

## Determination of Cr in water and sediment of Haidian Creek by cloud point extraction-flame atomic absorption spectrometry

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### ABSTRACT

A new method using cloud point extraction-flame atomic absorption spectrometry was established by using ammonium pyrrolidine dithiocarbamate as a chelating agent and the cloud point phenomenon of a complexed anion-non-ionic surfactant mixture (Sodium dodecyl sulfate-Triton X-114 mixture). It was used for determining the morphology of chromium in the water and sediments of Haidian Creek. The experimental conditions inorganic electrolytes, pH of a solution, dosage of reagent, the temperature of a water bath, and heating time were optimized according to their effect on the determination of absorbance. The interference of common coexisting ions is discussed. The results show that under the optimized conditions, the standard curve for Cr(III) and Cr(VI) were both linear in the range of  $0-9 \times 10^{-3}$   $\mu\text{g/L}$ . The detection limits for Cr(III) and Cr(VI) were 2.3 and 2.7  $\mu\text{g/L}$ , the correlation coefficients of the standard curve were 0.9904 and 0.9911, and the relative standard deviations were 3.7% and 4.5% ( $C = 0.04$   $\mu\text{g/mL}$ ,  $n = 11$ ), respectively. Compared with the common coexisting ions,  $\text{Fe}^{3+}$  produced greater interference that cannot be neglected. A hybrid masking agent was prepared by mixing diethyltriaminepentaacetic acid and 30% triethanolamine solution at 1:25 ratio and then used in experiments. It could mask the interference of  $\text{Fe}^{3+}$  in the samples. The proposed method was successfully applied in the determination of chromium in water and sediment samples collected from Haidian Creek. It had recovery rates of 86%–98% and 90%–104% for Cr(VI) and Cr(III) respectively, and it gave satisfactory results.

*Keywords:* Cloud point extraction; Surfactant compounding; Chromium form; Flame atomic absorption spectrometry

### 1. Introduction

Atomic absorption spectrometry [graphite furnace atomic absorption spectrometry (GFAAS) and flame atomic absorption spectrometry (FAAS)] has become the main method for determining the content of trace heavy metals [1]. Compared with GFAAS, FAAS has higher precision and stability, as well as lower cost, but it lacks sensitivity, and its detection limits can reach only mg/L levels [2]. During the determination of trace heavy metals in environmental samples, the detection limits often need to be at  $\mu\text{g/L}$  level or

lower. Here, however, the interference of the sample matrix is greater. The toxicity and harm caused by heavy metals are not only related to their content, but they also depend on the element morphology, which requires the morphological analysis of heavy metal elements. These have limited the application of FAAS in the real-sample analysis [3].

Cloud point extraction (CPE) is a new liquid-liquid extraction technique that has emerged in recent years. It does not use volatile organic solvents and it does not affect the environment [4]. It has many advantages such as environmental protection, safety, easy procedure, and the ease of using instruments simultaneously, which have attracted

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the attention of the majority of analysts. It has been successfully applied in the separation and enrichment of trace heavy metals and in the morphological analysis [5,6]. As an important method of separation and pre-concentration, CPE can be used in conjunction with many detection techniques such as atomic absorption spectrometry, spectrophotometry, mass spectrometry (MS), electrothermal atomic absorption spectrometry (ETAAS), and inductively coupled plasma emission spectrometer (ICP) [7–10]. In recent years, CPE has been one of the important sample pre-treatment technologies for morphological analysis of metal elements and thus has become a popular research area. Coupling CPE with FAAS not only can enrich heavy-metal ions, but it can also increase the sensitizing effect on FAAS because of solvents such as surfactants and the nitric acid-ethanol solution used to dilute the surfactant phase [11–13]. Furthermore, it can maintain the high precision and reliability of FAAS. Consequently, analysts hypothesize that there is a strong complementary between CPE and FAAS.

Chromium, which occurs in different valence states, is known to have completely different chemical and toxicological behaviors in the natural environment [14]. For example, Cr(III) is a trace element essential to the normal metabolism of glucose, protein, and fat in organisms. On the contrary, Cr(VI) is recognized as a highly toxic substance that can be teratogenic, mutagenic, and carcinogenic [15]. Since chromium is not easily degraded in the environment, most of it is released into the environment from industrial production and is eventually retained in the water and sediment. Therefore, studying the chemical forms of chromium in water and sediments is of great significance to protecting the aquatic environment, controlling damage to aquatic organisms, and maintaining food safety and human health. In the present work, we used ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent and the cloud point of a complexed anionic-non-ionic surfactant to establish a new, selective CPE-FAAS method for determining the forms of chromium in the water and sediment collected from Haidian Creek. It provides an effective technical means for the monitoring and protection of the water environment in Haikou.

## 2. Materials and methods

### 2.1. Apparatus

A TAS-990 AFG atomic absorption spectrophotometer with a chromium hollow-cathode lamp (Beijing Purkinge General Instrument Co., Ltd., Beijing, China) was used for the determination of chromium in the surfactant-rich phase. The working parameters for the measurements were 359.8 nm wavelength, 3 mA lamp current, 0.4 nm slit width, 1.7 L/min acetylene flow rate, and 6 mm burner height.

A PHS-3E precision acidity meter (Shanghai Electronics Science Instrument Co., Ltd., Shanghai, China) was used for pH measurements. A DZKW-D-1 thermostated water bath (Beijing Medical Equipment Factory, Beijing, China) was used to maintain the desired temperatures for the CPE experiments, and the phase separation was accelerated using a KQ 5200 DE ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd., China). An automatic tensiometer (Shanghai

Zhongchen Digital Technology Co., Ltd., China) was used to measure the change in surface tension and critical micelle concentration (CMC) of the mixed surfactant systems at different concentrations. All glassware and plastic centrifuge tubes were previously soaked in freshly prepared 30% (v/v) nitric acid for 24 h and rinsed thoroughly with deionized water before use.

### 2.2. Chemicals and reagents

Standard stock solutions of Cr(III) and Cr(VI) at concentrations of 1,000 mg/L were obtained from the National Standard Material Research Centre (Beijing, China). Working standard solutions (50 mg/L) were prepared by diluting the standard stock solution gradually.

The corresponding pH buffer solutions were prepared by using a 100 mL phosphoric acid/acetic acid/boric acid mixture ( $4 \times 10^{-2}$  mol/L) with a specified volume of 0.2 mol/L NaOH solution.

A 5% (w/v) solution of the non-ionic surfactant Triton X-114 (Sigma-Aldrich, Steinem, Germany) and a 5% (w/v) solution of the anionic surfactant sodium dodecyl sulfate (SDS; Sinopharm Chemical Reagent Co., Ltd., Beijing, China) were used without further purification.

A 4.0% (w/v) solution was prepared by dissolving 4.0 g of APDC (Shanghai Yuanye Biological Technology Co., Ltd., Shanghai, China) in water in a 100 mL volumetric flask.

A 0.1 mol/L ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving the appropriate amount of EDTA (Shanghai Hengyuan Biological Technology Co., Ltd., Shanghai, China). It was calibrated with 0.1 mol/L  $Zn^{2+}$  standard solution. Nitric acid/ethanol solution (1:9) was used to decrease the viscosity of the surfactant-rich phase. All other reagents were of analytical grade or purer. Ultrapure water obtained from a pure-water system in the lab was used throughout the entire experiment.

For the interference study, we used commercial standard stock solutions for atomic absorption, which contain 1 mg/L of the interference elements ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Al^{3+}$ , and  $Fe^{3+}$ ; National Standard Material Research Centre, Beijing, China).

### 2.3. CPE procedure

Extraction of Total Cr: For CPE, an aliquot of the standard was placed in the centrifuge tube, and then 4 mL of 0.4% (w/v) APDC solution, 4.5 mL of buffer solution (pH 7.96), and 2 mL of 5% (w/v) Triton X-114-SDS solution were added. Saturated  $Na_2SO_4$  solution (2.5 mL) was used to reduce the cloud point temperature. The mixtures were diluted with water to 50 mL, allowed to stand for 10 min to complete the reaction, and then incubated in a thermostatic water bath maintained at 70°C for 55 min. Separation of the phases was accelerated in an ultrasonic water bath at 25°C for 20 min and at an ultrasound frequency of 40 kHz at 200 W.

Afterward, the aqueous phase was readily decanted by inverting the tube. To decrease the viscosity of extracts and to facilitate sample handling, 3 mL of nitric acid/methanol solution (1:9) was added to the remaining surfactant-rich phase. Subsequently, the total amounts of chromium in the extract phases were determined by FAAS under optimized

conditions. Standard solutions used for constructing the calibration curves and the blank samples were processed in the same manner.

Extraction of Cr(VI): First, an aliquot of the standard solution was placed in the centrifuge tube, and then 4 mL of 0.1 mol/L EDTA, 4 mL of 0.4% (w/v) APDC solution, and 4.5 mL of Britton–Robinson buffer solution (pH 3.0) were added. The rest of the steps in the above section for the extraction of total Cr were then repeated. The Cr(III) content was calculated by subtraction of Cr(VI) content from the total chromium content. Standard solutions used for constructing the calibration curves and the blank samples were processed in the same manner.

#### 2.4. Sample collection and pre-treatment

In accordance with the sample collection standard GB 17378.3 2007 [37], water samples were collected from Haidian Creek directly empties into the sea in Hainan Province (China).

To ensure the quality of the samples collected at the three water sampling points, representative samples at each point from three depths (0.3, 1.3, and 2.3 m) were mixed. Each representative sample was then stored in a polyethylene bottle (1.5 L capacity), which had been soaked in 10% nitric acid for 24 h and then rinsed with ultrapure water before use. Stream samples were filtered through a 0.45 mm cellulose nitrate membrane to remove the suspended particulate matter and then stored at 4°C.

By using a grab sampler, three samples of sediment at the surface were collected around each sample point and then transported to the lab. They were placed in a dry plate after removal of the gravel, sand, shells, and plant residues, and then air-dried in dry shade. Each representative sample was prepared by mixing three samples obtained at each point, ground in an agate mortar, gradually reduced by quartering method, and then finally passed through a 250-mesh screen [16]. It was then stored in a cool, dry place, away from light, for later use.

#### 2.5. Sample determination

##### 2.5.1. Water samples

Water samples (20.0 mL) were pipetted into 50 mL centrifuge tubes and then analyzed according to the measurement steps for the different forms.

##### 2.5.2. Sediment samples

After lye digestion, according to the United States Environmental Protection Agency (U.S. EPA) 3060A [17], 20.0 mL of digestion solution was pipetted into a centrifuge tube. Subsequently, 6 mL of a masking agent obtained by mixing diethyltriaminepentaacetic acid and 30% triethanolamine solution at 1:25 ratio were added, in accordance with the operation steps for analysis of the different forms.

### 3. Results and discussion

#### 3.1. Efficiency of the surfactant mixture

The lower the CMC, the greater is the effect of the surfactant used. In CPE, a low concentration of surfactant can

facilitate phase separation and improve the efficiency of enrichment [18, 36].

Studies have shown that the surfactant complex has a synergistic effect, which can significantly improve its performance, and that the interaction between anionic surfactant and non-ionic surfactant is strong [19,20]. Therefore, an extraction system for a mixed micellar medium composed of Triton X-114 and SDS was selected in this work after comparison. Under normal pressure and at 298 K, the average surface tension ( $\gamma$ ,  $n = 3$ ) of a series of single surfactants and of mixed surfactants at different concentration ratios was determined through the platinum plate method (results are shown in Fig. 1). We can see that  $\gamma_{\text{cmc}}$  decreased to its minimum at  $\alpha = 0.7$  ( $\alpha = n_{\text{Triton X-114}}/n_{\text{Triton X-114-SDS}}$ ), indicating that the mixed system has interfacial activity much higher than that of any single surfactant. This also shows that the efficiency of the reaction improved because of the synergistic effect of the composite system. Therefore,  $\alpha = 0.7$  was selected as the best ratio for the mixed micelle system.

#### 3.2. Effect of surfactants and $\text{Na}_2\text{SO}_4$ dosage

Adding ionic surfactant to a non-ionic surfactant increases the turbidity point and the hydrophilicity of the solution, but it also makes phase separation more difficult [21]. Since salt addition can decrease the cloud point temperature of micellar solutions [22], we added different inorganic electrolytes (KBr, KCl, NaCl,  $\text{K}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4$ ) to determine its contribution to the efficiency of cloud point reduction. The results show that adding a small amount of  $\text{Na}_2\text{SO}_4$  can markedly reduce the cloud point temperature and that using  $\text{Na}_2\text{SO}_4$  as an additive can reduce the cloud point. Triton X-114-SDS solution and  $\text{Na}_2\text{SO}_4$  were added according to the experimental procedure for studying the effects of their different dosages on Cr(III) or Cr(VI) determination (results are shown in Figs. 2 and 3, respectively). We found that during the determination of Cr(III) or Cr(VI), both had maximum absorbances when the dosages of TX-114-SDS solution and  $\text{Na}_2\text{SO}_4$  were 2.0 and 2.5 mL, respectively.

#### 3.3. Effect of pH and buffer usage

The key step in CPE is the use of a chelating agent for heavy-metal ions to form a water-insoluble chelate; meanwhile, the pH of the extraction system has an important effect on the formation and chemical stability of metal chelates [23]. According to the analytical steps of CPE, we investigated the effect of pH and buffer usage on the absorbance of total Cr or Cr(VI), using nitric acid and sodium hydroxide to adjust the system pH (results are shown in Figs. 4 and 5). When the pH ranged from 6.5 to 7.96, the absorbance increased with the increase in pH, reaching the maximum at pH 7.96, and then it decreased gradually in the pH range of 7.96–9.0 (Fig. 4). Therefore, pH 7.96 was selected as the acidity of the system for the determination of total Cr in this work. The absorbance increased with the increase in pH when the pH ranged from 1.5 to 3.0, reaching the maximum at pH 3.0; but it decreased gradually when the pH exceeded 3.0. Therefore, pH 3.0 was chosen as the system acidity for the determination of Cr(VI) (Fig. 5).

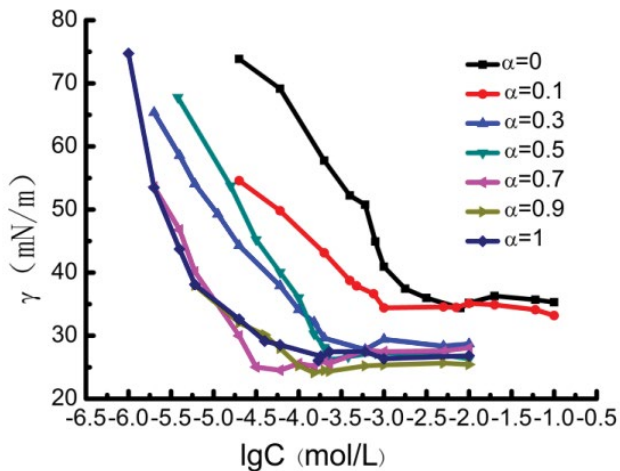


Fig. 1. Representative plot of surface tension vs. logarithm of surfactant concentration for different ratios at 298°K.

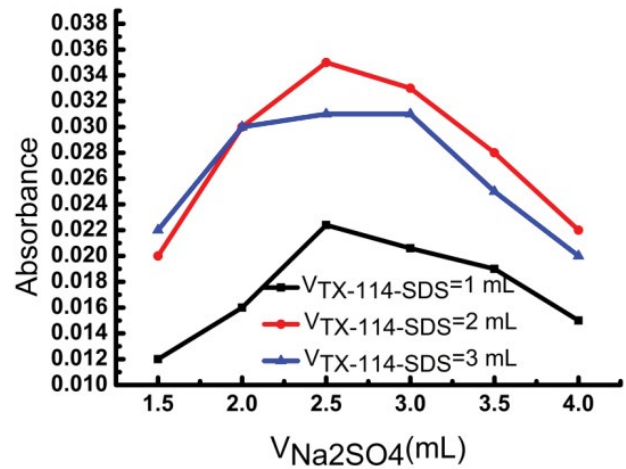


Fig. 3. Effects of the surfactant mixture and sodium sulfate dosage on Cr(VI) extraction.

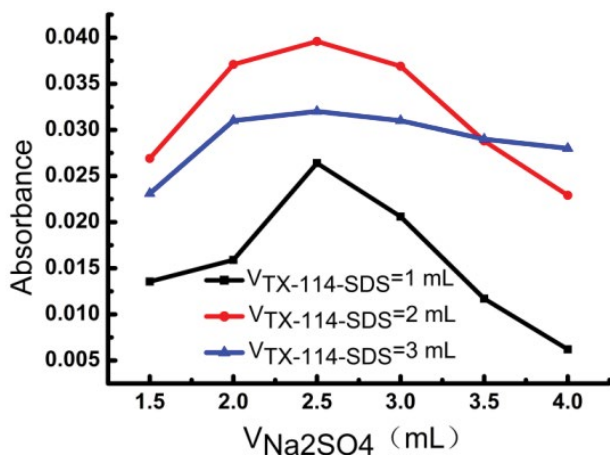


Fig. 2. Effects of the surfactant mixture and sodium sulfate dosage on Cr(III) extraction.

According to the analytical steps of CPE, different amounts of buffer solution were added to study the effects on Cr(III) and Cr(VI) extraction. The results (Fig. 6) show that the absorbance increased with the increase in the amount of buffer when there was less than 4.5 mL buffer. When there was more than 4.5 mL buffer, the absorbance decreased with the increase in the amount of buffer. Therefore, the amount of buffer was 4.5 mL in further experiments.

#### 3.4. Effect of ammonium pyrrolidine dithiocarbamate dosage

Chelating agents are one of the important reagents that affect the formation of metal chelates and CPE efficiency [24]. In accordance with the CPE steps, different amounts of APDC were added to observe its effect on the determination of Cr(III) and Cr(VI) absorbance values (results are shown in Fig. 7). We can see that the absorbance increases with the amount of APDC at amounts less than 4 mL, reaching the maximum when the amount of APDC reaches 4 mL.

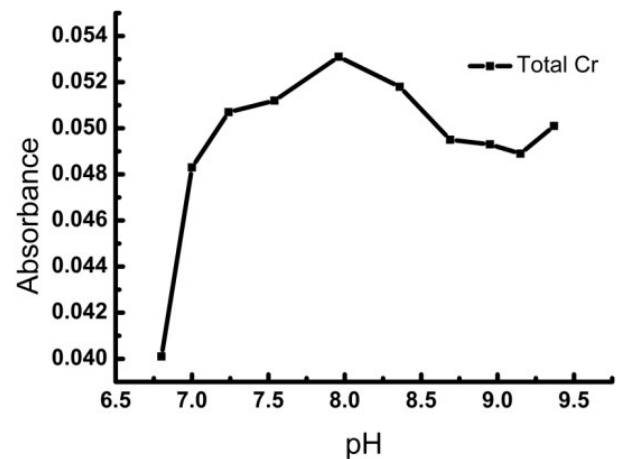


Fig. 4. Effect of pH on the extraction of total Cr.

Therefore, 4 mL of APDC (4%) solution was selected for further experiments.

#### 3.5. Effect of masking of ethylenediaminetetraacetic acid

EDTA can chelate Cr(III) effectively without affecting Cr(VI) [25–26]. Therefore, Cr(III) was masked with EDTA in the determination of Cr(VI). Different amounts of EDTA were added to investigate the effect of masking Cr(III) at pH 3.0 (results are shown in Fig. 8). We can see that the absorbance of Cr(VI) did not change generally with the increase in the amount of Cr(III) when 4 mL of 0.1 mol/L EDTA solution was added. This indicates that under these experimental conditions, 4 mL of 0.1 mol/L EDTA solution is enough to mask Cr(III) and that it has no effect on the determination of Cr(VI).

#### 3.6. Effects of incubation time and temperature

The effect of incubation temperature on the CPE of Cr(III) or Cr(VI) was studied (results are shown in Fig. 9). We found no obvious change in absorbance of Cr(III) in the

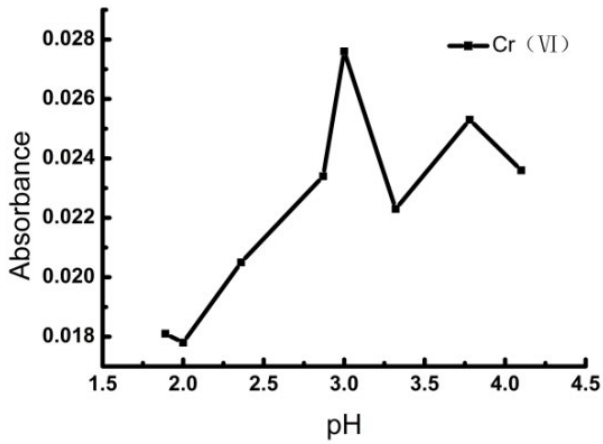


Fig. 5. Effect of pH on the Cr(VI) extraction.

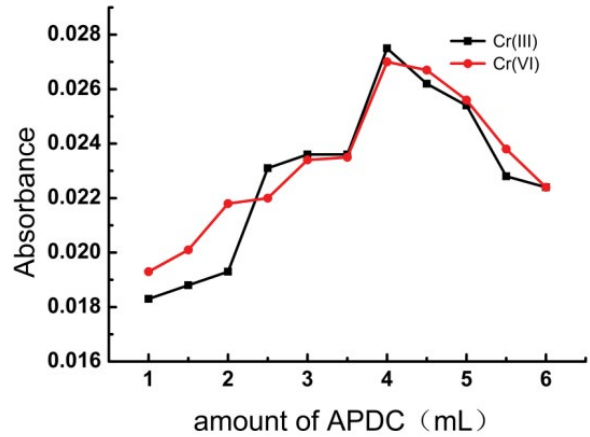


Fig. 7. Effect of APDC dosage on extraction.

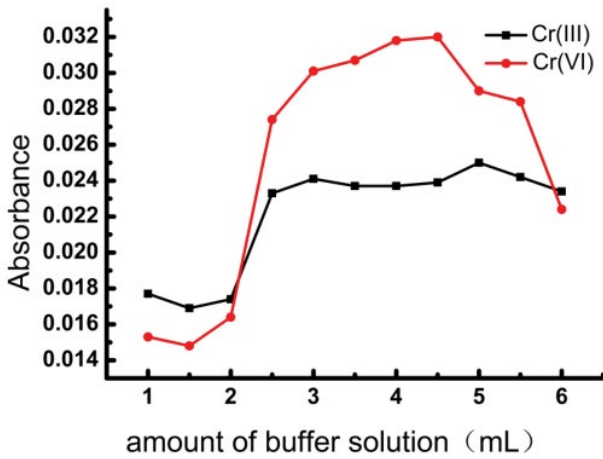


Fig. 6. Effect of the buffer solution dosage on extraction.

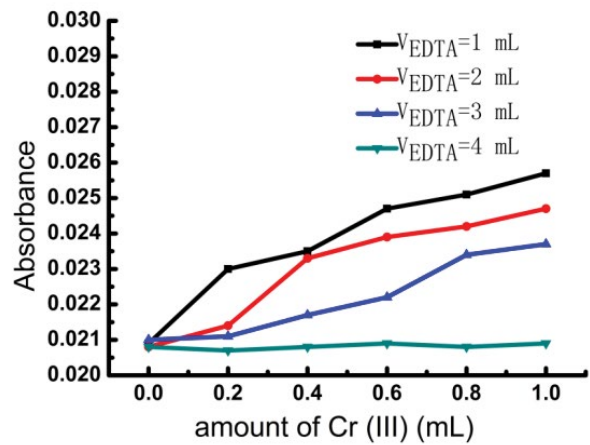


Fig. 8. Effect of masking of the reagent EDTA on Cr(III).

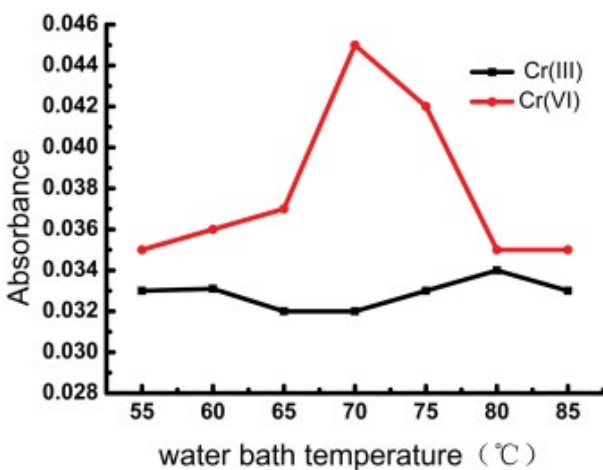


Fig. 9. Effect of water bath temperature on the extraction.

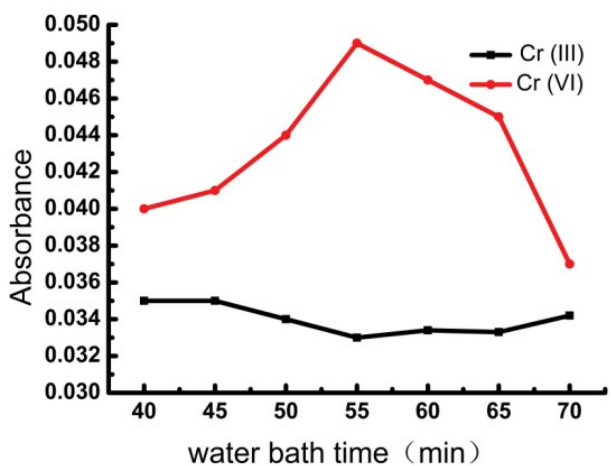


Fig. 10. Effect of incubation on the extraction.

range of 55°C–85°C, but the absorbance of Cr(VI) increased markedly, reaching the maximum at 70°C and then decreasing gradually. Hence, the incubation temperature of 70°C was selected. At this temperature, we studied the effect

of the incubation time (results are shown in Fig. 10). We can see that the effect of incubation time within the range of 40–70 min is similar to that of incubation temperature: the absorbance of Cr(III) apparently did not change. The

absorbance of Cr(VI) was higher than that of Cr(III), reaching a maximum when the incubation time was 55 min, and then it slightly decreased. Thus, 55 min was chosen for further experiments.

### 3.7. Effect of ultrasound extraction time

In order to improve the separation effect of the surfactant phase and aqueous phase, the effect of centrifugation and ultrasonic shaking were compared [27]. The results show that the latter phase separation better. The effect of different ultrasonic oscillation times shows that the phase separation was completed after ultrasonic vibration for 15 min. Therefore, 20 min of ultrasonic oscillation was chosen as the time for good separation of the two phases in further experiments [38–43].

### 3.8. Interference of coexisting ions

Because of the complexity of the marine environment matrix and the presence of various metal ions, the degree of chelation of Cr(III) and Cr(VI) by APDC is affected; hence, the recovery of common coexisting cations were determined during the determination of Cr(III) and Cr(VI) [28]. The results show that common ions such as  $K^+$ ,  $Mg^{2+}$ , and  $Na^+$  have little effect on the determination.  $Mn^{2+}$  had no effect at concentration ratios below 50:1;  $Cu^{2+}$ ,  $Al^{3+}$ ,  $Cd^{2+}$ , and  $Pb^{2+}$  had no effect at concentration ratios below 20:1, but  $Zn^{2+}$  and  $Fe^{3+}$  have a great impact due to negative interference (results are shown in Table 1). In particular, the

Table 1  
Effect of coexisting ions on the pre-concentration and determination of Cr(III) and Cr(VI)

Coexisting ions	The ratio of coexistent ions to chromium	Recovery (%)	
		Cr(III)	Cr(VI)
$K^+$	1,000	103.0	98.0
$Na^+$	600	98.3	100
$Mg^{2+}$	600	93.5	103.6
$Mn^{2+}$	50	89.2	95.7
$Cu^{2+}$	20	92.4	96
$Al^{3+}$	20	83.2	97.4
$Cd^{2+}$	20	103.7	103
$Pb^{2+}$	20	98.1	106
$Zn^{2+}$	10	92.5	90.3
$Fe^{3+}$	10	74.8	75.9

Table 2  
Linear equations,  $r^2$  values, RSDs, LODs, and enrichment factors of Cr(III) and Cr(VI)

Species	Linear range ( $\mu\text{g/L}$ )	Regression equation	$r^2$	RSD* (% , $n = 11$ )	LOD ( $\mu\text{g/L}$ )	Enrichment factor
Cr(III)	$0-9 \times 10^3$	$y = 0.0372x + 0.0237$	$990.4 \times 10^{-3}$	3.7	2.5	$169.1 \times 10^{-1}$
Cr(VI)	$0-9 \times 10^3$	$y = 0.0139x + 0.0095$	$991.1 \times 10^{-3}$	4.5	2.3	$60.4 \times 10^{-1}$

\*RSD was obtained for Cr(III) and Cr(VI) concentrations of 0.04  $\mu\text{g/L}$ .

coexistence of  $Fe^{3+}$  in the sediment had substantial interference in the application, which may be related to the frequent traffic and the mooring of ships in the waters under study. After several investigations, a masking agent was prepared by mixing diethylenetriamine pentaacetic acid with 30% triethanolamine at a ratio of 1:25 in order to eliminate this interference. It was successfully applied to the determination of the sample (results are shown in Table 4).

### 3.9. Figures of merit

Under the optimized experimental conditions, the detection of Cr(III) and Cr(VI) by CPE-FAAS with good analytical characteristics was established. For this method, the standard curve, correlation coefficient, relative standard deviation (RSD), the limit of detection (LOD), and enrichment factor were obtained (results are shown in Table 2). The RSDs resulting from the analysis of 11 replicates of standard solution were 3.7% and 4.5%. The detection limits, calculated as the concentration equivalent to three times the standard deviation of the blank divided by the slope of the calibration curve, were 2.5 and 2.3  $\mu\text{g/L}$  for Cr(III) and Cr(VI), respectively. The enrichment factors were calculated as the ratio of the slope of the pre-concentrated samples to that of the samples obtained without pre-concentration. The enrichment factors thus obtained for Cr(III) and Cr(VI) were 16.91 and 6.04, respectively.

The results of the proposed method were compared with those of the reported methods for the determination of Cr(III) or Cr(VI). Analytical properties under comparison, such as detection limit, linear range, and RSD%, are presented in Table 3. According to the table, Cr(III) and Cr(VI) can be determined through the methods described in the references and in this paper. The instruments used in ICP-MS in the literature are costly and have a high operating requirement. The instruments used in our study are relatively inexpensive and simple to operate. Our proposed method has shown satisfactory results such as a low limit of determination, good relative precision, and good sensitivity.

### 3.10. Analytical applications

After verification of the accuracy and precision of the method, we investigated using FAAS the method's applicability to the determination of Cr(III) and Cr(VI) in-stream and surface sediments from the three-stream sections. A 20 mL portion of each sample was pre-concentrated. Cr(III) and Cr(VI) standards were added to evaluate the matrix effect.

The stream samples were analyzed directly without any sample pre-treatment. The results (Table 4) indicate that for trace analysis, the recoveries of Cr(III) and Cr(VI) were

Table 3  
Comparison of the analytical figures of merit for the determination of Cr(III) or Cr(VI) through different methods

Detection	Agents	Linear range (mg/L)		Detection limit (mg/L)		RSD (%)		Literature
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
ICP-MS	APDC	$(0.3-5) \times 10^{-4}$	$(2-100) \times 10^{-4}$	0.01	$25 \times 10^{-3}$	3	0.6	[30]
FAAS	AC	$(4-200) \times 10^3$		$1 \times 10^3$		4.8		[31]
ETAAS	DDTC		0.1–0.5		$5 \times 10^{-2}$		3.5	[32]
HPLC	TAN	50–5,000	50–5,000	7.5	3.5	1.2	0.9	[33]
ET-AAS	DPC		$(3-300) \times 10^{-3}$		1		3.5	[34]
GFAAS	PMBP	100		0.021		3.5		[35]
FAAS	APDC	0–9	0–9	$25 \times 10^{-4}$	$23 \times 10^{-4}$	3.7	4.5	This work

AC, alizarin-3-methyliminodiacetic acid; TAN, 1-(2-thiazolylazo)-2-naphthol; DPC, 1,5-diphenylcarbazine; PMBP, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one.

Table 4  
Spiked recoveries of Cr(III) and Cr(VI) ions from actual stream samples after application of the proposed method ( $n = 3$ )

Stream	Added (mg/L)	Found (mg/L)		Recovery (%)		RSD (%)
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
1	0	0.33	0.02			2.30
	1	1.31	0.96	98	94	1.96
2	0	0.41	ND			2.04
	1	1.37	0.94	104	92	1.65
3	0	0.27	ND			1.83
	1	1.23	0.88	95	86	2.13

ND: Not detected.

Table 5  
Spiked recoveries of Cr(III) and Cr(VI) ions from surface sediment samples after application of the proposed method ( $n = 3$ )

Surface sediment	Added (mg/L)	Found (mg/L)		Recovery (%)		RSD (%)
		Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
1	0	77.03	3.40			5.36
	1	77.93	4.36	90	96	4.08
2	0	74.69	1.15			5.38
	1	75.61	2.09	92	94	1.70
3	0	75.82	1.32			3.14
	1	76.83	2.30	101	98	5.23

within the ranges of 95%–104% and 86%–94%, respectively. The surface sediment was analyzed following U.S. EPA Method 3060A, and then 6 mL of masking agent was added before the proposed procedure for masking  $\text{Fe}^{3+}$  so that the testing results would be more accurate (see Table 5). The masking agent consisted of diethylenetriaminepentaacetic acid (3.54 g) dissolved in a solution of triethanolamine (30%, v/v). The recovery rates were in the range of 90%–101% for Cr(III) and 94%–98% for Cr(VI).

The results obtained show that the developed CPE method can be applied to the pre-concentration and determination of trace amounts of Cr(III) and Cr(VI) in an actual stream and surface sediment samples.

#### 4. Conclusions

The chelating agent APDC can improve the efficiency of the anionic-non-ionic surfactant mixture (SDS-Triton X-114 mixture). Using the optimized conditions, we established a new CPE-FAAS method for the determination of the forms of Cr in water and sediment in Haidian Creek. The analytical method has good characteristics, maintaining the high precision and reliability of the FAAS method, as well as utilizing the cloud point of surfactant in the extraction and enrichment. In addition, it can improve the detection limit of the FAAS method from the mg/L to the  $\mu\text{g/L}$  level. The detection limit for Cr(VI) is lower than



that (0.004 mg/L) of the basic project analytical method of the National Surface Water Environmental Quality Standard (Diphenylcarbazide Spectrophotometry) [29]. It is an effective technique for the monitoring of chromium contamination in environmental water and sediments, and it provides satisfactory results.

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