



Suspended nanoparticles in surfactant media as a microextraction technique for simultaneous separation and preconcentration of cobalt, nickel and copper ions for electrothermal atomic absorption spectrometry determination

Shayessteh Dadfarnia*, Farid Shakerian, Ali Mohammad Haji Shabani

Department of Chemistry, Faculty of Science, Yazd University, Yazd 89195-741, Iran

ARTICLE INFO

Article history:

Received 15 October 2012

Received in revised form

20 November 2012

Accepted 5 December 2012

Available online 13 December 2012

Keywords:

Suspended nanoparticles in surfactant media

Microextraction

Alumina nanoparticles

ABSTRACT

The aim of this study was to describe a new method of microextraction based on the suspension of alumina nanoparticles in the surfactant media for simultaneous separation and preconcentration of the ultra-traces of cobalt, nickel and copper ions. In this technique, the alumina nanoparticles were suspended in the non-ionic surfactant solution of Triton X-114. The analytes in the sample solution were adsorbed onto the nanoparticles. After the phase separation based on the cloud point of the mixture at 40 °C, the nanoparticles settled down in the surfactant rich phase. Then 120 μL of nitric acid (3.0 mol L^{-1}) was added to the surfactant rich phase which caused desorption of the analytes. Finally, the liquid phase was separated by centrifugation from the nanoparticles and was used for the quantification of the analytes by the electrothermal atomic absorption spectrometry (ETAAS). The parameters affecting the extraction and detection processes were optimized. Under the optimized experimental conditions (i.e. $\text{pH} \sim 8$, Triton X-114, 0.05% (v/v); temperature 40 °C), a sample volume of 25 mL resulted in the enhancement factors of 198, 205 and 206 and detection limits (defined as $3S_b/m$) of 2.5, 2.8 and 2.6 ng L^{-1} for Co(II), Ni(II) and Cu(II) respectively. The sorbent showed high capacity for these metal ions ($30\text{--}40 \text{ mg g}^{-1}$ sorbent). The method was successfully applied to the determination of the analytes in natural water samples.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The sample preparation step in an analytical process has been recognized as the main bottleneck of the analysis, especially when trace determination is the purpose [1,2]. Despite the invaluable advances in the separation and quantification methods of the analysis, the conventional liquid–liquid extraction (LLE) is still the most widely used sample preparation technique [3,4]. However, it requires a large amount of organic solvent and is time consuming. To overcome the disadvantages, researches have been directed toward the development of the techniques that are environment friendly, and reduce the costs of analysis through reduction or complete elimination of the organic solvent as well as miniaturized sample preparation method [5]. As a result, a high proportion of the recent analytical publications deals with the novelties in microextraction techniques, such as cloud point extraction (CPE) [6–9], stir bar sorptive extraction (SBSE)

[10–12], solid phase microextraction (SPME) [13–15], and liquid phase microextraction (LLME) [16–18]. The SPME was introduced by Pawliszyn in the early 1990s [19,20] which was widely used in sample preparation. The SPME methods have the advantages of rapidity, simplicity, being solvent free and compatibility with most detection systems. However, it has the drawbacks of fiber breakage, stripping of coating, bending of the needle and limited suitability for the extraction of trace metal ions.

One important demand shared by the fundamental research on solid phase extraction and microextraction is the development and characterization of the new sorbents. The main goals of the researchers on this field are improvement of the capacity, sensitivity and detection limit attainable, and enhancement of the thermal, chemical and mechanical stability of the sorbents [21,22].

The nanosized materials can be considered as promising sorbents due to their special properties such as high sorption capacity, simplicity and rapidity of the sorption/desorption process. Alumina nanoparticles are one of the most important metal oxide materials widely used for structural, microelectronic, and membrane applications as well as water and wastewater

* Corresponding author. Tel.: +98 35 1821 2667; fax: +98 35 1821 0644.
E-mail address: sdadfarnia@yazduni.ac.ir (S. Dadfarnia).

treatment purposes [23]. Unmodified and modified alumina nanoparticles with different organic ligands have been used for the separation and preconcentration of the metal ions [24–30]. However, one of the limitations of the use of the nanosized materials as sorbents is the slow flow rate of the sample through the column packed with these particles. The flow rate can be facilitated by using a pump, but pumping the sample through the column makes the nanoparticle dislodged by passing through the foam which is used to retain the sorbent in the column. Consequently, most of the reports concerning the use of the nanoparticles as sorbents are based on the modification of the nanoparticles with different ligands, which cluster them together and retain them in the column. Also, some glass particles are added to these sorbents to prevent them from packing the column too tight [31]. On the other hand, the use of the nanoparticles in the batch mode extraction is not attractive since the rate of their settlement is very slow, and the separation of the sorbent from the large aqueous sample volume is difficult. In order to overcome the above mentioned problems, we introduced a new microextraction method named suspended nanoparticles in the surfactant media. Co(II), Ni(II) and Cu(II) were used as the model inorganic ions in the development and evaluation of the method. In this procedure 10 mg of the alumina nanoparticles was added to the sample solution containing 0.05% (v/v) of Triton X-114 as the nonionic surfactant. The mixture was put in an ultrasonic bath for about a few minutes, causing further dispersion and suspension of the nano-alumina. The analytes were quickly adsorbed on the alumina nanoparticles at this point. The phase separation was based on the cloud point of the mixture followed by centrifugation. The nanoparticles easily settled down in the surfactant rich phase and the aqueous phase was decanted. Then, 120 μL of nitric acid (3.0 mol L^{-1}) was added to the surfactant rich phase and the analytes were desorbed. Finally, the mixture was centrifuged and the liquid phase was used for the determination of the analytes by ETAAS.

2. Experimental

2.1. Reagents and chemicals

The reagents used throughout this study were of the analytical reagent grade obtained from Merck Company (Darmstadt, Germany). The standard stock solutions of nickel (II) (1000 mg L^{-1}), cobalt (II) (1000 mg L^{-1}) and copper (II) (1000 mg L^{-1}) were prepared separately by dissolving the proper amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 1% nitric acid solution. Working solutions were prepared daily by serial dilution of the stock solutions. Deionized water was used throughout the sample preparation process and all the solutions were stored in clean polypropylene (Nalgene, Lima, OH, USA) containers. Aluminum oxide nanopowder, < 50 nm particle size (TEM), was purchased from the Sigma-Aldrich company. All glasswares were kept in 10% nitric acid overnight and subsequently rinsed several times in deionized water before use. A Pd/Mg modifier was prepared from the palladium modifier solution for ETAAS and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ according to the method given in the literature[32].

2.2. Instrumentation

A Varian Zeeman spectra atomic absorption spectrometer (model 220Z) was used for all metal measurements. The Varian hollow cathode lamps of cobalt, nickel and copper were used as the light sources, and were operated at currents of 4, 7 and 4 mA, wavelengths of 232.0, 242.5 and 327.4 nm and spectra bandwidths of 0.2, 0.2 and 0.5 nm, respectively. The furnace tube was a

Table 1

Temperature program of electrothermal atomic absorption for determination of analytes.

Steps	Co(II) temperature (°C)	Ni(II) temperature (°C)	Cu(II) temperature (°C)	Time (s)	Gas flow (L min^{-1})
Drying	85	85	85	5	3.0
	95	95	95	40	3.0
	120	120	120	10	3.0
Ashing	750	800	800	8	3.0
Atomization	2300	2400	2300	3.1	0
Tube cleaning	2300	2400	2300	2	3.0

standard platform tube with a pyrolytic coating. The Zeeman background correction was used for all measurements. The furnace temperature programs applied were as recommended by the manufacturer (Table 1). Peak height measurement was used for all the quantifications. The pH measurements were carried out with a Metrohm pH meter (model 827, Switzerland) using a combined glass calomel electrode. The sample injection volume was 10 μL in all the experiments.

2.3. Procedure

10 mg of alumina nanoparticles was added to 25 mL of a standard or sample solution containing cobalt, nickel and copper. It was made 0.05% with respect to Triton X-114 and the pH was adjusted to 8 using diluted ammonia solution. The mixture was then put in an ultrasonic bath for a few minutes ($\sim 2 \text{ min}$), causing further dispersion and suspension of the alumina nanoparticles. At this stage, the analytes were adsorbed onto the alumina nanoparticles. The mixture was heated in a thermostated water bath at 40°C until the solution became cloudy ($\sim 5 \text{ min}$). The phases were separated by centrifuging the solution for 6 min at 4000 rpm. At this stage, the aqueous and the surfactant rich phase were separated and the nanoparticles containing the analytes were settled in the surfactant rich phase. The phases were further cooled in an ice-water bath, causing increase in the viscosity of the surfactant rich phase, and the aqueous phase was easily decanted. Then, 120 μL of nitric acid (3.0 mol L^{-1}) was added to the tube which caused desorption of the analytes into the surfactant rich phase. The mixture was centrifuged and finally, the supernatant solution was transferred into an electrothermal cup, and 10 μL of it along with 10 μL of the modifier was injected into the graphite tube of ETAAS for the quantification of each analyte.

2.4. Preparation of water samples

The water samples were filtered through a $0.45 \mu\text{m}$ Millipore filter. The pH was adjusted to ~ 8 using dilute ammonia solutions and treatments according to the given procedure

3. Results and discussion

Initial experiments indicated that the alumina nanoparticles suspended in the aqueous phase can easily settle down in the surfactant rich phase. On this basis, a microextraction method was designed and the possibility of simultaneous extraction of the Co(II), Ni(II) and Cu(II) as a model component was examined. In order to obtain high enrichment factors, the effects of different parameters affecting the extraction were optimized using a univariable approach.

Download English Version:

<https://daneshyari.com/en/article/7683625>

Download Persian Version:

<https://daneshyari.com/article/7683625>

[Daneshyari.com](https://daneshyari.com)