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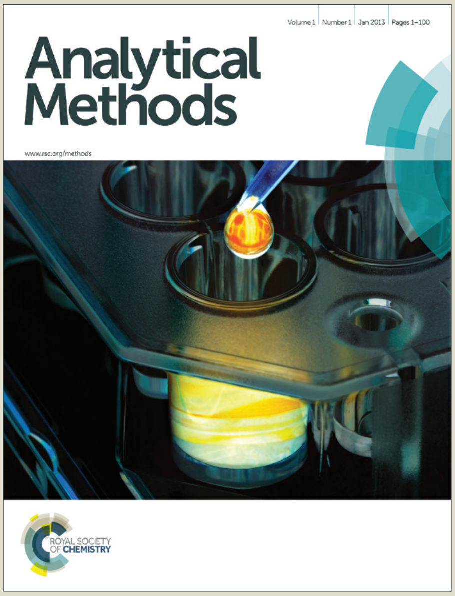

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Supramolecular solvent-based microextraction of copper and lead in water samples prior to reacting with synthesized Schiff base by flame atomic absorption spectrometry determination

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Abstract: A supramolecular solvent made up of reverse micelles of nonanoic acid, dispersed in a continuous phase of tetrahydrofuran (THF) and water, were proposed for the simple, rapid and efficient microextraction of copper (Cu) and lead (Pb) in water samples prior to flame atomic absorption spectrometry determination. A new Schiff base was synthesized and used as the chelating agent in this study. Some important extraction parameters such as the pH, Schiff base concentration, the composition and volume of the supramolecular solvent and vortex time were evaluated, obtaining the most favorable results. Under the optimized conditions, the calibration curves were linear in the range of 10-800 μg L^{-1} for Cu and 10-500 μg L^{-1} for Pb, respectively. The limits of detection (LOD) were 0.29 μg L^{-1} and 0.45 μg L^{-1}, with the enrichment factors of 27 and 22 for Cu and Pb, respectively. Recoveries of Cu and Pb spiked into water samples were in the range of 91.2%-102.1%. The results showed that the proposed method was suitable for the determination of Cu and Pb in water samples.

Keywords: Supramolecular solvent, Schiff base, flame atomic absorption spectrometry, Copper, Lead

1. Introduction

In recently years, pollution of the environment by large amount of toxic elements has been considered as a result of human activities.[1] More and more waste water containing hazardous heavy metals were released into the river, which are harmful to human's body and the environment around. So, determination of the toxic metals such as Cu and Pb in water samples is of significative. Cu is a ubiquitous trace metal in the biosphere, it is an essential and necessary micronutrient for many biological systems at very low levels. However, it becomes toxic at high levels due to its association with cell membranes, preventing the transport across the wall cell.[2,3] Pb is known to be a toxic metal, which can be accumulates in human body throughout the lifetime.[4] It can cause adverse effect on metabolic processes of human beings and has been proved to be a carcinogenic agent.[5] Therefore, determination and monitoring of Cu and Pb at trace levels is of significant importance.

Direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. Thus, preconcentration and separation techniques are still very necessary. Various techniques including solid phase extraction (SPE),[6,7] liquid-liquid extraction (LLE),[8] dispersive liquid-liquid microextraction (DLLME)[9-11] and cloud point extraction (CPE)[12-14] have been applied for preconcentration and separation of trace amounts of Cu and Pb from environmental samples.

In this work, a new extraction technique, supramolecular solvent-based microextraction, was developed as the effective, rapid and inexpensive extraction method for the determination of Cu and Pb in water samples.

Supramolecular solvents are introduced to design water-immiscible liquids made up of supramolecular assemblies dispersed in a continuous phase.[15] They are produced from amphiphile solutions by two well-defined self-assembly processes occurring on two scales, molecular and nano. First, amphiphilic molecules self-assemble in the solution above a critical aggregation concentration. Then, the generated nanostructures self-assemble in larger aggregates with a wide size distribution in the nano and micro scale regimes by the action of an external stimulus and separate from the bulk solution by a mechanism that remains elusive.[16-18]

The supramolecular solvents proposed in this work for the extraction of Cu and Pb was produced from an isotropic solution of reverse micelles of nonanoic acid in THF by addition of water. Schiff base ligands bearing nitrogen and oxygen donor atoms have been shown to exhibit interesting ionophoric properties, in particular towards heavy metal ions.[19] The application of Schiff base in different separation and preconcentration techniques were investigated.[20-22] This work reports the synthesis of a new Schiff base by using a Schiff base reaction between 4-aminoantipyrine and p-dimethylaminobenzaldehyde (DMAB). According to our knowledge, using the Schiff base as chelating agent for supramolecular solvent-based microextraction of Cu and Pb has not been reported before. Below, the main results obtained in optimization studies, analytical features evaluation and analysis of real water samples are presented and discussed.

2. Experimental

2.1 Chemicals

Stock standard solution (1000 μg mL^{-1}) of Cu and Pb were obtained from the National Institute of Standards (Beijing, China). Britton-Robinson buffer solution was composed of phosphoric acid, boric acid and acetic acid. 4-aminoantipyrine and DMAB (Aladdin, China) were used for the synthesis of the Schiff base. Octanoic acid， nonanoic acid, decanoic acid and THF were analytical grade and purchased from Sigma (St. Louis, Mo., USA). Purified water was obtained using an Aike water purification system (Chengdu, China) and used as experimental water throughout the research. All the other reagents used were of analytical grade.

2.2 Apparatus

Flame atomic absorption spectrometer (Z-2000, Hitachi, Japan) was used for the determination of metal ions. A vortex oscillator (Shanghai, China) was used to assist the supramolecular solvent-based microextraction procedure. A centrifuge with calibrated centrifugal tubes (Shanghai, China) was used for the phase separation process.

2.3 Supramolecular solvent production

The supramolecular solvent was produced by the following procedure. 800 μL of nonanoic acid, 13 mL THF and 20 μL HCl (2 mol L^{-1}) was added in a 50 mL of plastic centrifuge tube, respectively. After this, the mixture was diluted to 50 mL by bidistilled water, and then fiercely stirred by a vortex oscillator for 5 min, time in which the supramolecular solvent spontaneously formed into the bulk solution. Then, the mixture was centrifuged at 3500 rpm for 5 min to speed the supramolecular solvent separation up, which is less dense than water. After this, the solvent was withdrawn using a syringe with a long needle, transferred to a hermetically close storage glass vial to avoid THF losses and stored at 4 ℃. Under these conditions, the supramolecular solvent produced was stable for at least one month.

2.4 Synthesis of Schiff base

The Schiff base was synthesized by the following method: First, solutions of 4-aminoantipyrine (2.03 g, 10 mmol) in ethanol (30 ml) and DMAB (1.49 g, 10 mmol) in ethanol (50 ml) were prepared, respectively. Then, the solution of DMAB was slowly added into the 4-aminoantipyrine and the mixture was refluxed at 65 ℃for 3 h. The yellow precipitate was filtered off and recrystallized three times from methanol. Finally, the product was dried for one day by the method of vacuum drying. The reaction scheme of the synthesis was shown in Fig. 1.

2.5 Supramolecular solvent-based microextraction

In this method, Cu and Pb react with Schiff base yielding hydrophobic complexes in aqueous phase, which are then extracted into the supramolecular solvent phase. For the supramolecular solvent-based microextraction under optimum conditions, an aliquot of 10 mL of sample solution or standard solution containing Cu and Pb (100 μg L^{-1}), 10 μg mL^{-1} of Schiff base, 1 mL of buffer solution (pH 7.0) and 1 mL of supramolecular solvent were placed in a graduated centrifuge tube. Then the mixed solution was fiercely stirred by a vortex oscillator for 5 min. Separation of the two phases was accelerated by centrifugation for 10 min at 3500 rpm. The aqueous phase was then carefully removed by using a syringe with a long needle. And the supramolecular solvent phase was diluted with methanol solution containing 1.0 mol L^{-1} HNO_3 to 1 mL and determined by FAAS.

3. Results and discussion

3.1 FT-IR spectroscopy analysis of the synthesized Schiff base

FT-IR spectroscopy analysis has been widely employed for the characterization of organic functional groups bonded organic and inorganic solid phases. The FT-IR spectra of DMAB and the synthesized Schiff base are given in Fig. 2. From the Fig. 2, we can get the following information: First, stretching vibration absorption at 1750 cm^{-1} is the characteristic absorption peaks of C=O in the aldehyde group. But it has disappeared. This result demonstrated that DMAB has reacted completely, which may indirectly illustrate the formation of C=N. Second, the stretching vibration absorption at 1647 cm^{-1} is belong to C=N in synthesized Schiff base. Third, the stretching vibration absorption at 1454 cm^{-1}, 1503 cm^{-1}, 1579 cm^{-1} and 1590 cm^{-1} are the characteristic absorption peaks of C-H in the benzene ring. Based on the above analysis, we can infer that the Schiff base has been synthesized successfully.

3.2 Effect of pH

The pH plays a unique role on the metal complex formation and subsequent extraction. For this reason, the effect of pH on the extraction efficiency was investigated in the range of 1-11. Fig. 3 shows the effect of pH on the extraction of the Cu and Pb complexes. It was found that the maximum extraction efficiency was obtained at the pH 7.0. So, a pH of 7.0 was selected in subsequent experiments.

3.3 Effect of the Schiff base concentration

In order to investigate the concentration of Schiff base on the extraction efficiency of Cu and Pb, different concentrations of the Schiff base in the range of 1-20 μg mL^{-1} were used. As shown in Fig. 4, the recovery of Cu and Pb increased by increasing Schiff base concentration up to 10 μg mL^{-1}. Hence, 10 μg mL^{-1} of Schiff base was used in subsequent experiments

3.4 Effect of the composition and volume of the supramolecular solvent

Three types of organic acid including octanoic acid, nonanoic acid and decanoic acid were selected to the supramolecular solvent production. Its formation occurs through two sequential self-assembly processes. First, the organic acid molecules aggregate as reverse micelles in THF. Then, under the addition of water, they rearrange in larger reverse micelles that separate from the bulk solution, as an immiscible liquid, through a mechanism that remains elusive. The immiscible liquid is made up of reverse micelles, THF and water. And the effect of three types of supramolecular solvent on the recovery of Cu and Pb were investigated. As shown in Fig. 5, compared with octanoic acid and decanoic acid, supramolecular solvent formed by nonanoic acid and THF could obtain the best extraction efficiency. Therefore, it was selected as the best extraction solvent for this study. And the effect of the volume of this supramolecular solvent on the presented method was also investigated. As it is shown in Fig. 6, 1 mL of the supramolecular solvent was chosen as the optimum volume for this study.

3.5 Effect of the vortex time

Vortex process plays an important role in this study. Firstly, it was used to accelerate the supramolecular solvent spontaneously formed into the bulk solution. According to our experiments, 5 min of vortex time was appropriately for the formation of the supramolecular solvent. Secondly, a vortex process was applied to mix the solution thoroughly and obtain good extraction efficiency. For this reason, the vortex time was investigated in the range of 0-10 min. As can be seen from Fig. 7, the recovery of Cu and Pb was increased by increasing the vortex time up to 5 min. Therefore, 5 min of vortex time was chosen as the optimal time in this study.

3.6 Analytical features

Under the optimized conditions, the analytical performance of the proposed method was evaluated. A calibration curve was constructed by preconcentrating of 10 ml of sample solutions with supramolecular solvent. The calibration graph was linear in the range of 10-800 μg L^{-1} and 10-500 μg L^{-1} for Cu and Pb, respectively. The limit of detection (LOD), defined as $C_L=3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank, and slope of the calibration graph, respectively), are 0.29 μg L^{-1} and 0.45 μg L^{-1} for Cu and Pb. Other analytical features of the proposed method such as calibration equation, correlation coefficient and the relative standard deviation (RSD) were also investigated. The results were shown in Table 1.

3.7 Interference study

The effect of other ions in the extraction of Cu and Pb was studied under optimized conditions. To perform this study, 10 mL of solution containing 50 µg L^{-1} of Cu and Pb and different concentrations of other interfering ions were prepared and subjected to the extraction procedure. The tolerance limit was defined as the foreign ion concentration causing a change in the absorbance of less than ±5%. The results are shown in Table 2. And these results showed that the presence of large amounts of foreign ions commonly presents in water samples have no significant effect on the supramolecular solvent-based microextraction of Cu and Pb in water samples.[23-24]

3.8 Analysis of real samples

Three types of water samples including tap water, river water and industrial wastewater were analyzed to assess their content in Cu and Pb. The samples were filtered to remove the suspended solids and then 10 ml of each of the samples were preconcentrated by proposed method in this study. The results (Table 3) demonstrated that the proposed method can be successfully applied for the preconcentration and determination of Cu and Pb in water samples.

4. Conclusions

In this study, a supramolecular solvent made up of reverse micelles of nonanoic acid, dispersed in a continuous phase of THF and water, was proposed as a simple, rapid and efficient microextraction of Cu and Pb in water samples prior to flame atomic absorption spectrometry determination. The Schiff base used in this study is easy to be synthesized, and it is proved to be an efficient chelating reagent for Cu and Pb. An obvious higher extraction efficiency of Cu and Pb was obtained by a vortex-assisted process. The presented method can be successfully employed for the determination of Cu and Pb in water samples.

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Table 1 The performance characteristics of the proposed method

Analyte	Linear range (μg L^{-1})	Regression equation	R^2	LOD (μg L^{-1})	RSD (%) (n=6)
Cu	10-800	$A=8.2\times10^{-4}C+0.005$	0.999	0.29	2.3
Pb	10-500	$A=3.96\times10^{-4}C+0.0015$	0.999	0.45	3.6

Table 2 Tolerance limits for ions interfering with the determination of 50 µg L^{-1} Cu and Pb (n=6)

Ions	Interfering ion to analyte ratio
K^+, Na^+	1000
Ca^{2+}, Mg^{2+}	2500
Al^{3+}, Fe^{3+}, Mn^{2+}	1500
Hg^{2+}, Cr^{3+}	1000
Cd^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}	800
Cl^-, HCO_3^-, SO_4^{2-}, PO_4^{3-},	2000
NO_3^-, CH_3COO^-	1500

Table 3 Determination of Cu and Pb in water samples

Samples	Added (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
	Cu	Pb	Cu	Pb	Cu	Pb
Tap Water	0	0	not detected	not detected	-	-
	50	50	48.5	48.3	97	96.6
	100	100	96.5	93.4	96.5	93.4
River Water	0	0	21.5	11.6	-	-
	50	50	67.4	58.5	91.8	93.8
	100	100	123.6	109.5	102.1	97.9
Industrial Waste Water	0	0	41.5	20.6	-	-
	50	50	90.5	68.2	98	95.2
	100	100	132.7	116.5	91.2	95.9