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Vortex and air assisted liquid–liquid microextraction as a sample preparation method for high-performed liquid chromatography determinations



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ABSTRACT

A novel, simple and sensitive method based on vortex and air assisted liquid–liquid microextraction (VAALLME) technique coupled with high-performance liquid chromatography (HPLC) has been developed for quantitative analysis of β-naphthol, naphthalene and anthracene as model analytes. Unlike the dispersive liquid–liquid microextraction (DLLME), dispersive solvent and centrifuging step were eliminated in proposed technique. In this technique, extraction solvent was dispersed into the aqueous sample solution by using vortex. Phase separation was achieved via motion of air bubbles from the bottom to top of the extraction tube, which promoted the analytes transfer into the supernatant organic phase. Influential parameters on the extraction efficiency such as type and volume of extraction solvent, salt type and its concentration, vortex and aeration times, and sample pH were evaluated and optimized. The calibration curves showed good linearity ($r^2 > 0.9947$) and precision ($RSD < 5.0\%$) in the working concentration ranges. The limit of detection (LOD) for β-naphthol, naphthalene and anthracene were 10, 5.0 and 0.5 ng mL^{-1} , respectively. The recoveries were in the range of 97.0–102.0% with RSD values ranging from 2.2 to 5.2%.

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1. Introduction

Most samples are not suitable for direct introduction into analytical instruments. For this reason, the sample preparation procedure is an important step in an analytical study. However, selection of sample preparation procedure depends on the analytes properties, the matrix, concentration level of analytes in the sample, the analytical techniques to be employed and their capabilities [1]. In the last two decades many extraction approaches for minimizing the environmental pollution emphasis on reducing organic solvent consumption in the extraction process.

Solid-phase microextraction (SPME) is the first microextraction technique that used to extract the analytes from a solution or headspace of sample [2–4]. SPME is a solventless procedure, which has double role of clean-up and pre-concentration of interested analytes. Limitations of the SPME for quantitative analysis are include: (a) longer extraction time, (b) limited volume of extractant phase (fiber coating), (c) carryover and memory effects,

(d) fragility of the fibers and (e) the limited lifetime of fibers that results to increase analysis cost.

Liquid–liquid extraction (LLE) is one of the most common sample preparation techniques. LLEs involving a few milliliters or less of extraction solvent are termed microscale liquid–liquid extraction (MLLE). The fundamentals of MLLE techniques are similar to LLE with advantages of simpler automation and less solvent consumption. In 1996, a new microextraction technique namely single-drop microextraction (SDME) was introduced simultaneously by Liu and Dasgupta [5] and Jeannot and Cantwell [6].

Later, other types of liquid–liquid microextraction (LLME) techniques such as headspace liquid–phase microextraction (HS-LPME) [7–9], hollow fiber liquid–liquid microextraction (HF-LLME) [10–12], vortex-assisted liquid–liquid microextraction (VALLME) [13–15] and salt-assisted liquid–liquid microextraction (SALLME) [16–18] were developed. These methods have many advantages such as reduction in sample and solvent quantity, high enrichment factor and clean-up step.

In 2006, Assadi and co-workers [19] developed a novel microextraction technique, termed dispersive liquid–liquid microextraction (DLLME), which is based on a ternary component solvent system like homogeneous liquid–liquid extraction (HLLME) and cloud point extraction (CPE). In this method, the extraction is performed by an interaction between the sample and a cloud of

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fine extractant drops after injection of an appropriate mixture of extraction and disperser solvents into the aqueous sample. After formation of cloudy solution, the surface area between extracting solvent and aqueous sample increases which lead to quick extraction. Therefore, the extraction time becomes very short.

The air-assisted solvent extraction (AASX) method was used in engineering processes to remove of metals and organic contaminants from wastewater. In this method, a solvent-coated bubble is used to contact between organic and aqueous phases [20,21]. Aeration causes the extraction solvent to form a thin layer on bubbles and leads to increases the contact area between two phases [22]. Due to increasing interfacial area between extraction solvent and aqueous phase, analytes can be extracted into the organic phase in short time with higher efficiency.

Recently, an air-assisted liquid–liquid microextraction method (AALLME) as a new version of DLLME was developed for extraction and preconcentration of phthalate esters in aqueous samples [23]. Due to elimination of disperser solvent in AALLME method, volume of extraction solvent was decreased in comparison with DLLME. In order to increase the contact between analytes and extraction solvent, the mixture of aqueous sample solution and extraction solvent was sucked and injected with a syringe for several times in a conical test tube.

In this work, a novel vortex and air assisted liquid–liquid microextraction (VAALLME) technique was developed for determination of trace levels of β -naphthol, naphthalene and anthracene in wastewater samples. Unlike DLLME method, extraction was performed without using disperser solvent and centrifuging step. After mixing of sample solution and extraction solvent by using vortex, the cloudy mixture was transfer to a long tube and subjected to aeration process. Aeration leads to phase separation and increases analytes transfer to organic phase. Finally, upper organic phase was removed and injected to high-performance liquid chromatography (HPLC) system. The influences of the different experimental parameters on the extraction efficiency of model analytes are studied and optimized.

2. Experimental

2.1. Chemicals and materials

Acetonitrile (HPLC grade), methanol, cyclohexane, octanol, 2-decanol, sodium carbonate, ammonium acetate, sodium chloride, sodium hydroxide and orthophosphoric acid were purchased from Merck Chemical Company (Darmstadt, Germany). Naphthalene, β -naphthol and anthracene were obtained from Sigma-Aldrich (USA). All solutions were prepared with deionized water from a Milli-Q system (Millipore, USA).

2.2. Chromatographic conditions

The HPLC system (Shimadzu Corporation, Kyoto, Japan) which consisted of a quaternary pump (LC-10ATvp), UV–vis detector (SPD-M10Avp), vacuum degasser and system controller (SCL-10Avp) was used. A manual injector with a 10 μ L sample loop was applied for loading the sample. Class VP-LC workstation was employed to acquire and process chromatographic data. A reversed-phase C_{18} analytical column (Shim-Pack VP-ODS, 250 mm \times 4.6 mm i.d., Shimadzu, Japan) was used.

The mobile phase consisted of water and acetonitrile (40:60, v/v). Prior to preparation of the mobile phase, water and acetonitrile were degassed separately using a Millipore vacuum pump. The UV detector was set at 254 nm. The chromatograms were run for 15 min at a flow rate of 1.0 mL min^{-1} at ambient temperature.

2.3. Sample preparation

Standard stock solutions were prepared by dissolving each analyte in methanol with concentration of 100 $\mu\text{g mL}^{-1}$. Working standard solutions at different concentrations were prepared freshly by mixing the appropriate volumes of the stock solutions and diluting with deionized water.

Wastewater samples were collected from Shazand Petrochemical Corporation (Arak, Iran). Samples were filtrated through a 0.45 μm PTFE membrane and were adjusted to the pH of 7.0 prior to extraction.

2.4. VAALLME procedure

10 mL of sample or standard solution was transferred into a 50 mL conical polypropylene centrifuge tube. 1 g of sodium carbonate and 500 μL of octanol/cyclohexane (50:50, v/v) as extraction solvent were added and then the mixture was vortexed (DRAGON LAB MX-S, Beijing, China) at 2500 rpm for 2 min. The cloudy mixture was transferred into a long glass tube and subjected to aeration process by using an air pump (model XP-2200A, China) until phase separation occurs and aqueous phase was clear. Then the organic phase was moved to the top of the tube by using water injection. Finally, 10 μL of organic phase was withdrawn and injected into the HPLC system for analysis. The schematic diagram of extraction process was illustrated in Fig. 1.

3. Results and discussion

Various parameters such as type and volume of extracting solvent, vortex and aeration times, salt type and its concentration and sample pH can be affected on extraction efficiency. The effects of these parameters on extraction were studied and optimized.

3.1. Selection of extraction solvent

In order to select suitable extraction solvent several parameters must be considered: (a) no interference with analytes signal, (b) high extraction efficiency for analytes, (c) low solubility in aqueous solution and (d) compatibility with detection system. Various extraction solvents such as octanol, 2-decanol, cyclohexane, and mixture of octanol/cyclohexane at different ratios were examined. The results were illustrated in Fig. 2. Low extraction efficiency of 2-decanol and octanol as extraction solvent can be attributed to high viscosity of these solvents, which decrease the diffusion coefficients of the analytes. In addition, polarity of extraction solvent is another important parameter. Therefore, different ratios of octanol and cyclohexane were used. According to results, mixture of octanol/cyclohexane (50:50 v/v) was selected as appropriate extraction solvent.

3.2. Volume of extraction solvent

Fig. 3 shows the influence of extraction solvent volume on the analytes extraction. It can be observed that the peak areas of analytes increased with increasing extraction solvent volume up to 200 μL and then decreased. In lower extraction solvent volumes (< 200 μL), extraction of analytes are not completed. In the other hand, enrichment factor (EF) decreases with increasing volume of the extraction solvent. Therefore, 200 μL was selected as the optimum volume in this study.

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