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Ultrasound-assisted supramolecular dispersive liquid–liquid microextraction based on solidification of floating organic drops for preconcentration of palladium in water and road dust samples

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ABSTRACT

A novel ultrasonic-assisted supramolecular dispersive liquid–liquid microextraction based on solidification of a floating organic droplet (UASMDLLME-SFO) was proposed for the microextraction of Pd(II) prior to its determination by flame atomic absorption spectrometry (FAAS). A supramolecular solvent made up of reverse micelles of 1-dodecanol in tetrahydrofuran (THF) was injected into the aqueous sample solution. Reverse micelle coacervates were produced in situ through self-assembly processes. Sonication accelerated mass transfer of the target analyte into the supramolecular solvent phase. Some parameters such as type and volume of the extraction solvent, pH, volume of the disperser solvent, ultrasound extraction time, reagent concentration, and salt concentration were investigated. Under optimum conditions, a detection limit 0.63 μg L^{-1} with preconcentration factor of 93 and the relative standard deviation (RSD, n = 10) 3.2% were achieved. The accuracy of the method was confirmed by analyses using the geological standard reference materials (GBW07291peridotite). The recoveries of the analytes in water and road dust samples were in the range of 96–104%.

1. Introduction

Palladium is one of the noble metals and possesses specific characteristics such as high melting point, corrosion resistance and extraordinary catalytic properties [1]. Palladium and its alloys have found essential importance in many different fields for an extensive range of applications such as in the automobile, electronics, metallurgy, catalytic converters, dental and medical prostheses, and jewelry manufacture. Some palladium compounds have been reported as highly toxic and carcinogenic to humans, and easily transported to biological material and ultimately intensified along the food chain [2]. Therefore, very sensitive techniques are necessary for determination of trace amounts of Pd ions such as electrothermal atomic absorption spectrometry, inductively coupled plasma-optical emission spectroscopy and flame atomic absorption spectrometry techniques. Some of these techniques are time-consuming and expensive, but flame atomic absorption spectrometry presents desirable characteristics such as low cost, operational facilities, high analytical frequency and good selectivity, but direct determination of metal ions at trace levels is limited due to insufficient sensitivity of this technique as well as matrix interferences occurring in environment samples. Thus, preconcentration and separation techniques are still very necessary. Different kinds of methods have been reported for separation and preconcentration of Pd(II) prior to its detection, such as solid phase extraction (SPE) [3], liquid–liquid extraction (LLE) [4], flow injection extraction (FIE)[5], cloud point extraction (CPE) [6] and dispersive liquid–liquid microextraction (DLLME) [7].

However, there are some shortcomings in these techniques e.g., like time-consuming, long extraction times, and large volumes of solvents which are expensive, toxic and contaminant for the environment due to their high vapor pressure. The use of toxic, flammable and environmentally damaging solvents is one of the major drawbacks of recent analytical techniques and much attention has been paid towards the use of green solvents such as ionic liquids. However, they are very expensive and their handling poses some difficulties because of their high viscosities. In respect to the use of other organic solvents friendly to the environment, recently a new mode of liquid-phase microextraction, the so called supramolecular solvent (SUPRAS) has been developed [8–10]. The SUPRAS is a water-immiscible liquid consisting of reverse micelles that aggregate at nanoscale dimensions dispersed in a continuous phase and provides different types of interactions with the organic compound and hydrophobic complex of metals with ligands. Thus it can be used as the most suitable system for extraction processes [11–13]. However, this technique is tedious, labor-intensive and a time-consuming procedure. Recently, ultrasound-assisted emulsification microextraction (USAEME) was introduced by Requeiro and his

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Table 1
Effect of type of extraction solvent on the extraction recovery of Pd (II).

Supramolecular solvent	Recovery (%) ± S.D.[a]
1-Decanol	85.0 ± 2.1
1-Undecanol	80.1 ± 2.3
Decanoic acid	76.3 ± 2.7
1-dodecanol	95.3 ± 2.5

[a] Mean of three experiments ± standard deviation.

coworkers [14]. It is well known that ultrasound has the potential to increase the speed of homogenization, emulsification, and mass transfer between immiscible phases [15].

A combination of ultrasound and supramolecular based DLLME technique provides enhanced sensitivity and a high preconcentration factor. The advantages of this method are simplicity of operation, high recovery, very short extraction time due to the very large surface area between the organic and aqueous phases. Leong and Huang suggested a new method of DLLME based on the solidification of the floating organic droplet (DLLME-SFO) [16]. A small volume of an organic solvent with a melting point near room temperature is floated on the surface of an aqueous solution and can be easily collected by solidifying at a low temperature [17,18]. Due to the fact that 1-dodecanol possesses lower density than water, a novel combination of ultrasound-assisted supramolecular solvent and dispersive liquid–liquid microextraction based on the solidification of floating organic drop (UASMDLLME-SFO) as a rapid method for the routine control of this contaminant in different matrices has been introduced. In this method, an appropriate amount of reverse micelles of 1-dodecanol in tetrahydrofuran was injected rapidly into the aqueous sample by a syringe then the mixture was sonicated. The large contact surface between the extraction solvent and the sample speeds up the mass transference processes. Hence, extraction can be achieved within a few seconds. In the present study, the applicability of UASMDLLME-SFO was evaluated for preconcentration Pd(II) in water and road dust samples.

2. Experimental

2.1. Instrumentation

The determination of palladium was carried out using a Varian Spectra AA 220FS Atomic Absorption Spectrometer (Australia, http://www.varianinc.com) equipped with an air–acetylene burner. For background correction, a deuterium lamp was used. Measurements were in the peak area mode at wavelength at 244.8 nm and slit of 0.2 nm. The lamp was operated at 5 mA. Measurements of pH values were made with a pH-meter, Model 692 from Metrohm (http://www.metrohm-ag.com, Herisau, Switzerland) with a glass combined electrode. A refrigerated centrifuge (Hettich, Universal 1320 R) equipped with an angle rotor (6-place, 5000 rpm, Cat. No. 1628 A) was applied to the separation. A 50/60 Hz, 350 W ultrasonic bath with temperature control (EURONDA S.P.A., Italy) was used.

2.2. Reagent

All reagents used were of analytical grade. All solutions were prepared using doubly distilled water. Pd(II) stock solution (1000 mg L^{-1}) was prepared by dissolution of the proper amount of $PdCl_2$ (Merck, Darmstadt, Germany) in 3:1, HCl/HNO_3 (v/v) and then diluted with double distilled water. The working standard solutions were obtained by dilutions of the stock solution with deionized water immediately prior to the analysis. A solution of 1×10^{-3} mol L^{-1} 1-(2-Pyridylazo)-2-naphthol (PAN) was prepared by dissolving an appropriate amount of this reagent in ethanol. Solvents containing 1-Decanol, 1-Undecanol, Decanoic acid, 1-dodecanol and THF were obtained from Merck (Darmstadt, Germany).

2.3. Sample preparation

The water samples containing well water, tap water, waste water and river water were analyzed according to the recommended procedure. The samples were filtered through a 0.45 μm membrane filter immediately after sampling to remove suspended particulate matter.

An amount of 1.0 g of homogenized dust sample (collected from different roadsides in Tehran) was weighed accurately and digested with 50 ml HCl/HNO_3 in a beaker by refluxing the mixture for 5 h. The solution was centrifuged. The filtered solution was diluted with distilled water up to 50 mL and pH of solution was adjusted. The obtained solution was analyzed following the experimental procedure.

2.4. UASMDLLME-SFO procedure

An aliquot of 10 ml sample solution containing 30 μg L^{-1} Pd(II), PAN (1.5×10^{-5}) was poured into a 50 mL tube. After adjusting pH to 3, 450 μL of extraction solution consisting of 1-dodecanol (100 μL) and THF (350 μL) was injected into the sample solution by using a 1 mL syringe rapidly, then the mixture was sonicated in an ultrasonic bath for 1 min. During this process, a turbid solution was the result. The hydrophobic complex was extracted from the supramolecular solvent. The mixture was centrifuged at 4000 rpm for 5 min to accelerate the complete separation of the two immiscible liquids. The test tube was then placed in an ice bath (5 min) and then the supramolecular solvent collected into a conical vial and melted immediately. Then, the extractant was dissolved in 100 μL of ethanol. Subsequently, 50 μL of the final solution was injected into FAAS for the determination by using the microsample introduction system.

3. Results and discussion

3.1. Supramolecular solvent condition

The extraction solvent should have several characteristics such as low volatility, low toxicity, low melting point near room temperature, good solubility in disperser solvent and a density less than that of water. Based on these considerations, 1-Decanol (mp 6.4 °C), 1-undecanol (mp 15.9 °C), Decanoic acid (mp 31.5 °C) and 1-dodecanol (mp 24 °C) in THF were tested. The extraction recovery values have shown that 1-dodecanol was solvent suitable (Table 1). The volume of the extraction solvent is one of the important factors. For this purpose, solutions containing different volumes (25–200) μL of 1-dodecanol and a constant volume of THF (350 μL) were used. As can be seen in Fig. 1, the maximum extraction recovery was obtained using 100 μL of the extraction solvent. 1-dodecanol, like other alkyl carboxylic acids, is slightly soluble in water (0.004 g L^{-1} at 20 °C) and very soluble in

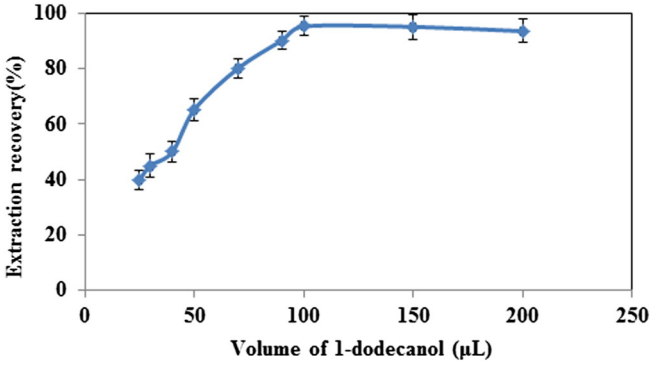

Fig. 1. Effect of the volume of 1-dodecanol on the extraction recovery of Pd(II). Conditions: sample volume: 10 mL; volume of disperser solvent (THF), 350 μL; pH 3; Pd(II) concentration: 30 μg L^{-1}.