillary electrophoresis (CE). The most common LPME categories include single-drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME), and hollow-fiber liquid phase microextraction (HF-LPME). The relevance of LPME techniques has motivated the publication of a number of detailed reviews [18–22]. SDME seems to be more appropriate to prepare samples for the determination of phenolic species and other analytes by GC [20], although some researchers have reported on the use of HF-LPME for this purpose [23,24]. Other authors have opted to use DLLME to pretreat samples for the determination of phenolic compounds [8,11,25–30]. To extract phenols from water, it is essential to acidify the aqueous matrix, in order to obtain the molecular form of the analytes and improve their extraction. Nevertheless, phenolic compounds present a wide range of hydrophobicity, which impacts their recovery; the log K_{OW} values vary from 1.46 for phenol to 5.12 for pentachlorophenol, and by using DLLME, recovery values of 13.1 and 81.8% for phenol and pentachlorophenol were observed, respectively [11]. On the basis of these data, it seems that the extraction of more polar phenolic compounds from water is not a straightforward task, which is probably the reason why most of the work based on LPME has described attractive results only for the more hydrophobic compounds, mainly chlorophenols [8,11,25,27–30]. For the more polar phenolic compounds, even the best extraction conditions for conventional DLLME provide the extraction of a small amount of the analyte, not to mention that they require higher sample volumes. In an attempt to achieve an extraction method capable of processing a larger sample volume (100 mL), Zhang et al. [12] used a special glass device. These authors designated the procedure as two-step LPME for the extraction of nitrophenols, chlorophenols, and phenol and obtained very satisfactory results.

Notwithstanding the several LPME procedures available to prepare samples for the determination of nitrophenols and chlorophenols, no reports have been published about the microextraction of cresols. Hence, the present study aimed to develop a two-stage method for the microextraction of phenol and cresols from water matrices. The first stage consisted of solvent extraction employing a simple commercial volumetric flask and *n*-octanol, whereas the second stage was comprised of an alkaline extraction. After the determination of the best conditions for analysis, the LPME method was successfully employed for the quantification of phenol, *o*-cresol, *m*-cresol, *p*-cresol and 2,4-dimethylphenol in different environmental water samples. It is important to note that these analytes were investigated in order to evaluate the possibility of water or soil contamination. Therefore, for the first time determination of the highly polar compounds, such as phenol and cresols, in a soil extract sample was carried out by LPME.

2. Experimental

2.1. Reagents, solutions, and materials

The phenol (Ph), *o*-cresol (*o*-Cr), *m*-cresol (*m*-Cr), *p*-cresol (*p*-Cr), and 2,4-dimethylphenol (2,4-DMP) standards were acquired from Sigma-Aldrich (St. Louis, USA) at purity greater than 99.0%. Methanol (HPLC grade) was purchased from J.T. Baker (Mexico City, Mexico). Acetonitrile (HPLC grade) was supplied by Carlo Erba (Rodano, Italy) and was used for the composition of the mobile phase. The analytical grade solvents, *n*-hexane, cyclohexane, butyl acetate, and *n*-octanol were obtained from Sigma-Aldrich (St. Louis, USA). All other reagents employed in the current study were of analytical grade and acquired from Merck, Carlo Erba, or J.T. Baker. High purity water (resistivity of 18 MΩ cm) was obtained with the aid of a reverse osmosis system from Quimis (Diadema, SP, Brazil), model Q842-210, followed by purification with a Simplicity UV water purifying system from Millipore (Molsheim, France). A Hanna potentiometer, model pH 21, coupled to an Ag/AgCl combined glass electrode was used to measure the pH values.

All of the glassware was kept in a 2.5% (v/v) alkaline detergent solution for at least 24 h, washed with water obtained from the reverse osmosis system, then with high purity water, and dried in a dust-free environment. Stock standard solutions at a concentration of 1000 mg L^{-1} were prepared in methanol and stored in amber glass vials at 4 °C. Working solutions containing the five phenolic compounds at concentrations ranging between 2.50 and 250 μg L^{-1} were prepared on a daily basis by dilution of the stock standard solution with high purity water. Before the chromatographic determinations, the standards and the samples were filtered through disposable 0.45 μm PTFE membranes with a diameter of 25 mm (from Millipore).

2.2. Chromatographic conditions

A liquid chromatography system from Waters (Milford, MA, USA) was employed, equipped with a quaternary pump (Waters 600E), a degasser (In Line AF), a thermostatted column compartment (Module II), an automatic sampler (20 μL, Waters 717 Plus), and a diode-array detector (Waters 2998). The signals were acquired at 270 nm with the aid of the software Empower 2. An octadecylsilane (C18) column from Kromasil AzkoNobel (Bohus, Sweden) (250 mm × 4.6 mm, particle size of 5 μm) was connected to a C18 guard column and employed at 40 °C. The mobile phase consisting of a 60:40 mixture of 1.0% acetic acid and acetonitrile was filtered through a 0.45 μm PTFE membrane (Millipore) and used in the isocratic mode at a flow rate of 1.0 mL min^{-1}.

2.3. Microextraction procedure

Fig. 1 illustrates the procedure employed for the microextraction and describes the optimized analytical conditions.

First, a solution containing *Ph*, *o*-Cr, *m*-Cr, *p*-Cr, and 2,4-DMP at 100.0 μg L^{-1} was employed to establish the best extraction conditions. The following parameters were evaluated, in triplicate: solvent (*n*-hexane, cyclohexane, butyl acetate, and *n*-octanol), NaOH concentration in the acceptor phase (0.10, 0.15, 0.25, 0.40, and 0.60 mol L^{-1}), stirring time (2.5, 5.0, 10.0, 20.0, and 30.0 min), volume of *n*-octanol in the extraction phase (100, 300, 500, 700, and 900 μL), HCl concentration in the donor phase (0.01, 0.05, 0.10, and 1.00 mol L^{-1}), extraction temperature (5.0, 10.0, 20.0, 30.0, 40.0, 50.0, and 60.0 ± 0.2 °C), and NaCl concentration in the donor phase (2.50, 5.00, 10.0, and 20.0%). The temperature was controlled by insertion of the volumetric flask in a glass jacket connected to a thermostatic bath (Fig. 1). Volumes of 25, 50, and 100 mL of the standard solution were also tested.