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Separation and preconcentration system based on ultrasonic probe-assisted ionic liquid dispersive liquid–liquid microextraction for determination trace amount of chromium(VI) by electrothermal atomic absorption spectrometry

Hao Chen[a], Ping Du[a], Jie Chen[b], Shenghua Hu[b], Shengqing Li[a,c,*], Hanlan Liu[a]

[a] Department of Chemistry, College of Science, Huazhong Agricultural University, Wuhan 430070, China
[b] Narcotics Control Department of Wuhan Municipal Public Security Bureau, Wuhan 430014, China
[c] The Supervision, Inspection & Testing Center of Microbial Products Quality (Wuhan), Ministry of Agriculture, China

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ABSTRACT

A novel method of ultrasonic probe-assisted ionic liquid dispersive liquid–liquid microextraction combined with electrothermal atomic absorption spectrometry (ETAAS) was developed for the determination of chromium(VI) species in water samples. In this procedure, the hydrophobic chelate of chromium(VI) with ammonium pyrrolidinedithiocarbamate (APDC) was extracted into the fine droplets of 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF_6]), which was dispersed into the aqueous sample solution by ultrasonication using an ultrasonic probe. Several variables such as the volume of [Hmim][PF_6], sample pH, concentration of APDC, and extraction time were investigated in detail. Under the optimum conditions, the limit of detection of the proposed method was 0.07 ng mL^{-1} for Cr(VI) and the relative standard deviation for five-replicated determination of 2.0 ng mL^{-1} Cr(VI) was 9.2%. The proposed method has been also successfully applied to the determination of chromium(VI) species in lake and tap water samples.

1. Introduction

Chromium species exist mainly in two oxidation states in the environment, Cr(III) and Cr(VI), which have contrasting physiological effects [1]. Chromium(III) is essential to normal carbohydrate, lipid and protein metabolism. In contrast, chromium(VI) can induce carcinogenesis because of its possibility to cross biological membranes easily and react with protein components and nucleic acids inside the cell [2]. The US Environmental Protection Agency (EPA) recommends that the concentration of Cr(VI) in drinking water should be less than 0.1 μg mL^{-1}. Thus, it is crucially important to determine the species of Cr(VI) in environmental sample.

Separation and preconcentration steps are often required before the determination of trace or ultra-trace chromium species in water samples. Although the conventional liquid–liquid extraction [3] was still employed herein, new techniques such as solid phase microextraction [4], liquid phase microextraction [5,6] and cloud point extraction [2,7–8] are well known for this purpose. These techniques have advantages of simple procedure, high extraction efficiency and low consumption of toxic organic solvents.

A new procedure termed as dispersive liquid–liquid microextraction (DLLME) has received much attention for sample pretreatment after 2006 [9]. There are many reports about the application of DLLME for the analysis of organic compounds. It has also been successfully applied to the analysis of inorganic Cd [10], Pb [11,12,13], Co [14,15,16], Ni [15], Cu [13,17], Pd [14], Au [18], Se [19], As(III) and Sb(III) [20] in water or biological samples. Most recently, DLLME has been conducted to the speciation analysis of chromium [21], As(III) and As(V) [22], butyltin and phenyltin [23] in water samples. High enrichment factors of 275 and low detection limit of 0.07 ng mL^{-1} for Cr(VI) were reported, applying the method of DLLME combined with microsample introduction-flame atomic absorption spectrometry to the preconcentration and determination of Cr(VI) in 25 mL sample solution [21].

Ionic liquids (ILs) are considered as environmentally benign replacements for traditional organic solvents for their unique chemical and physical properties as negligible vapor pressure, tunable viscosity and miscibility with water and organic solvents. They have gained high interest in analytical chemistry as reviewed by Liu et al. [24]. Several methods of ionic liquid-based microextraction have been developed for the determination of Pb [25,26], Mn [27], Hg [28–31], Cd [32], Zn [33], V [34], Co [35], and some lanthanoids

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* Corresponding author at: Department of Chemistry, College of Science, Huazhong Agricultural University, 1 Shizishan St., Hongshan District, Wuhan 430070, China. Tel.: +86 027 87287442; fax: +86 027 87287442.
E-mail address: sqingli@mail.hzau.edu.cn (S. Li).

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Table 1
Operating condition for ETAAS.

Parameters	
Element	Cr
Wavelength (nm)	357.9
Slit (nm)	0.4
Current (mA)	3.0
Dry temperature (°C)	100 (ramp 20 s, hold 10 s)
Ashing temperature (°C)	1000 (ramp 10 s, hold 30 s)
Atomization temperature (°C)	2300 (ramp 0 s, hold 4 s)
Cleaning temperature (°C)	2400 (ramp 1 s, hold 1 s)
Sampling volume (μL)	2

[36]. We have developed a new method of ultrasound-assisted ionic liquid-based dispersive liquid–liquid microextraction for the preconcentration of Cd in water samples prior to the ETAAS detection [37]. The proposed procedure employed an ultrasonic probe to accelerate the formation of a cloudy dispersive extraction mixture within 1 min and did not need any dispersive organic solvent comparing with the normal DLLME.

The aim of the present work was to combine the ultrasonic probe-assisted ionic liquid-based DLLME with ETAAS for the determination of chromium(VI) in water samples. The possible affecting factors such as the volume of $[Hmim][PF_6]$, sample pH, concentration of complexing reagent, extraction time and salt effect were studied.

2. Experimental

2.1. Apparatus

A TAS-986 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., China) with a deuterium background correction was used for the determination of chromium. The operating conditions for ETAAS are given in Table 1. Fine droplets of ionic liquid were made by JYD150 ultrasonic cell disruptor (Shanghai Touching Science & Technology Co. Ltd., China). A TG-16 centrifuge (Gongyi City Yuhua Instrument Co. Ltd., China) was used to accelerate the phase separation. The pH values were measured with a PHS-3C pH meter (Shanghai precision & Scientific Instrument Co. Ltd., China) supplied with a combined glass electrode.

2.2. Standard solutions and reagents

Stock standard solutions of $1.0\,mg\,mL^{-1}$ Cr(VI) and Cr(III) were prepared by dissolving corresponding $K_2Cr_2O_7$ and $Cr(NO_3)_3$ (Sinopharm Chemical Reagent Limited Company, China) in ultra pure water. The ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate ($[Hmim][PF_6]$), was purchased from Shanghai Chengjie Chemical Co., Ltd. Solution of ammonium pyrrolidinedithiocarbamate (APDC, 4%, m/v) was prepared every day by dissolving 0.08 g of APDC (Shanghai Reagent Factory, China) in 2.0 mL ultra pure water. The pH values were adjusted by addition of $0.1\,mol\,L^{-1}$ ammonia or hydrochloric solutions before used. Other reagents used in this work were all of analytical reagent grade and ultra pure water (18.2 MΩ cm) prepared by Purelab ultrapure water system (ELGA Purelab, UK) was used throughout. The pipettes and vessels used were kept in 20% (v/v) nitric acid for at least 24 h and then washed with ultra pure water.

2.3. Analytical procedure

An 8.0 mL of ultra pure water containing $5.0\,ng\,mL^{-1}$ of chromium(VI) was placed in a screw cap glass conical tube and 10 μL of 4% (m/v) APDC solution was added. After 50 μL of $[Hmim][PF_6]$ was added, the mixed solution was vibrated by the ultrasonic probe at 45 W for 1 min. A cloudy solution formed and the test tube was immersed in ice water for 10 min. During this stage, the hydrophobic chelate of Cr(VI) was extracted into the fine droplets of $[Hmim][PF_6]$. Then the mixture was centrifuged at 6000 rpm for 5 min to achieve phase separation. After this step about 4 μL of the $[Hmim][PF_6]$ were sedimented at the conical bottom of the test tube. Two microlitres of this sedimented phase was removed using a 10 μL microsyringe and injected directly into the graphite tube for analysis. The absorbance of chromium was recorded, and the peak height was measured for quantification.

2.4. Sample preparation

Tap water from our laboratory and lake water from South Lake (Wuhan, China) were collected for this work. The water samples were filtered through a 0.45 μm micro-pore membrane before use and stored in dark at 4°C.

3. Results and discussion

3.1. Optimization of ultrasonic probe-assisted ionic liquid DLLME

3.1.1. Effect of [Hmim $[PF_6]$ volume

During the ionic liquid-based DLLME process, IL volume is a critical factor to obtain a high volume ratio of the phases. Enrichment factor was used to assess the effect of IL volume on the microextraction. It was defined as the ratio of concentration of Cr(VI) in sedimented IL phase to initial concentration of Cr(VI) in the aqueous sample. The volume of $[Hmim][PF_6]$ on the enrichment factor was studied and the results were shown in Fig. 1. When the initial volume of $[Hmim][PF_6]$ increased from 50 to 80 μL added to the 8.0 mL aqueous sample, the sedimented volume of IL phase increased from 4 to 28 μL. The enrichment factor declined as the phase ratio of acceptor-to-donor increasing although the extraction efficiency enhanced with this change. Subsequently, high enrichment factor would be obtained at low volume of the extraction solvent so as the sedimented amount of $[Hmim][PF_6]$ satisfies the sampling volume of ETAAS. Thereby, the initial volume of 50 μL for $[Hmim][PF_6]$ was adopted in the following experiments.

3.1.2. Effect of ultrasonication, cooling and centrifugation time

In the process of ultrasonic probe-assisted ionic liquid dispersive liquid–liquid microextraction, mass-transfer takes place in all of the ultrasound-assisted dispersing, cooling and centrifuging

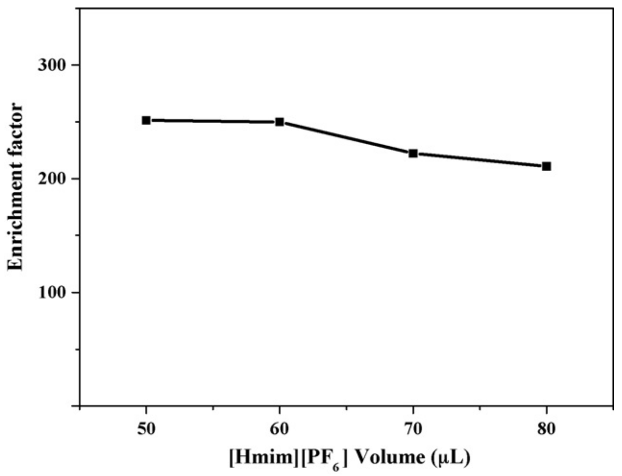

Fig. 1. Effect of IL volume on the enrichment factor. Extraction conditions: 8.0 mL of $5.0\,ng\,mL^{-1}$ Cr(VI) solution, pH 6.0; 0.005% (m/v) APDC.

steps. The effect of time on the dispersion of ionic liquid and phase separation was investigated in respect to obtaining high extraction efficiency.

The time of ultrasonication plays an important role in the dispersion, which affects the extraction efficiency of the analytes. An ultrasonic probe was immersed into the mixture of sample solution and extraction solvents in this experiment. During the ultrasonication, the solution became turbid due to the dispersion of fine solvent droplets of [Hmim][PF_6] into the aqueous phase. Enough time will make the ionic liquid dispersed well and favor the mass-transfer process of the analytes from the aqueous bulk to the IL droplets. However, too long time may increase the temperature of the solution in the test tube. It was found that 1 min was enough for the dispersing step.

Dependence of enrichment factor upon cooling time was studied within a range of 1–30 min. It took about 5–6 min to form an intensively cloudy mixture in the test tube. The results displayed that after the formation of the cloudy solution, the cooling time had no notable effect on the enrichment factor. It indicated that the cooling time of 10 min was adequate to achieve good transfer of Cr(VI) complex from the aqueous phase to the IL droplets.

The effect of centrifugation time on analytical signal was tested in a range of 2–10 min. The obtained results show that, over 5 min, analytical signal was constant indicating complete centrifugation of IL droplets to the conical bottom of the test tube. So, a centrifugation time of 5 min at 6000 rpm was selected for subsequent experiments.

3.1.3. *Effect of the pH*

The pH value of the aqueous solution is a crucial factor for a hydrophobic complex formation and its transfer from the aqueous phase to the extraction solvents and was studied in the pH range of 1–8. It can be seen from Fig. 2 that the signal of Cr(VI) achieved maximum at the value of 5–6, while that of Cr(III) was negligible in the whole range of pH values tested. This difference makes it possible to separate Cr(VI) from the sample solution through the ultrasound-assisted [Hmim][PF_6]-based DLLME. Careful control of 6.0 was carried out for this purpose in the following experiments.

3.1.4. *Effect of APDC concentration*

Ammonium pyrrolidinedithiocarbamate (APDC) reacts with Cr(VI) much faster than with Cr(III) at room temperature because it is difficult to displace the Cr(III)-coordinated water molecules in the aqueous phase by the dithiocarbamate ligand [38]. Results of former experiments showed that 5 min was enough for complete formation of Cr(VI)–APDC complex. In this experiment, this reaction occurred together with mass-transfer during the ultrasonication (1 min) and cooling (10 min) stages. The effect of APDC concentration upon the absorbance signal of Cr(VI) was optimized. The maximum absorbance was obtained in the range of 0.005–0.08% (m/v) APDC according to Fig. 3. Therefore, 0.005% (m/v) of APDC was selected in the procedure of ultrasonic probe-assisted ionic liquid DLLME.

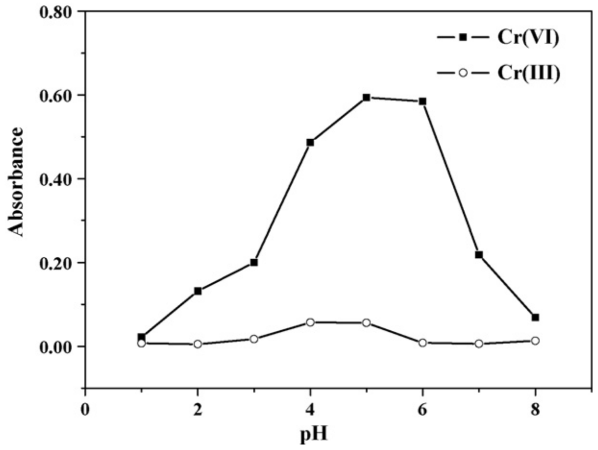

Fig. 2. Effect of pH on the absorbance of Cr(VI) and Cr(III). Extraction conditions: 8.0 mL of sample solution; Cr(VI) and Cr(III), 5.0 ng mL^{-1}; 0.005% (m/v) APDC; 50 μL of [Hmim][PF_6].

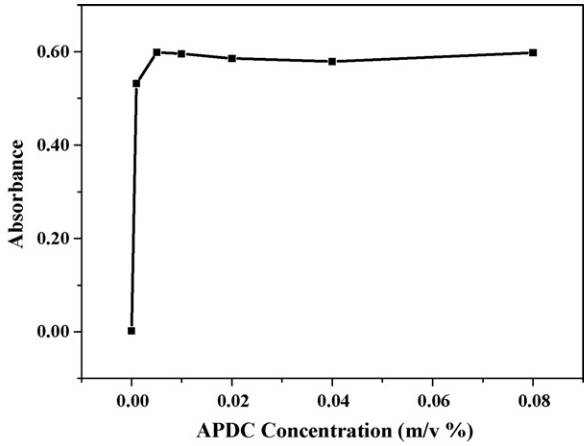

Fig. 3. Effect of APDC on the absorbance of Cr(VI). Extraction conditions: 8.0 mL of 5.0 ng mL^{-1} Cr(VI) solution, pH 6.0; 50 μL of [Hmim][PF_6].

3.1.5. *Effects of salt and coexisting ions*

The influence of ionic strength was examined by studying the absorbance in the presence of known concentration of NaCl and the rest of the experimental conditions were kept constant. The obtained results showed that the overall process was not affected significantly by salt as the concentration of NaCl up to 5% (m/v).

The possible interferences of common coexisting ions on the determination of Cr(VI) were investigated to demonstrate the selectivity of the developed method of ultrasonic probe-assisted ionic liquid DLLME. In these experiments, solutions of 5.0 ng mL^{-1} of Cr(VI) containing the added coexisting ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount causing a change in the absorbance of Cr(VI) no higher than 5%, are given in Table 2. The results showed good tolerance of coexisting ions studied in water samples. It stated that the developed method was applicable to the analysis of Cr(VI) in some environmental water samples as shown later.

3.2. *Analytical figures of merit*

The analytical characteristics of the method were evaluated under the optimum experimental conditions and Table 3 shows them. The calibration graph, obtained by implementing the proposed method with a series of Cr(VI) standard solutions ranged in 0.5–8.0 ng mL^{-1}, was linear with a correlation coefficient (R^2) of 0.9991. The regression equation was $A = 0.1192C + 0.002$, where A

Table 2
Tolerance limits of coexisting ions in the determination of Cr(VI) (5.0 ng mL^{-1}).

Coexisting ions	Foreign ion to Cr ratio
K^+, Na^+	40,000
Ca^{2+}, Mg^{2+}	4000
Pb^{2+}	200
Mn^{2+}, Zn^{2+}, Fe^{3+}	100
Cu^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+}, Al^{3+}	50

Table 3
Analytical characteristics of proposed method for determination Cr(VI).

Parameter	Analytical feature
Linear range (ng mL^{-1})	0.5–8.0
Regression equation	$A = 0.1192C + 0.002$
R^2	0.9991
Limit of detection (ng mL^{-1}) (3σ, $n = 5$)	0.07
RSD (%) ($n = 5$, 2.0 ng mL^{-1})	9.2
Enrichment factor[a]	300

[a] Calculated as the slope ratio of two calibration curves for Cr(VI) with and without preconcentration.

Table 4
Determination of Cr(VI) in water samples (mean ± S.D., $n = 3$).

Samples	Added (ng mL^{-1})	Founded (ng mL^{-1})	Recovery (%)
Lake water	–	1.44 ± 0.09	–
	0.5	1.92 ± 0.04	96
	5.0	5.24 ± 0.27	102
Tap water	–	nd[a]	–
	0.5	0.49 ± 0.05	98
	5.0	5.10 ± 0.19	100

[a] Not detected.

is the absorbance and C is the concentration of Cr(VI) in ng mL^{-1}. The limit of detection, calculated as the concentration of absolute amount of analyte yielding a signal equivalent to three times the standard deviation of the blank signal ($n = 5$), in accordance with IUPAC recommendation, was 0.07 ng mL^{-1} for the determination of chromium(VI) in 8 mL of sample solution. The relative standard deviation (RSD) for five-replicate measurement of 2.0 ng mL^{-1} Cr(VI) was 9.2%. And the enrichment factor, if it was assessed from the slope ratio of calibration graph after and before ultrasonic probe-assisted ionic liquid DLLME, was obtained as high as 300 for the analysis of 8.0 mL water sample.

3.3. *Water sample analysis*

Ultrasonic probe-assisted ionic liquid DLLME combined with ETAAS was applied to the determination of Cr(VI) in South Lake water (Wuhan, China) and tap water. The recovery experiments were carried out order to validate the accuracy of the proposed procedure. The results were given in Table 4. As could be seen, the recoveries of Cr(VI) for the three spiked samples were in the range of 96–102%. The results demonstrated that the proposed method was suitable for the determination of Cr(VI) in real water samples.

4. Conclusions

A novel method of ultrasonic probe-assisted ionic liquid ultrasound-assisted dispersive liquid–liquid microextraction combined with ETAAS, using [Hmim][PF$_6$] as the only extraction solvent, is described for the determination of Cr(VI) in water samples. The presented method employs an ultrasonic probe-based sonication to accelerate the dispersion of IL droplets and mass-transfer of Cr-APDC complex from the aqueous phase to the extraction solvents. It is no need of dispersive solvent comparing with normal DLLME. In addition, it has low limit of detection for Cr(VI) (0.07 ng mL^{-1}) and high enrichment factor for the analysis of small volume (8.0 mL) of water samples.

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