

Simultaneous preconcentration of cadmium and chromium(III) in water samples by cloud point extraction and their determination by flame atomic absorption spectrometry

Lifen Meng, Jinyan Ning and Yaling Yang

ABSTRACT

A sensitive and simple method for flame atomic absorption spectrometry determination of traces of cadmium and chromium(III) species in water samples after preconcentration by cloud point extraction has been developed. A novel complex agent of alizarin complexone with cadmium (Cd) and chromium (Cr(III)) was quantitatively extracted in surface primary alcohol ethoxylate-rich phase at 33 °C. The effects of experimental conditions including pH of sample solution, concentration of chelating agent and salt, equilibration temperature and time, and foreign ions were evaluated in order to enhance sensitivity of the method. Under optimal conditions, the low limit detections were 6.7 and 3.2 µg/L, and the enrichment factors were 24 and 20 for Cd and Cr(III), respectively. The relative standard deviations were 3.8 and 2.5% for Cd and Cr(III), respectively ($n = 11$). The high recoveries of the spiked Cd and Cr(III) ions were obtained in the range of 90–116%. The proposed method has been successfully applied for the determination of Cd and Cr(III) in water samples.

Key words | alizarin complexone, cadmium, chromium(III), cloud point extraction, flame atomic absorption spectrometry, primary alcohol ethoxylate

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INTRODUCTION

Chromium occurs naturally in the Earth's crust, but its extensive use in various industrial processes and products has led to widespread chromium contamination in the environment (Sarkar *et al.* 2006; Zhang *et al.* 2009). It is well known that the toxicological as well as the biological properties of the element chromium depend strongly on its chemical forms (Hashemi & Daryanavard 2012). Cadmium is classified as a prevalent toxic element with a biological half-life in the range of 10–30 years, and is known to damage organs such as kidneys, liver and lungs, even at a very low concentration level (Davis *et al.* 2006; Wen *et al.* 2009). Therefore, an accurate and reliable method should be applied for the determination of chromium and cadmium species. Different approaches have been reported for the speciation analysis of Cr(III) and Cd. These include the combination of powerful separation techniques such as flame atomic absorption spectrometry (FAAS) (Narin *et al.* 2008), inductively coupled plasma atomic emission spectrometry (Liang *et al.* 2006), inductively coupled plasma optical emission spectrometry (Menegario *et al.* 2005),

inductively coupled plasma-mass spectrometry (Rahman *et al.* 2005), UV-visible spectrophotometry (Wen *et al.* 2011), electrothermal atomic-absorption spectrometry (Zhu *et al.* 2005), electrochemical fluorometry (Hosseini & Belador 2009) and chemiluminescence (Yang *et al.* 2003).

Development of a new preconcentration procedure is essential. Various preconcentration methods prior to FAAS or graphite furnace atomic absorption spectrometry have been developed, including ion exchange, membrane filtration, solid phase extraction, single-drop microextraction (Jiang & Lee 2004), solvent bar microextraction (Xia *et al.* 2004; Fan & Zhou 2006), hollow fiber liquid-phase microextraction, cloud point extraction (CPE) (Wu *et al.* 2008) and liquid-liquid extraction (Rezaee *et al.* 2006; Luconi *et al.* 2006; Singh *et al.* 2007; Li & Zhai 2008; Zhou *et al.* 2011). CPE is an alternative separation technique based on the phase behavior of non-ionic and ionic surfactants in aqueous solutions, which show phase separation after an increase in temperature or a salting-out agent (Lindqvist 1995). Above the cloud point (CP), the micellar solution

separates into a surfactant-rich phase with a small volume and a diluted aqueous phase (Ghaedi *et al.* 2009). To date, CPE has been widely used for extracting heavy metal ions with FAAS (Doroschuk *et al.* 2004).

So far, non-ionic surfactants, such as the Triton X series (Ohashi *et al.* 2005, 2007; Purkait *et al.* 2005; Mustafina *et al.* 2006; Wu *et al.* 2007), PONPE series and Igepal series (Mustafina *et al.* 2006; Shen & Shao 2006), are the most widely used surfactants for CPE. These surfactants have been successfully applied to extract metal ions (Moran *et al.* 2000; Tang *et al.* 2004). However, in the European Union, environmentally unfriendly surfactants with an aromatic group, which have poor biodegradability, are forbidden (Chen *et al.* 2012). Therefore, using a surfactant which reduces pollution to the environment is considered a better way to complete the CPE procedure.

AEO-9 is a primary alcohol ethoxylate, a non-ionic surfactant, with no aromatic group, which has low viscosity, lower CP, low skin irritation, is odorless, has excellent biodegradability and is environmentally friendly. Its unreacted alcohol content is very low. From the commercial information the CP for AEO-9 is in the range 50–83 °C. However, it was found that salting-out electrolytes lowered the CP of non-ionic surfactant AEO-9 due to the dehydration and then the precipitation of surfactant molecules; in this work, (NH₄)₂SO₄ decreased the CP of AEO-9 solution. Hence its CP is about 33 °C. To our knowledge, AEO-9 has never been applied in CPE for the determination of metal ions.

In this research, the CPE coupled with FAAS was applied for preconcentration and determination of trace amounts of chromium and cadmium. Alizarin complexone (AC) was selected as the chelating agent and AEO-9 as surfactant. The parameters influencing CPE were investigated in detail. The method was successfully applied to the analysis of chromium and cadmium in water samples.

MATERIALS AND METHODS

A vortex instrument was employed for the CP experiments (Shanghai, China) and a flame atomic absorption spectrometer (AA-6300C, Shimadzu, Japan) was used to determine the concentration of metal. A centrifuge (Shanghai, China) was used to complete the phase separation process.

All the reagents used were of analytical reagent grade and all solutions were prepared in deionized water. A stock standard solution of chromium and cadmium at a

concentration of 1,000 µg/mL was obtained from the National Institute of Standards (Beijing, China). AEO-9, ammonium sulfate and AC (Aladdin, China) were used.

Acetate buffer solutions (CH₃COO⁻/CH₃COOH) were prepared by mixing appropriate volumes of 1 M acetic acid and 1 M sodium acetate solutions for pH 3.0. Phosphate buffer solutions (H₂PO₄⁻/HPO₄²⁻) were prepared by mixing appropriate volumes of 1 M sodium dihydrogen phosphate and 1 M sodium hydrogen phosphate at pH 7.0. Ammonium buffer solutions were prepared by mixing appropriate amounts of 1 M ammonia and 1 M ammonium chloride solutions at pH 9.0.

General procedure

For the CPE experiments, 10 mL of aqueous solution containing 10 µg/mL of Cr(III) and Cd ions (pH = 7.0), 5.0 µg/mL AC (500 µL), 100 µL AEO-9 and 0.5 g (NH₄)₂SO₄ were placed in a 10 mL screw cap glass centrifuge tube with a conical bottom. Then, the glass centrifuge tube was vortex mixed for 1 min. Afterwards, the glass centrifuge tube was put in a water-bath at 33 °C for 5 min. The cloudy solution was separated by centrifugation at 3,000 rpm for 10 min. After phase separation, the aqueous phase was then removed from the centrifuge tube by a syringe. The surfactant-rich phase was diluted with deionized water to 2.0 mL and then the analyte contents were determined by FAAS.

RESULTS AND DISCUSSION

Effect of pH on CPE

The formation of metal complexes and their chemical stability are the two important effective factors for the CPE, and the pH of the sample solution plays a critical role in metal chelate formation and subsequent extraction efficiency. Thus, the effect of pH ranging from 3.0 to 9.0, using acetate buffer solutions for pH adjustment, on extraction efficiency of Cr(III) and Cd, was evaluated and the results are shown in Figure 1. As can be seen, the optimum pH for Cr(III) and Cd maximum extraction efficiency was 7.0. So, pH 7.0 was chosen as the optimum for further experiments.

Effect of the AC concentration on CPE

The effect of AC concentration in the range of 1.5 to 10.0 µg/mL was investigated while the other experimental variables

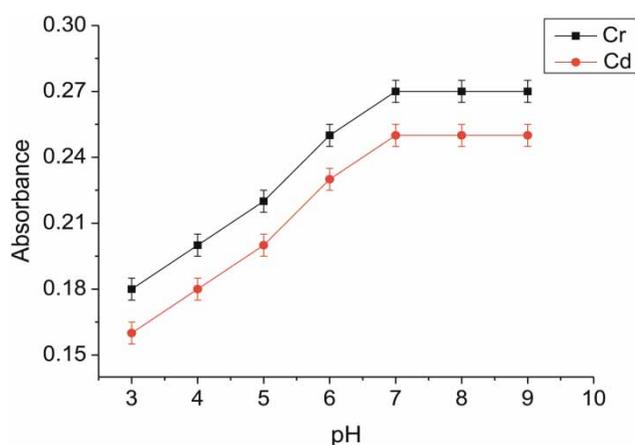


Figure 1 | Effect of pH on the CPE; sample volume, 10 mL; equilibration temperature, 33 °C; equilibration time, 5 min; pH, 7.0; ligand, AC 5.0 µg/mL.

remained constant. The results are illustrated in Figure 2. It can be seen that with an increase in AC concentration, the absorbance increases and a maximum is obtained after the AC concentration approaches 5.0 µg/mL and remains constant up to 10.0 µg/mL. Therefore, 5.0 µg/mL AC concentration was employed for further experiments.

Effect of temperature and time on CPE

It is important to use the shortest equilibration time and the lowest temperature for the extraction and separation of phases. The equilibration temperature and time for recovery were in the range of 30–45 °C and 5–10 min. The maximum extraction recovery was obtained at 33 °C for 5 min. Therefore, 33 °C and 5 min were selected for further experiments.

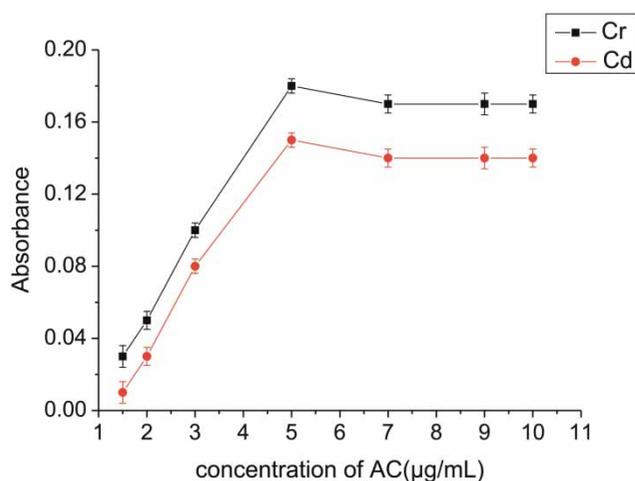


Figure 2 | Effect of AC concentration on CPE; sample volume, 10 mL; equilibration temperature, 33 °C; equilibration time, 5 min; pH, 7.0; ligand, AC 5.0 µg/mL.

Effects of foreign ions

The effects of representative potential interfering species were tested. The tolerance limits of the co-existing ions, defined as the largest amount making a change to the recovery of Cr(III) and Cd ions $\pm 5\%$, are given in Table 1. They show that the recovery is quantitative and satisfactory in the presence of most foreign cations, and the major cations in the water samples have no obvious influence on CPE of Cr(III) and Cd ions under the selected conditions.

Analytical characteristics

The analytical characteristics of the method were evaluated under optimum conditions. The enrichment factor (EF), relative standard deviations (RSDs) and limits of detection are factors to evaluate a developed analytical method (Table 2). With the optimized system, the calibration graph of Cr(III) and Cd was linear in the range of 10–500 µg/L. The calibration equation is $A = 6.5 \times 10^{-3} C + 0.0016$ with

Table 1 | Effects of the matrix ions on extraction efficiency of the Cr(III) and Cd ions

Ions	Molar ratio (ions)		Recovery (%)	
	Cr(III)	Cd	Cr(III)	Cd
K ⁺	1,000	800	98.4	95.4
Ba ²⁺	1,000	1,000	96.5	99.8
Co ²⁺	800	1,000	101.5	99.0
Na ⁺	800	1,000	103.5	100.1
Zn ²⁺	1,000	500	102.9	108.7
Fe ³⁺	1,000	500	98.9	103.4
Cl ⁻	800	1,000	95.6	93.5
NO ₃ ⁻	500	800	97.8	92.9
SO ₄ ²⁻	200	800	99.7	98.5

Table 2 | Performance of the presented CPE method

Parameter	Optimum value	
	Cr(III)	Cd
Recovery (%)	90–116	90–116
EF	24	20
Linear range (µg/L)	10–500	10–500
RSD (%)	3.8	2.5
Limit of detection (µg/L) (<i>n</i> = 11)	6.7	3.2

a correlation coefficient of 0.9983 and $A = 4.3 \times 10^{-3} C + 0.0014$ with a correlation coefficient of 0.9992 for Cr(III) and Cd, respectively, where A is the absorbance and C is the Cr and Cd concentration in $\mu\text{g/L}$. The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 11$) of the reagent blank, for Cr and Cd were 6.7 and 3.2 $\mu\text{g/L}$ respectively. The relative standard deviations for Cr and Cd were 3.8% and 2.5% respectively ($n = 11$). The relative recoveries of the spiked Cr(III) and Cd ions were in the range of 90–116%. The enhancement factor, defined as the ratio of the slope of pre-concentrated samples to that obtained without preconcentration, were 24 and 20 for Cr and Cd, respectively.

Table 3 | Determination of Cr(III) and Cd in water samples

Sample	Metal amount ($\mu\text{g/L}$)		Recovery (%)
	Added	Found	
River water			
Cr(III)	0.0	not detected	–
	10.0	9.7 ± 0.2	97.0
	20.0	19.8 ± 0.3	99.0
Cd	0.0	not detected	–
	10.0	9.8 ± 0.2	98.0
	20.0	21.5 ± 0.3	107.5
Tap water			
Cr(III)	0.0	not detected	–
	10.0	9.6 ± 0.2	96.0
	20.0	21.5 ± 0.3	107.5
Cd	0.0	not detected	–
	10.0	9.9 ± 0.3	99
	20.0	19.7 ± 0.2	98.5

Table 4 | Comparison of AEO-9 with other reported surfactants

Surfactants	Sample volume (mL)	Element	Preconcentration time (min)	RSD (%) ($n = 9$)	Low limit detection ($\mu\text{g/L}$)	Reference
TritonX-114	10	Cr(III)	>15	2.7	7.5	Wang et al. (2010)
	10	Cd	30	2.0	4.3	Bosch Ojeda et al. (2010)
CTAB	10	Cr(III)	12	2.2	12	Hashemi & Daryanavard (2012)
TritonX-100	10	Cr(III)	>15	2.1	6.5	Zhu et al. (2004)
TMN-6	5	Cr(III)	10	4.2	2.9	Sun & Liang (2008)
AEO-9	10	Cr(III)	5	3.8	6.7	This paper
		Cd	5	2.5	3.2	

Applications of the presented procedure

Under the recommended experimental conditions, the proposed method was applied for the determination of Cr(III) and Cd in environmental samples, which were from the Luolong River. All the water samples were spiked with Cr(III) and Cd standard solutions at different concentration levels to assess the matrix effects. Non-spiked samples were also sampled. The results are shown in Table 3. This shows that the developed method applied to determine Cr(III) and Cd in water samples is feasible.

Comparison with other methods

Table 4 compares the characteristic data of the AEO-9 with other reported reagents for the determination of Cr(III) and Cd in the literature. As can be seen, the proposed method possesses a lower limit of detection and preconcentration time than most reported reagents with 10 mL of the sample solution and is suitable to determine trace amounts of Cr(III) and Cd in water samples. The type of samples and matrix does not affect the determination of Cr(III) and Cd.

CONCLUSION

The methodology of chromium and cadmium determination in water samples has been demonstrated based on CPE of Cr(III) and Cd with AC in the presence of the surfactant AEO-9 and sequential determination by FAAS. The developed method is characterized by simplicity, selectivity, safety, low cost and high preconcentration factor, because of the distinct and advantageous features of CPE. The proposed method has been successfully employed for the determination of Cr(III) and Cd in water samples collected

from the Luolong River, with low detection limit, good accuracy and precision.

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