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Determination of metal ions by ultrasound-assisted hollow fiber liquid-phase microextraction technique

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A novel approach, ultrasound-assisted hollow fibre liquid-phase microextraction (UA-HF-LPME) was used for the preconcentration of Copper (Cu), cadmium (Cd) and chromium (Cr) of environmental samples by flame atomic absorption spectrometry (FAAS). The method was based on the extraction of the analytes from environmental samples (donor phase) into 15μL of nonanoic acid supported by a porous-walled polypropylene hollow fibre by ultrasound-mixing. Ultrasound-mixing was used as an assisted method to accelerate the mass transfer and minimize fluid loss. Under the optimal conditions, the detection limits of this method for Cr, Cu, and Cd were 0.28, 0.35, and 0.19 μg/L, respectively. The relative standard deviations for Cr, Cu, and Cd were 2.0, 2.6 and 1.8% (C=0.5μg/L, n=9). The relative recoveries of Cr, Cu, and Cd in well water and wastewater samples at the spiking level of 10μg/mL ranged from 80.5 to 96.4%. The method is successfully applied for these metals content evaluation in environmental samples with satisfactory results and high enrichment factors (200).

Keywords: Ultrasound-assisted hollow fibre liquid-phase microextraction, Environmental samples, Metal ions, Flame atomic absorption spectrometry.

INTRODUCTION

Environmental contamination by heavy metal ions in aquatic ecosystems has been increasing with industrial growth and development in recent years. Among all heavy metals, cadmium ion is considered as an extremely toxic metal ion when its concentration in water exceeds 0.01 mg/L which is the permissible limit for human consumption [1]. The main emissions of cadmium occur from waste incineration and fuel burning, but it is also used in foundry and metallurgic industries, batteries, plastics, fertilizers and other materials. Inhaling cigarette smoke has proven to cause expose to cadmium [2]. Copper is an essential element for many biological systems, which plays an important role in carbohydrate and lipid metabolism. In general, copper at nearly 40μg L^{-1} is required for normal metabolism of many living organisms; however, in higher levels it is considered to be toxic and severe oral intoxication will affect mainly the blood and kidneys [3]. Direct determinations of trace or ultra-trace levels of heavy metals in environmental samples are difficult because of their extremely low concentrations in interfering matrices [4]. To overcome these problems, the combination of a separation and preconcentration procedure with flame atomic absorption spectrometry (FAAS) is useful [5,6].

Therefore, a separation and preconcentration technique is extensively applied to the FAAS determination of metal ions [7], hollow fibre liquid-phase microextraction (HF-LPME) is an excellent pretreatment method that is highly compatible with FAAS and overcomes many of the disadvantages of traditional extraction techniques, such as solid-phase extraction (SPE) [8], solid-phase microextraction (SPME), co-precipitation [9],liquid–liquid extraction (LLE) [10,11] and dispersive liquid–liquid microextraction (DLLME) [12]. Hollow fibre liquid-phase microextraction (HF-LPME) technique, originally proposed by Pedersen-Bjergaard and Rasmussen [13] has gained considerable interest in the analytical area and has been widely applied to a variety of environmental and biological samples. In HF-LPME procedure, the analytes are extracted from an aqueous sample (donor phase) into an organic acceptor phase supported by a porous-walled polypropylene hollow fibre [14-16]. The volume of sample in HF-LPME can range between 5mL and greater than 1L, however, the volume of the extraction solvent (acceptor phase) is, in most cases, in the range 2-30μL [17], thus, the very high analyte enrichment factor can be obtained. Although classical HF-LPME procedure take long time (more than 30 min), and the repeatability is not good, the major advantages of HF-LPME are simplicity, negligible volume of solvents used, high enrichment factor, large pH tolerance range, excellent sample clean-up

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and low cost [18]. In general, most HF-LPME reports performed using stirring to help mass transfer were very slow [19-21]. Ultrasound-assisted hollow fibre liquid–liquid–liquid microextraction was reported by Yu-Ying Chao [22] for the determination of chlorophenols in water samples. However, to the best of our knowledge, ultrasound-mixing has not yet been applied for determination metal ions in environmental samples using hollow-fibre liquid phase microextraction.

In this work, a novel approach, ultrasound-assisted hollow fibre liquid-phase microextraction (UA-HF-LPME) was used for the preconcentration of Cd, Cu, and Cr from environmental samples by FAAS. Ultrasound-mixing was used as an assisted method to accelerate the mass transfer and minimize fluid loss. The factors affecting preconcentration of the metal ions such as sample pH, eluent type and concentration, extraction solvent type and concentration, fibre length, equilibrium time and matrix effects were investigated in detail.

EXPERIMENTAL

Chemicals and reagents

All reagents used were of analytical grade. All solutions were prepared with ultra-high purity (UHP) water from a Milli-Q system (18.2 MΩ cm). Laboratory glassware was kept overnight in 10% HNO_3 solution. Standard stock solutions of metal ions (1000 mg L^{-1}) were prepared by dissolving their nitrate salts in 1 mol L^{-1} HNO_3. The standard working solutions of metal ions were prepared by dilution of their stock solutions. Buffer solutions are CH_3COOH-CH_3COONa (pH =4-6), CH_3COONH_4 (pH=7) and NH_3/NH_4Cl (pH=8-10). 1-octanol, nonanoic acid, caprylic acid, capric acid and 1-undecanol of analytical standard were obtained from Aladdin Chemistry (Shanghai, China).

Instrumentation and materials

A ultrasound instrument was employed for experiments (Shanghai, China) and flame atomic absorption spectrometer (AA-6300C, Shimadzu, Japan) were used for the determination of the concentration of metals. A centrifuge with centrifugal vials (Shanghai surgical instrument factory, 80-2, Shanghai, China) was used for phase separation. A vortex agitator (Kylin-Bell Lab Instruments Co. Ltd., Jiangsu,China) was used for vortex-mixing. The porous hollow fibre used to support the organic phase was Q3/2 polypropylene (Wuppertal, Germany) with 600 lm inner diameter, 200 μm of wall thickness and pores of 0.2μm. A 1.0 mL microsyringe (model 702SNR) with a sharp needle tip was used for the injection of the extraction solvent into the hollow fibre lumen. Instrumental parameters were adjusted according to the manufacturer’s recommendations.

Preparation of hollow fibre and UA-HF-LPME extraction procedure

The hollow fibre was cut into 5 cm length pieces. Before use them, each piece was sonicated for 5 min in acetone in order to remove any contamination in the fibre and then, dried in air. The fibre was soaked in nonanoic acid for 15 s to impregnate the pores, and the lumen of the prepared fibre piece was filled with 15μL nonanoic acid using a microsyringe carefully. Both open ends of the fibre were sealed by a piece of aluminium foil. Then the hollow fibre was bent to a U-shape and immersed in the 5 mL sample solution (pH 5.0, adjusted with CH_3COOH-CH_3COONa buffer solution) containing 10μg mL-1of each metal ion(Cu、Cd、Cr). The sample was ultrasound-mixed for 2 min at room temperature. Then, the fibre was removed from the sample solution, and its closed end was cut. The 0.5mL methanol was injected into one of its end by a microsyringe. Finally the extract was filtered by a 0.45μm membrane and injected into the FAAS system for analyses. A fresh hollow fibre was used for each extraction to decrease the memory effect [23].

Sample Preparation

Well water and wastewater samples were collected from Kunming, China. The samples were filtered through a 0.45 μm membrane filter.

RESULTS AND DISCUSSION

Optimization of the UA-HF-LPME procedure

Several different experimental parameters that can influence the extraction efficiency were investigated in our experiments. The optimization procedure was done as described in UA-HF-LPME procedure.

Selection of organic extraction solvent and eluent

The type of organic solvent used in HF-LPME is an essential consideration for an efficient extraction of target analyte from aqueous solution. Firstly, it should provide high solubility for the target analytes, and should have a low solubility in water. Addition, the ideal organic extraction solvent should have a low volatility and an appropriate viscosity to prevent diffusion and volatile loss.

Compared with the other extractant, long chain alcohols and acids have those particular properties, which have special extraction efficiency for the analytes. Thus, five organic solvents (1-octanol, nonanoic acid, caprylic acid, capric acid, 1-undecanol) with different viscosities, volatilities and partition coefficients were evaluated in this work. As shown in Fig. 1, nonanoic acid was the most suitable extraction solvent as it resulted in the highest response. Nonanoic acid has larger viscosity, less volatility and better compatibility in polarity with metal ions, those characteristics attributed to lower solvent loss during extraction and higher recovery.

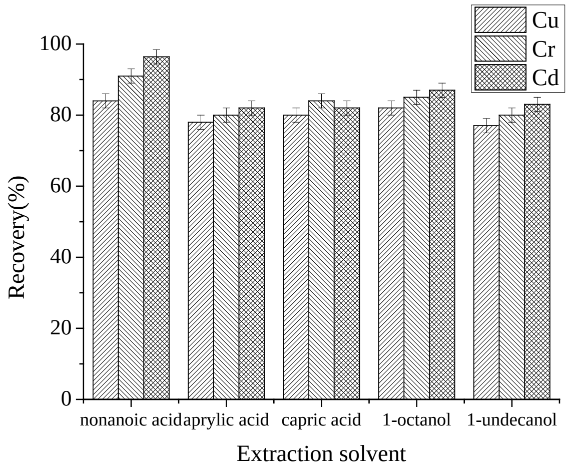

Fig. 1. Effect of extraction solvent on the recovery

The selection of eluent is critical and it affects the extraction efficiency and the enhancement factor. The elution of analytes could be inconvenience owing to irreversible binding of some elements. An appropriate eluent should desorb the metals or chelate complexes and be suitable for the subsequent determination technique. The studied eluents include methanol, ethanol and acetonitrile, The results were shown in Fig. 2, which proved methanol was the best eluent for Cu, Cr and Cd.

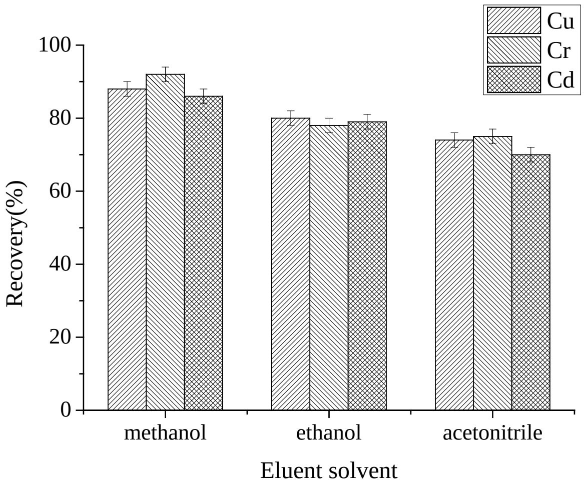

Fig. 2. Effect of eluent solvent on the recovery

Effect of fibre length

In general, a short fibre length will provide a high enrichment factor for the concentration of trace analytes in HF-LPME procedure. However, too short fibre membranes cannot provide sufficient extractant to promote analytes transport to extraction solvent. Thus, the fibre lengths of 2, 4, 5, 6, 8, and 10cm were examined. The results in Fig. 3 indicated that 5 cm was sufficient, and no significant effect was found when the fibre length ranged from 6 to 10 cm. accordingly, an HF length of 5 cm which containing approximately 20μL extraction solvent was selected for the subsequent experiments.

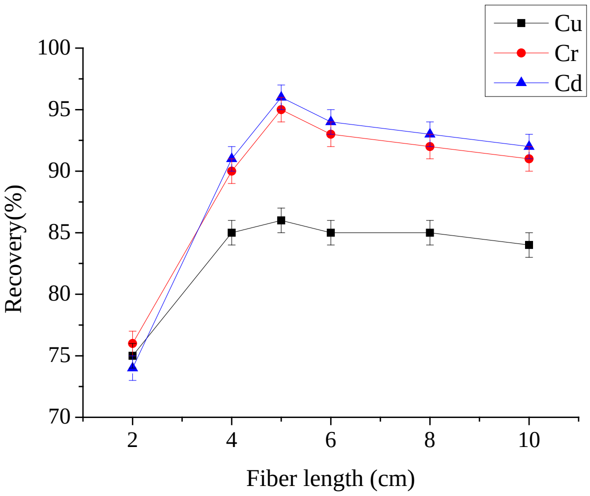

Fig. 3. Effect of fiber length

Effect of pH on UA-HF-LPME

The formation of metal complexes and its chemical stability are the two important effective factors for the HF-LPME and the pH of the sample solution plays a critical role on metal chelate formation and subsequent extraction efficiency. Thus, the effect of pH ranged from 3.0 to 9.0 using acetate buffer solutions for pH adjustment on extraction efficiency of Cr, Cu, and Cd was evaluated and the results are shown in Fig. 4. As can be seen, the optimum pH for Cr, Cu, and Cd maximum extraction efficiency was 5.0. So, in subsequent experiments, pH 5.0 was chosen as the optimum for further experiments.

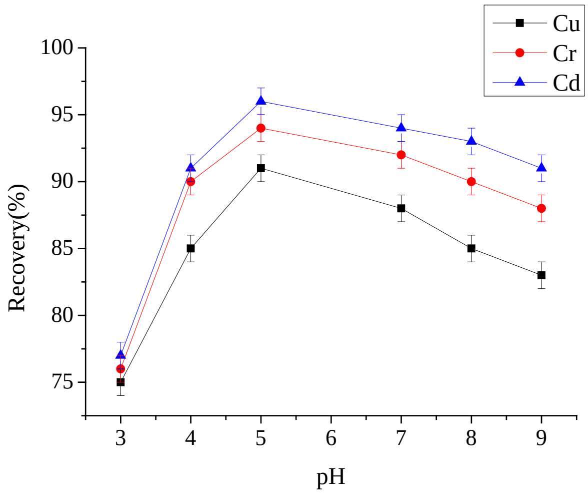

Fig. 4. Effect of pH

Effect of the ultrasound-mixing time

In our study, the extraction can be accelerated by ultrasound-mix of the sample solution. Similar results were observed with ultrasound-mixing times between 1 and 10 min (Fig. 5). Significant effect was observed on the extraction recovery when the ultrasound-mixing time was increased. This may be due to the fact that the analytes were thrown out from fibre membrane because of the high shear forces. Therefore, an ultrasound-mix time of 2 min at 3000 rpm was selected for further experiments.

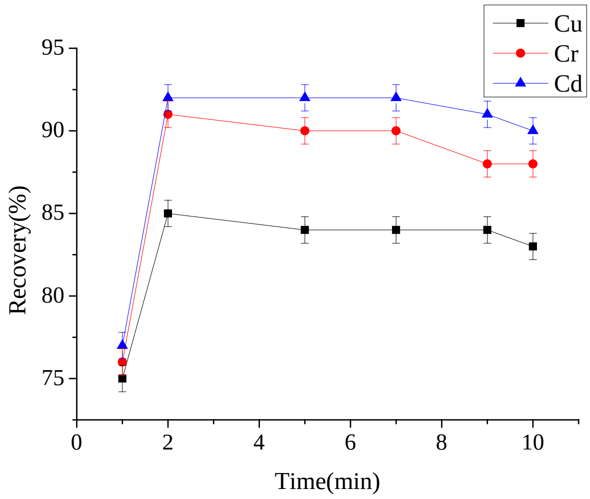

Fig. 5. Effect of the ultrasound-mixing time

Comparison of the proposed method with other reported methods

Table 1 provides a comparison between the proposed method and other reported pretreatment techniques coupled with FAAS from the viewpoint of sample preparation, recovery, extraction time, solvent amount. As listed in Table 1, the analytical performance of this novel extraction is certain advantages and feasibility.

Analytical Figures of Merits

The analytical characteristics of the method were evaluated under the optimum experimental conditions. The relative standard deviations (RSD) and the limits of detection (LOD) are effective factors to evaluate a developed analytical method. With the optimized system, the calibration graph of Cr ,Cu and Cd was linear in the range of 10 to 1,000 µg/L. The calibration equation is $A=2.8 \times 10^{-2}C+0.0031$ with a correlation coefficient of 0.9997 for Cr , $A=3.6 \times 10^{-2}C+0.028$ with a correlation coefficient of 0.9968 for Cd and $A=7.9 \times 10^{-2}C+0.003$ with a correlation coefficient of 0.9999 for Cu, where A is the absorbance and C is the Cu,Cr or Cd concentration in µg/L. The detection limits, defined as the concentration equivalent to three times the standard deviation of the reagent blank, for Cr ,Cu and Cd were 0.28,0.35 and 0.19µg/L, respectively. The relative standard deviations for Cr ,Cu and Cd were 2.0, 2.6 and 1.8% (C=0.5µg/L, n=9). The relative recoveries of Cr ,Cu and Cd in well water and wastewater samples at the spiking level of 10µg/mL ranged from 80.5 to 96.4%.

Analysis of Real Samples

The environmental samples which are Well water and wastewater were analyzed to evaluate the feasibility of the described preconcentration method. The obtained results are shown in Table 2. The obtained values are in good agreement with the certified values. The determination of Cr, Cu and Cd in well water and wastewater samples was made together with the recovery studies. The recoveries for spiked metal ion concentrations were found in a range of 80.5-96.4% which indicate that the method is applicable for the determination of analytes in real samples with various matrices.

CONCLUSION

A novel ultrasound-assisted hollow fibre liquid-phase microextraction (UA-HF-LPME) method has been developed for determination of three metal ions in environmental samples. The target analytes were enriched very quickly into the acceptor phase with continuous ultrasound-mixing instead of stirring. Coupled with flame atomic absorption spectrometry detection, the method has been proven to be simple, rapid, and reliable for metal ions in environmental samples. In future work, it will be extended in separation and preconcentration of different inorganic and organic species.

Table 1. Comparison of the proposed method with other reported methods

Analytes	Method	Recovery (%)	Extraction time (min)	Solvent amount	References
Pd,Ag	SPE		4		[24]
Cu,Ni,Co	SDSPE	80.7-97.5	2	0.5mL	[25]
Cu,Cr,Cd	UA-HF-LPME	80.5-96.4	2	20µL	This work

Table 2. Analysis of metal ions well water and wastewater

Samples	Element	Added (µg L^{-1})	Found (µg L^{-1})	Recovery (%)
Well water	Cu	0	ND	
		5	4.5±0.3	90
		10	8.7±0.2	87.0
	Cr	0	ND	
		5	4.8±0.2	96.0
		10	9.6±0.2	96.0
	Cd	0	ND	
		5	4.2±0.4	84
		10	8.2±0.2	82.0
Waste water	Cu	0	ND	
		5	4.2±0.4	84.0
		10	8.5±0.3	85.0
	Cr	0	ND	
		5	4.8±0.2	96.0
		10	9.6±0.2	96.0
	Cd	0	ND	
		5	4.5±0.3	90.0
		10	8.07±0.2	80.5

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ОПРЕДЕЛЯНЕ НА МЕТАЛНИ ЙОНИ ЧРЕЗ УЛТРАЗВУК-ПОДПОМАГАНА ТЕЧНА-МИКРОЕКСТРАКЦИОННА ТЕХНИКА С КУХИ ВЛАКНА

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(Резюме)

Един нов подход, ултразвук-подпомагана течно-микроекстракционна техника с кухи влакна (UA-HF-LPME) се използва за преконцентриране на мед (Cu), кадмий (Cd) и хром (Cr) от проби от околната среда чрез атомно абсорбционна спектрометрия (FAAS). Методът се основава на екстракция на аналитите от проби на околната среда (фаза донор) в 15 μL на нонанова киселина, поддържана от полипропиленови кухи влакна с порести стени, с ултразвуково смесване. Ултразвуковото смесване се използва като метод за подпомагане и ускоряване на масопреноса и свеждане до минимум на загубата на течност. При оптимални условия, границите на откриване на този метод за Cr, Cu, Cd и са 0.28, 0.35 и 0.19 μg/L съответно, относителните стандартни отклонения за Cr, Cu, Cd са 2.0, 2.6 и 1.8% (C = 0,5 μg/L, n = 9). Относителните нива на регенерирация на Cr, Cu и Cd в проби от кладенчова вода и отпадни води в границите на 10 μg/L варират от 80,5 до 96,4%. Методът се прилага успешно за оценка на съдържанието на тези метали в проби от околната среда със задоволителни резултати и високи фактори на обогатяване (200).