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Application of vesicular coacervate phase for microextraction based on solidification of floating drop

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ABSTRACT

A new, efficient and environmentally friendly method for the analysis of parabens as model compounds was developed using solidified floating vesicular coacervative drop microextraction (SFVCDME). A supramolecular solvent consisting of vesicles of decanoic acid in the nano- and microscale regimes was firstly used as the solvent in solidification of floating drop microextraction. The solvent was produced from the coacervation of decanoic acid aqueous vesicles in the presence of tetrabutylammonium (Bu_4N^+). Methylparaben (MP), ethylparaben (EP), and propylparaben (PP) were extracted on the basis of hydrophobic and π–cation interactions and the formation of hydrogen bonds. Microliter volume of vesicular coacervative droplet was delivered to the surface of the aqueous sample, and the sample was stirred for a desired time. The sample vial was cooled by immersing it into an ice bath for 3 min. The solidified solvent was transferred into a suitable vial and melted immediately. Twenty microliter of the vesicular coacervative solvent was directly injected to high-performance liquid chromatography-ultraviolet detection, with no need to dilution or solvent evaporation. Several parameters affecting the microextraction efficiency including sample temperature, stirring rate, pH, salt effect, volume of the solvent and extraction time were investigated and optimized. Under optimum conditions, preconcentration factors and relative recoveries of the studied compounds were obtained in the range of 81–174 and 91–108%, respectively; and the performance of the method was comparable with that of solid-phase extraction as the reference method.

1. Introduction

The esters of *p*-hydroxybenzoic acid are commonly known as parabens, including methyl paraben, ethyl paraben, propyl paraben and butyl paraben. They are widely used as preservatives in a large number of cosmetic, food and pharmaceutical products. Although combinations of two or more parabens are often used to increase the ability of the system to withstand microbial contamination [1–3], there are numerous formulations that contain only one of them. Parabens are extensively used in formulations of personal care products due to having neutral pH, no perceptible odor or taste, and having no discoloration or hardening effect [4,5]. Generally, parabens are stable in the air, and are resistant to hydrolysis in hot and cold water as well as in acidic solutions ($1 \leq pH < 7$). Recently, use of preservatives in consumer products has been the subject of criticism because of their possible side-effects on human health. The Council Directive 76/768/EC of the European Community permits their use with a maximum concentration of 0.4% (w/w) for each one and total maximum concentration of 0.8% (w/w), expressed as *p*-hydroxybenzoic acid [6].

Determination of parabens can be performed by various techniques, such as gas chromatography–mass spectrometry (GC–MS) [7], high-performance liquid chromatography (HPLC) [8–10], microemulsion electrokinetic chromatography (MEEKC) [11,12], and capillary electrochromatography (CEC) [9]. HPLC is the most common method used for detecting these compounds, which is often combined with a pretreatment procedure to remove nonpolar matrices. In order to determine and analyze the parabens in different samples, an extraction or pre-concentration step is often required.

Sample preparation prior to the chromatographic analysis is one of the most crucial steps in the whole analytical procedure to obtain accurate and sensitive results [13–16]. There are several recent reviews on the methodological approach to improve analytical performances [17,18]. Solid-phase microextraction and liquid-phase microextraction (LPME) have emerged as new attractive alternatives for sample preparation, which leads to saving time, labor, and solvent consumption, and therefore can improve the analytical performance of the procedure. Recently, several different types of LPME have been developed, including single drop microextraction (SDME) [19,20], hollow fiber LPME [21–24], and dispersive

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liquid–liquid microextraction (DLLME) [25,26]. Microextraction techniques are fast, simple, inexpensive, environmentally friendly, and compatible with many analytical instruments.

Surfactants are organic compounds that are amphiphilic, and contain both hydrophobic and hydrophilic groups. Therefore, they are soluble in both organic and aqueous solvents. Many surfactant-based extraction methods have been reported up to now [27–33].

The cloud point extraction (CPE) was the first extraction method in which non-ionic surfactants have been used. In this technique, a small volume of the surfactant-rich phase enables that the extraction and preconcentration of the analytes to be performed in a single step. The cloud point refers to the phase separation of neutral surfactants induced by temperature [34]. Non-ionic and zwitterionic surfactants have been used for cloud point extraction. The term "coacervation extraction" or "micelle-mediated extraction" is reserved for the phase separation of ionic amphiphiles induced by other conditions. Cationic surfactants, *e.g.* alkyltrimethylammonium bromides, are known to undergo coacervation in the presence of saturated sodium chloride and 1-octanol. Anionic surfactants such as alkyl sulfates, sulfonates, and sulfosuccinates undergo pH-induced coacervation. Hence, cationic and anionic surfactants can be used for coacervative extraction. Among the four types of surfactants, anionic surfactant-mediated extraction is predominant [35].

The surfactant-rich phase is a nano-structured liquid, recently named as supramolecular solvent (SUPRAS), which is generated from the amphiphiles through a sequential self-assembly process occurring on the molecular and nano-scales [36–42]. Recently, Rubio et al. reviewed both theoretical and practical aspects of using supramolecular solvents in analytical extractions reported over the last decade [43].

The tetrabutylammonium-induced liquid–liquid phase separation in vesicular solutions of alkyl carboxylic acids recently described by Pérez-Bendito et al. [44], presents a high potential for the extraction of bisphenols. The main properties of the SUPRASs are the high concentration of amphiphiles, 1 mg μL^{-1}, and different types of the interactions offered by them for analyte extraction (*i.e.* ionic, hydrogen bonding, π-cation and hydrophobic).

In 2007, a new and simple liquid-phase microextraction method was developed based on solidification of floating droplet (LPME-SFD) by our research group [45] in which the extraction solvent had lower density than water, low toxicity, and proper melting point near room temperature (in the range of 10–30 °C). In this method, a small volume of an extraction solvent was floated on the surface of aqueous solution. The aqueous sample solution was stirred for a defined time. After the extraction, the floated droplet could be collected easily through solidification at low temperature. The solidified organic solvent could be melted quickly at room temperature, and subsequently determined by either chromatographic or spectrometric methods.

In 2008, Pérez-Bendito and coworkers described the potential of coacervates for SDME for the first time [46]. They investigated the parameters affecting the efficiency of single-drop coacervative microextraction (SDCME) using vesicular coacervates as the solvent and chlorophenols as model analytes. They found that, with the experimental setup proposed, maximal stirring rates should be kept at 300 and 600 rpm during the extraction of samples with drop volumes of 40 and 5.0 μL, respectively. The main limitation of SDCME was dislodging of the coacervate drops from the needle tip in higher stirring rates which caused an increase in the extraction time.

Herein, the potential of vesicular coacervates drop (melting point ≈ 10 °C) for LPME-SFD was explored. The effective parameters on the extraction efficiency of parabens including sample temperature, stirring rate, salt effect, pH, volume of the solvent, and the extraction time were investigated and optimized.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical grade. Methyl-, ethyl-, and propyl esters of 4-hydroxy benzoic acid were purchased from Sigma (St. Louis, MO, USA). Decanoic acid was purchased from Fluka (Buchs, Switzerland) and tetrabutyl ammonium hydroxide (Bu_4NOH, 40%, w/v in water) was obtained from Sigma. HPLC-grade methanol and acetonitrile were purchased from Caledon (Ontario, Canada). The ultra-pure water was prepared by a model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea).

Stock solutions of 1000 mg L^{-1} parabens were prepared by dissolving appropriate amount of compounds in methanol and then keeping them stable during three months by being stored in fridge at 4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with ultra-pure water to the required concentrations.

2.2. Apparatus

Chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a 20 μL sample loop and equipped with a Varian 9050 UV–vis detector. Chromatographic data were recorded and analyzed using ChromanaCH software version 3.6.4 (Tehran, Iran). The separations were carried out on an ODS column (250 cm × 4.6 mm, with particle size of 5 μm) from Teknochroma (Barcelona, Spain). A mixture of ultra-pure water and acetonitrile (55:45) for 15 min and then 100% acetonitrile for 10 min (for elution of coacervate phase) at a flow rate of 1.0 mL min^{-1} were used as a mobile phase and the analytes were detected at 254 nm.

2.3. Sample preparation

(a) Cosmetic samples: Five milligram of each sample (sunblock, aftershave gel and skin cream) was accurately weighed and dissolved in a solution mixture containing 2 mL methanol and 8 mL ultra-pure water. Then, 1 mL of a concentrated HCl solution (37 vol.%) was added to the solution and exposed to sonication for 10 min. The solution was diluted to 150 mL with ultra-pure water and finally the pH was adjusted at 6.0. Afterwards, 24 mL of the solution was transferred into an extraction vial.

(b) Water samples: Different water samples, including tap water from our lab (Tehran, Iran), river water (Niasar, Iran), pond water (Tehran downtown, Iran) and urban wastewater from downtown (Tehran, Iran) were collected and the SFVCDME method was applied to extract the parabens. Each water sample was filtered, in order to remove any suspended material. After being filtered, the urban wastewater sample was diluted 1:1 by ultra-pure water. For preconcentration, pH of the samples was adjusted at 6.0 using the described procedure before the analysis. Finally, the interference effect of calcium was removed by adding EDTA (2 mg L^{-1}) as masking agent before extraction, for water samples containing high concentration of calcium.

2.4. Vesicular coacervates preparation

Vesicular coacervates were prepared by mixing 5.15 g of decanoic acid and 3.9 g of tetrabutyl ammonium hydroxide in 200 mL distilled water at pH 7. In order to dissolve the decanoic acid, the mixture was stirred at 1200 rpm for 10 min. Finally, phase separation was achieved by centrifugation of the mixture for 5 min