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A new strategy to simultaneous microextraction of acidic and basic compounds

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ABSTRACT

The simultaneous extraction of acidic and basic pollutants from water samples is an interesting and debatable work in sample preparation techniques. A novel and efficient method named ion pair based surfactant assisted microextraction (IP-SAME) was applied for extraction and preconcentration of five selected acidic and basic aromatic species as model compounds in water samples, followed by high performance liquid chromatography–ultraviolet detection. A mixture including 1 mL of ultra-pure water (containing ionic surfactant as emulsifier agent) and 60 μL 1-octanol (as extraction solvent) was rapidly injected using a syringe into a 10.0 mL water sample which formed an emulsified solution. IP-SAME mechanism can be interpreted by two types of molecular mass transfer into the organic solvent (partitioning and ion pairing for non-ionized and ionized compounds, respectively) during emulsification process. The effective parameters on the extraction efficiency such as the extraction solvent type and its volume, type of the surfactant and its concentration, sample pH and ionic strength of the sample were optimized. Under the optimum conditions (60 μL of 1-octanol; 1.5 mmol L^{-1} cethyltrimethyl ammonium bromide (CTAB) as emulsifier agent and sample pH 10.0), the preconcentration factors (PFs), detection limits and linear dynamic ranges (LDRs) were obtained in the range of 87–348, 0.07–0.6 μg L^{-1} and 0.1–200 μg L^{-1} respectively. All of natural water samples were successfully analyzed by the proposed method.

1. Introduction

Aromatic compounds such as aniline, phenol and their derivatives are of great importance in environmental chemistry due to their toxic nature and their suspected carcinogenic properties [1–3]. They are used in several manufacturing processes, particularly in dye industry [4]. Also with the recent development of aniline and phenol-based herbicides, there has been a great deal of attention on aniline, phenol and their derivatives as environmental pollutants. Due to their high solubility in water, anilines and phenols can easily permeate through soil and contaminate ground water. Aniline is highly toxic and readily absorbed through the skin in dangerous amounts and is fatal if swallowed or if the vapors are inhaled [5].

Chlorinated anilines (CAs) such as 3-chloroaniline, 4-chloroaniline and 3,4-dichloroaniline have also been found as degradation products and intermediates of various phenylurea and phenylcarbamate pesticides [6]. Regarding the importance of these compounds, a rapid and sensitive method of analysis is needed to detect them in the environment.

Nitrophenols (NPs) might be released due to the photochemical reaction of benzene with nitrogen monoxide in highly polluted air. Therefore, nitrophenols are found as contaminants in wastewater, rivers, groundwater, soil, and in the atmosphere. Concentrations in the range of 4.6–100 μg L^{-1} have been found in rain water and in the tropospheric atmosphere [7].

Several analytical methods have been reported for determination of anilines, phenols and their derivatives such as gas chromatography (GC) [8,9] and capillary zone electrophoresis (CZE) [10]. The most popular technique for the analysis of aromatic amines and phenols in environmental water is high-performance liquid chromatography (HPLC) [11].

Although the development of modern analytical instruments allows great enhancement in aspects of analysis, the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples in many cases. Sample preparation is still a bottleneck for overall throughput because the steps involved often employ large volumes of hazardous organic solvents, are time consuming and/or expensive. Besides, there might also be the problem of contamination and sample loss [12–16].

Recently, liquid phase microextraction (LPME) was developed as a novel and disposable method for sample preparation [17]. LPME is a solvent-minimized sample preparation procedure, in which only several μL of solvent are required to concentrate analytes from

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various samples and also is compatible with GC, capillary electrophoresis (CE) and HPLC. In 2006 Assadi and co-workers [18] reported dispersive liquid–liquid microextraction (DLLME) as a new version of LPME technique which uses μL volumes of extraction solvent along with a few mL of disperser solvents. In this method, a cloudy solution is formed when a mixture of extraction and disperser solvents are injected into an aqueous sample containing the analytes of interest. Having formed the cloudy solution, the surface area between extraction solvent and aqueous sample is enlarged and equilibrium state is achieved quickly resulting in a short extraction time. In fact, this is the principal advantage of DLLME.

One of the major disadvantages of DLLME is the small partition coefficients of analytes between organic and aqueous phases due to presence of disperser solvent in the aqueous phase. A new format of DLLME based on surfactant, as disperser agent, was reported in 2010 [19,20]. In this method a mixture of aqueous solution including surfactant and extraction solvent is quickly injected into the sample solution so as to form an emulsified solution. The enriched analytes in the collected phase are determined by an appropriate analytical instrument after centrifugation. One of advantages of surfactant application is that it does not decrease the partition coefficient of the analytes considerably and also the toxicity of the surfactants is low.

The dispersion phenomenon can be qualitatively interpreted via the liquid–liquid interface chemistry. The interfacial tension is the parameter representing the uncompensated intermolecular forces acting in the bulk phase. The surfactants reduce interfacial tension (γ) between organic and aqueous phases making an increase in surface area during fine droplets formation as is described by the Young–Laplace equation

$$\Delta P = P_{\text{internal}} - P_{\text{external}} = \gamma \left(\frac{2}{R_{\text{sph}}} \right) \quad (1)$$

where R_{sph} is the radius of the spherical droplet and P_{internal} and P_{external} are the internal and external pressures of droplet, respectively. This simple form of the Young–Laplace equation shows that the interfacial tension reduction leads to a reduction in the droplet radius and forming finer droplets in a constant pressure difference.

In our previous study [19] cationic surfactant was used as emulsifier for microextraction of the chlorophenols in water samples. The chlorophenols are acidic compounds and are not extractable into organic solvents in alkaline medium. Occurring the ion-pair formation, chlorophenols can be extracted from alkaline solutions (containing cationic surfactants) into organic solvents. Therefore it is expected that the anionic surfactants is capable to form ion-pair with the protonated chloroanilines (CAs) in acidic medium resulting in CAs extraction into organic solvent.

In the present study, nitrophenols and chloroanilines are selected as acidic and basic model compounds, respectively, to consider their simultaneous extraction using ion pair based surfactant assisted microextraction (IP-SAME).

The eventual mechanism of IP-SAME to transfer protonated CAs by anionic surfactant in acidic medium and deprotonated NPs by cationic surfactant in alkaline medium to organic solvent is shown in Fig. 1. As can be seen, the mentioned equilibriums tend to right side of reaction, in (a) acidic, (b) alkaline medium and anionic surfactant-CA and cationic surfactant-NP ion pairs are formed, respectively. In the adjusted basic pH, CAs are in its neutral form and can be extracted into organic solvent, while, NPs are deprotonated and able to form ion pair with the cationic surfactant and extract into extraction solvent. Thus the mass transfer process occurs by a mechanism involving two parallel phenomena (partitioning and ion pairing) in proposed study.

The aim of the proposed study was to optimize various parameters, affecting the extraction efficiency of IP-SAME in simultaneous extraction of the CAs and NPs from water samples.

2. Experimental

2.1. Chemicals and reagents

3-Chloroaniline (3-CA, $pK_b = 10.48$, $\log K_{ow} = 1.88$), 4-chloroaniline (4-CA, $pK_b = 10.0$, $\log K_{ow} = 1.85$), 3,4-dichloroaniline (3,4-DCA, $pK_b = 11.1$, $\log K_{ow} = 2.8$), 4-nitrophenol (4-NP, $pK_a = 7.2$, $\log K_{ow} = 2.0$) and 3-nitrophenol (3-NP, $pK_a = 8.3$, $\log K_{ow} = 2.0$) [7,21–23] obtained from Sigma–Aldrich (Milwaukee, WI, USA). Cethyltrimethyl ammonium bromide (CTAB) was obtained from Merck (Darmstadt, Germany), and tetradecyl trimethyl ammonium bromide (TTAB), sodium dodecyl sulfate (SDS) and sodium tetradecyl sulfate (STS) were purchased from Sigma–Aldrich. 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). Toluene, 1-undecanol, 1-octanol and 1-dodecanol were purchased from Merck.

Stock standard solutions of analytes (1000 mg L^{-1}) were prepared by dissolving the proper amounts of them in HPLC grade methanol. Standard aqueous solutions were prepared by spiking ultra-pure water with 1.0, 10.0 and 50 mg L^{-1} of mixed standard solutions of analytes in methanol. All other chemicals used were of analytical grade.

2.2. Apparatus

An Agilent 1200 series liquid chromatograph (Centerville Road, Wilmington, USA) equipped with a UV–Vis diode array detector (DAD) was applied. The system was equipped with a Rheodyne 7125i injector with a 20-μL loop. An ODS-Zorbax column (250 cm × 4.6 mm, with 5 μm particle size) and an ODS-Zorbax guard column (4.6 mm × 1.25 cm) were applied to separate the analytes under gradient elution conditions. Firstly, a mixture of ultra-pure water and acetonitrile (50:50) for 15 min and then 100% acetonitrile for 10 min were used as mobile phase. The mobile phase flow rate was 1 mL min^{-1} and DAD monitoring wavelengths were chosen at 220, 220, 240, 240 and 240 nm for 4-NP, 3-NP, 4-CA, 3-CA and 3,4-DCA respectively. It is worthy to note that the optimization of the parameters were performed at fixed wave length of 230 nm and the figures of merit of the method were obtained at λ_{max} of each analyte by using DAD detector.

2.3. IP-SAME procedure

An aliquot of 10.0 mL water sample containing the analytes was poured into a 12 mL glass test tube which is designed for collection of low density solvents [24]. The pH of the solutions was adjusted to an appropriate level (pH 10.0). A mixture containing 1 mL CTAB (as emulsifier agent, 1.5 mmol L^{-1}) and 60 μL 1-octanol (as extraction solvent) was quickly injected into the sample solution using 1.0 mL gastight syringe. Cloudy solution was quickly formed as the fine droplet of the immiscible extraction solvent dispersed in the aqueous sample. This process greatly enlarged the contact area between the extraction solvent and aqueous phase, and the analytes were extracted into the formed fine droplets. The formed emulsion was centrifuged at 5000 rpm for 3 min to separate the phases. Twenty microliters of collected phase was taken using a 50 μL microsyringe and directly injected into the HPLC instrument.