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Vortex-assisted liquid–liquid microextraction of octylphenol, nonylphenol and bisphenol-A

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ABSTRACT

A new and fast equilibrium-based solvent microextraction technique termed vortex-assisted liquid–liquid microextraction (VALLME) has been developed and used for the trace analysis of octylphenol, nonylphenol and bisphenol-A in water and wastewater samples. According to VALLME, dispersion of microvolumes of a low density extractant organic solvent into the aqueous sample is achieved by using for the first time vortex mixing, a mild emulsification procedure. The fine droplets formed could extract target analytes towards equilibrium faster because of the shorter diffusion distance and larger specific surface area. Upon centrifugation the floating extractant acceptor phase restored its initial single microdrop shape and was used for high-performance liquid chromatographic analysis. Different experimental parameters were controlled and the optimum conditions found were: 50 μl of octanol as the extractant phase; 20 ml aqueous donor samples; a 2 min vortex extraction time with the vortex agitator set at a 2500 rpm rotational speed; centrifugation for 2 min at 3500 rpm; no ionic strength or pH adjustment. The calculated calibration curves gave high levels of linearity yielding correlation coefficients (r^2) greater than 0.9935. The repeatability and reproducibility of the proposed method were found to be good and the limits of the detection were calculated in the low μg l^{-1} level ranging between 0.01 and 0.07 μg l^{-1}. Matrix effects were determined by applying the proposed method to spiked tap, river water and treated municipal wastewater samples. The proposed method was finally applied to the determination of target pollutants in real wastewater effluent samples using the standard addition method.

1. Introduction

Analytical microextractions represent an important development in the field of sample preparation, addressing issues of simplicity, miniaturization and time efficiency [1]. Although different types of microextraction techniques were initially reported, it was the introduction of solid-phase microextraction (SPME) in 1990 [2] that initiated intensive research efforts in the area. Few years later, solvent microextraction (also known as liquid-phase microextraction or LPME) appeared in the literature [3–6], representing a miniaturization of the traditional liquid–liquid extraction (LLE) procedure whereby the solvent to aqueous phase ratio was greatly reduced. The general requirements for LPME were the use of an acceptor phase immiscible to the aqueous sample donor solution and analytes that were more soluble in the extractant phase than in the sample solution. Hitherto, different methodologies evolved from this approach including amongst others immersion [7] and headspace [8] single-drop microextraction, static and dynamic LPME [9] or even hollow fiber LPME [10,11].

Recently, a new LPME method termed dispersive liquid–liquid microextraction (DLLME), based on a ternary component solvent system similar to the one found in homogeneous liquid–liquid extraction and cloud point extraction, appeared in the literature [12]. For DLLME, a water-immiscible extractant solvent dissolved in a water-miscible dispersive solvent was rapidly injected into an aqueous donor solution leading to the formation of a cloudy solution consisting of fine droplets of the extractant solvent dispersed entirely in the aqueous (continuous) phase. Target analytes were extracted into these fine droplets, which could be subsequently separated by centrifugation and used for analysis. The main drawbacks associated with DLLME were the difficulty to automate and the necessity of using a third component (disperser solvent), which commonly decreased the partition coefficient of analytes into the extractant solvent [13]. Recently, dispersion of the extractant phase into the sample solution was also achieved using the so-called temperature-controlled ionic liquid DLLME method [14]. The method was based on the ability of an ionic liquid drop to disperse in an aqueous phase at higher temperatures, yet return to phase separation upon cooling and centrifugation. Although the method yielded high enrichment factors, analyte losses due to volatilization at higher temperatures were reported. Finally, the possibility of using ultrasound as a mean for dispersing the

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extractant acceptor phase (organic solvent [13,15] or an organic solvent/ionic liquid mixture [16]) into an aqueous donor phase was recently explored. In general, heterogeneous liquid–liquid systems are known to become uniform when subjected to ultrasonic irradiation. The process is also known as “homogenization” or “emulsification” and has been used as an alternative to the conventional LLE method [17]. Moreover, ultrasound was found to speed up this homogenization/emulsification step given that the formation of submicron size droplets greatly increased the contact surface between the two liquids, yielding fast and efficient analyte transfer. Nevertheless, in many cases analytical chemists have been reluctant to test ultrasound as a mean for improving liquid–liquid extraction given that it most often produces stable emulsions that result in long phase separation times. Problems were also encountered due to the use of cleaning baths as ultrasound irradiation production equipment which are notorious for their tendency to decline in power with time and their lack of uniformity in the transmission of ultrasound irradiation [18]. It should also be mentioned that even at these low frequencies and relatively short application times, analyte degradation may occur through large pressure and temperature gradients, high shear forces, or even by free radicals generation [19,20].

The aim of this research was to introduce a new and fast microextraction method whereby dispersion of the extractant phase into the aqueous is achieved for the first time using vortex mixing, a mild emulsification procedure. The resulting methodology was termed vortex-assisted liquid–liquid microextraction (VALLME) and was used for the extraction of trace amounts of alkylphenols (namely: octylphenol (OP) and nonylphenol (NP)) and bisphenol-A (BPA) used here as model compounds from water and wastewater samples. In general, alkylphenols are considered as degradation products of alkylphenolpolyethoxylates, a widely used class of nonionic surfactants with industrial and household applications [21,22]. OP and NP have been classified as endocrine disruptive compounds by several organizations, and are listed as a priority substance in the Water Framework Directive [23]. BPA on the other hand is commonly used as an intermediate in the production of polycarbonate and epoxy resins, flame retardants and other specialty products [24] and was found to exhibit weakly estrogenic activity as well as antiandrogenic activity [25]. Hitherto, different reports based on SPME or LPME coupled to high-performance liquid chromatography (HPLC) deal with the trace analysis of environmental samples containing these target analytes [21,26–32]. For the purpose of the present investigations, several experimental parameters affecting the extraction process (namely: organic solvent, agitation time, rotational speed of the vortex agitator, acceptor phase volume, aqueous sample volume, pH and salt addition) were initially controlled and optimized and the performance of the proposed method was then assessed. Matrix effects upon extraction were evaluated by analyzing spiked tap and river water as well as effluent water samples taken from a municipal wastewater treatment plant.

2. Experimental

2.1. Chemicals and samples

BPA and OP were purchased from Aldrich (Sigma–Aldrich, Gillingham, Dorset, UK). 1-octanol and NP Pestanal® (94% purity) were purchased from Riedel-de Haën (Seelze, Germany). All organic solvents used here were of pesticide grade. Deionized water was prepared on a water purification system (EASYpure®RF) supplied by Barnstead/Thermolyne Corporation (Dubuque, IO, USA). Stock solutions were prepared in methanol and stored at 4 °C in the dark when not in use. Working standards were prepared daily at the concentration levels of interest.

A 100 μl Hamilton (Bellefonte, BA, USA) HPLC 710 SNR model microsyringe was used to introduce the organic solvent into the aqueous sample and then collect it and inject it into the HPLC system for analysis.

River water samples were collected from the River Koiliaris situated in Chania-Crete (pH 7.5; chemical oxygen demand (COD) = 20 mg/l; total dissolved solids (TDS) = 100 mg/l). Wastewater effluent samples were collected from the municipal wastewater treatment plants of Chania (pH 7.6; COD = 15 mg/l; TDS = 508 mg/l) and Rethymno (pH 8.0; COD = 68 mg/l; TDS = 780 mg/l) situated in the North-West part of Crete, serving approximately 70,000 and 25,000 habitants, respectively. All samples were collected the day before being analyzed and were stored in the dark at 4 °C.

2.2. VALLME

Unless otherwise stated within the text, 20 ml aqueous samples spiked at a known concentration with all target analytes were placed in a round-bottom glass vial (diameter: ∼2 cm) and 50 μl of octanol were then slowly introduced acting as the extractant solvent. The mixture was then vigorously shaken using a vortex agitator (Reax Control, Heidolph, Germany) for 2 min at 2500 rpm (maximum setting). As a result fine droplets were formed facilitating mass transfer of the target analytes into the organic acceptor phase. Separation of the two phases occurred upon centrifugation at 3500 rpm for 2 min (Labofuge 400 Heraeus, Kendro Laboratory Products, Germany). The floating octanol phase could thus restore its original single microdrop shape and 30 μl could be easily collected with the help of a microsyringe and used for HPLC analysis. During optimization, all experiments were run at least in duplicate.

2.3. HPLC analysis

Separation and quantification was carried out using an HPLC system, manufactured by Shimadzu (Shimadzu Corporation, Kyoto, Japan), equipped with a fluorescence detector (FLD) and two solvent delivery pumps. A Nucleosil 100-5 C18 (250 mm × 4.6 mm × 5 μm; Macherey-Nagel, Duren, Germany) was used to separate the target analytes at 27 °C. The mobile phase was acetonitrile:water (80:20) with a flow rate of 1.0 ml min^{-1}. The excitation and emission wavelengths of the FLD were set at 277 and 300 nm respectively. The total analysis time was 15 min.

3. Results and discussion

3.1. Optimization of VALLME

Initially, several water immiscible solvents (namely: 1-octanol, toluene, *n*-hexane, octane and cyclohexane) were tested, having densities lower than that of water and differing in polarity and water solubility. Each time, 50 μl of the organic solvent to be tested was slowly added to a 20 ml aqueous sample spiked at 1 $\mu\text{g}\,\text{l}^{-1}$ with BPA and OP and 10 $\mu\text{g}\,\text{l}^{-1}$ with NP. Given that all solvents tested had densities lower than that of water, they resided in the top surface of the water sample in the form of a single microdrop. The mixture was then vigorously agitated using a vortex agitator (2 min; 2500 rpm) leading to drop breakage into fine droplets. In the present studies centrifugation (2 min at 3500 rpm) was chosen as a viable mean for separating the two phases of this liquid–liquid dispersion. Amongst the low density solvents tested, 1-octanol had the ability to “restore” its initial single microdrop shape and as such could be easily collected and used for HPLC analysis. Under the present experimental conditions, coalescence of the fine droplets into a coherent phase did not occur for the rest of the tested solvents which were left scattered on the top surface of the aqueous solution in the form of smaller satellite microdrops hindering thus