



# Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples

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## ABSTRACT

A sensitive and simple method for high-performance liquid chromatography (HPLC) determination of traces of chromium species in lake sediments after preconcentration by cloud point extraction (CPE) has been developed. Simultaneous preconcentration of Cr(III) and Cr(VI) in sediment samples was achieved by CPE with 1-(2-thiazolylazo)-2-naphthol (TAN) as the chelating agent and non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114) as the extractant. Baseline separation of the TAN chelates of Cr(III) and Cr(VI) was realized on a RP-C<sub>18</sub> column by using a mixture of methanol–water (69:31, v/v) solution and 4.5 mmol L<sup>-1</sup> CTMAB buffered with 0.03 mol L<sup>-1</sup> NaAc–HAc solution (pH 5.5) as the mobile phase at a flow rate of 0.8 mL min<sup>-1</sup>. The variables affecting the complexation and extraction steps were examined. The precision (R.S.D.) for seven replicate injections of a mixture of 100 µg L<sup>-1</sup> of Cr(III) and Cr(VI) was 1.2 and 0.9% for the retention time, 4.7 and 2.7% for the peak area, respectively. The concentration factor was 45 for Cr(III) and 40 for Cr(VI). The detection limit (LOD) of this method, calculated as three times the standard deviation of the blank signals was 7.5 µg L<sup>-1</sup> for Cr(III) and 3.5 µg L<sup>-1</sup> for Cr(VI), respectively. The proposed procedure was applied to the speciation of chromium in sediment samples with satisfactory results.

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## 1. Introduction

Chromium occurs naturally in the earth crust, but its extensive use in various industrial processes and products has led to widespread chromium contamination in the environment. It is well known that the toxicological as well as biological properties of element chromium depend strongly on its chemical forms. In fact, while Cr(III) is an essential component having a vital role in the metabolism of glucose, lipids and protein, Cr(VI) is considered to be a more toxic form [1]. Total chromium does not provide sufficient information to understand its toxicity, bioavailability, biotransformation and ways of circulation. Therefore, an accurate and reliable method for the determination of chromium species is more important than the total chromium measurement. Different approaches have been reported for the speciation analysis of Cr being the combination of a powerful separation technique in environmental and biological samples such as flame atomic absorption spectrometry (FAAS) [2,3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4], inductively coupled

plasma atomic emission spectrometry (ICP-OES) [5,6], inductively coupled plasma-mass spectrometry (ICP-MS) [7], electrothermal atomic-absorption spectrometry (ET-AAS) [8], electrochemical [9], fluorometry [10,11] and chemiluminescence [12].

Despite increasingly sensitive analytical instrumentation, the determination of Cr at trace levels usually requires previous preconcentration [13,14]. Cloud point extraction (CPE), based on the clouding phenomena of non-ionic surfactants, has become an alternative to conventional solvent extraction due to a number of possible advantages such as low cost, environmental safety, a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors. CPE occurs in aqueous solutions of non-ionic surfactants that become turbid when heated to a temperature known as the cloud-point temperature (CPT), thus forming a two-phase system. During the formation of the two phases, hydrophobic complexes can be entrapped “in situ” in the surfactant phase. Mere centrifugation and decanting of the aqueous phase can easily separate the two phases. The first use of the CPE technique for preconcentration of metals was pioneered by Watanabe et al. [15], who studied the extraction of manganese with 1-(2-pyridylazo)-2-naphthol (PAN) as a complexing agent. Extracting ligands such as 1-(2-thiazolylazo)-2-naphthol (TAN) [16], 8-hydroxyquinoline (8-HQ) [17] and lately,

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dibromophenylfluorone (Br-PF) [8] have been used for cloud point extraction in several procedures.

In recent years CPE has been used as a preconcentration step in conjunction with detection by atomic absorption spectrometry for the speciation analysis of Cr [3], Fe [18], Sb [19], As [20] and Sn [21] species. Atomic absorption spectrometry can easily detect the total amount of chromium, but it can not distinguish between Cr(III) and Cr(VI). Many of these methods have the disadvantage that one of the species is determined as the difference between total and the other chemical form of the element. The separation of element species prior to determination is necessary if independent results are to be obtained. In some cases, chromatographic systems techniques can be used for simultaneous determination of the most important element species in a single step [22].

The aim of the present work was to apply CPE as a preconcentration step for chromium species combined with high-performance liquid chromatographic determination. In the developed system, 1-(2-thiazolylazo)-2-naphthol (TAN) was used as the chelating agent and Triton X-114 as the extractant. Potential factors affecting the CPE preconcentration of Cr(III) and Cr(VI) were investigated in detail. The developed method was applied for chromium speciation in lake sediments with satisfactory results.

## 2. Experimental

### 2.1. Instrumentation

A Waters Breeze HPLC system (Waters, USA) equipped with a Waters 1525 Binary Pumps, a Waters 2487 Dual  $\lambda$  Absorbance Detector, and injector was employed to determine the concentration of Cr(III) and Cr(VI) species in extract phase. All separations were performed on a C18 column (Waters ODS 5  $\mu\text{m}$ , 150 cm  $\times$  4.6 mm i.d.) at room temperature. The Breeze software was used to acquire and process spectral and chromatographic data from the detector 2487. The chromatograms were monitored at 490 nm for optimization experiments and peak area measurements.

A thermostated water bath maintained at the desired temperatures (Jincheng guosheng Science Instrument, Jiangsu, China) was used for equilibration temperature experiments and the phase separation was accelerated with a centrifuge (Xiangyi Laboratory Instrument Co., Ltd., Hunan, China). All the pipettes and vessels used for trace analysis were soaked in 10% nitric acid for at least 12 h and subsequently at least three times with pure water.

### 2.2. Reagents

All chemicals were of analytical or better grade, and water used to prepare sample and buffer solutions was freshly deionized by EASYpure water purification system with a 0.2  $\mu\text{m}$  fiber filter (Barnstead, USA). Triton X-114 (>99%), cetyltrimethylammonium bromide (CTMAB) and TAN were purchased from Sigma (St. Louis, MO, USA) and used without further purification. A 2.0 mmol L<sup>-1</sup> of TAN solution was prepared by dissolving suitable amount of the reagent in methanol. A mixture of methanol (Chromatographic Grade, Acros Organics, Morris Plains, NJ)–water (69:31, v/v) and 4.5 mmol L<sup>-1</sup> CTMAB buffered with 0.03 mol L<sup>-1</sup> NaAc–HAc solution (pH 5.5) was employed as the mobile phase at a flow rate of 0.8 mL min<sup>-1</sup>. The pH of the sample solution was adjusted to 5.5 with 1 mol L<sup>-1</sup> acetic acid. The mobile phase was filtered through a 0.45  $\mu\text{m}$  filter, and was degassed in an ultrasonic bath for 20 min just prior to use. To ensure good day-to-day precision for the HPLC separation, methanol at 1.0 mL min<sup>-1</sup> was used to wash the HPLC column for 50 min to remove residual surfactant adsorbed on the column after 1-day experiment.

Stock standard solutions of Cr(III) and Cr(VI) at a concentration of 1000 mg L<sup>-1</sup> were prepared from Cr(NO<sub>3</sub>)<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, respectively. Working standard solutions were prepared by step-wise diluting the stock solutions just before use.

### 2.3. Procedure for cloud point extraction

For the CPE, aliquots of 10.0 mL of a solution containing the analytes, 2.0 mmol L<sup>-1</sup> TAN and 1.25% (v/v) Triton X-114 at a suitable pH 5.5 were heated in a thermostatic water bath maintained at 40 °C for 20 min. The mixture was centrifuged at 4000 rpm for 15 min for phase separation, and then cooled in an ice-bath for 10 min so that the surfactant-rich phase became viscous and was retained at the bottom of the tube. In this way, the supernatant aqueous phase was easily decanted. In order to reduce the viscosity and facilitate sample handling prior to HPLC separation, 0.5 mL of methanol was added to the remaining surfactant-rich phase.

### 2.4. Sample collection and preparation

The investigated area is located in the Chaohu Lake in the middle of Anhui Province (China). The localization of the main sampling sites is presented in Fig. 1. Sediment samples were collected from six sites of the Chaohu Lake. The samples were dried in an oven at 105 °C and homogenized with a sieve. Then a 1.0 g sediment sample was weighed and transferred into conical flask. Sample solution was obtained by exchanging the contaminated sediment with water in a 1:5 ratio (soil:deionized water) for 2 h in an end-over-end shaker, 4000 rpm for 15 min and filtering through 0.45  $\mu\text{m}$  Schleicher and Schuell syringe filters [23]. Then, cloud point extraction procedure given above was applied to the final solutions.

## 3. Results and discussion

### 3.1. Effect of pH on CPE

Cr(III) and Cr(VI) reacts with TAN in acidic medium to form hydrophobic complexes which are subsequently trapped in the surfactant micelles (e.g. Triton X-114) and separated from the aqueous phase. The formation of metal complexes and its chemical stability are the two important influence factors for the CPE 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 on extraction efficiency of Cr(III) and Cr(VI) was evaluated and the results are shown in Fig. 2. As can be seen, the optimum pH for Cr(III) and Cr(VI) maximum extraction efficiency was 5.5. In more acidic solutions, absorbance decrease may be attributed to some hydronium ions trapped in cage of TAN which avoids interaction between metal ion and TAN. On the other hand, when the pH of solution is higher than 5.5, the signal intensity of analyte is decreased obviously due to the degradation of TAN complexing. Hence, pH of 5.5 was preferred for all subsequent studies.

### 3.2. Effect of Triton X-114 concentration on CPE

The non-ionic surfactant Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud-point temperature (22–30 °C), low UV absorbance and high density of the surfactant-rich phase, which facilitates phase separation by centrifugation. The effect of Triton X-114 concentration was investigated within the range of 0.25–1.5% (v/v) on the extraction efficiency and the results are shown in Fig. 3. It was found that the extraction efficiency of analytes increased as the concentration of Triton X-114 increased from 0.5 to 1.25% (v/v), and remained

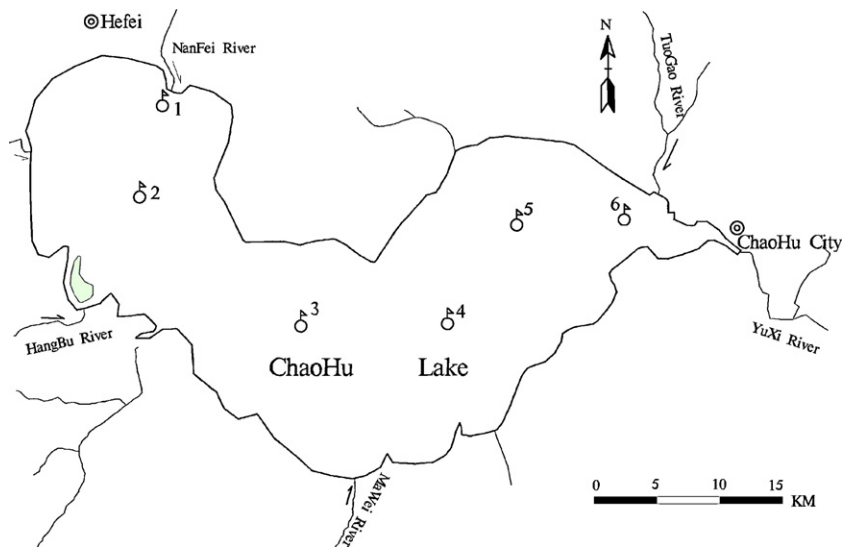


Fig. 1. Localization of sampling sites in ChaoHu Lake.

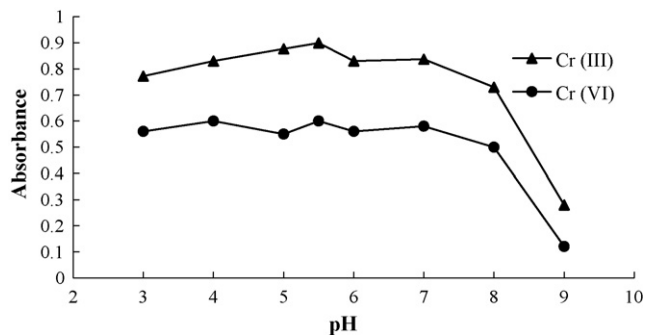


Fig. 2. Effect of pH on CPE. Other conditions: 0.2 mmolL<sup>-1</sup> TAN, 1.25% (v/v) Triton X-114, equilibration temperature 40 °C. HPLC conditions: methanol–water (69:31, v/v) buffered with 0.03 molL<sup>-1</sup> NaAc–HAc buffer (pH 5.5). The flow rate was 0.8 mL min<sup>-1</sup>. The monitoring wavelength was 490 nm.

constant between 1.25 and 1.5% (v/v) Triton X-114. So, a Triton X-114 concentration of 1.25% (v/v) was employed as the optimum surfactant concentration in order to achieve the highest possible enrichment factor.

### 3.3. Effect of TAN concentration on CPE

In this work, TAN was used as the chelating agent due to the highly hydrophobic nature of its metal complexes. A 10 mL solution containing 100 ng of Cr(III) and Cr(VI) in 1.25 (v/v) Triton X-114 at a medium buffer of pH 5.5 containing various amounts of TAN was

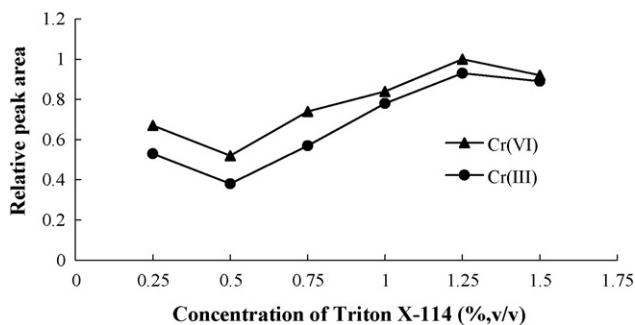


Fig. 3. Effect of Triton X-114 on CPE. Other conditions: 0.2 mmolL<sup>-1</sup> TAN, pH 5.5, equilibration temperature 40 °C. HPLC conditions as in Fig. 2.

subjected to the CPE process. As illustrated in Fig. 4, the CPE efficiency for Cr(III) and Cr(VI) increased rapidly as the concentration of TAN increased from 0.1 to 0.2 mmolL<sup>-1</sup>, then kept almost constant with further increase in the TAN concentration up to 0.3 mmolL<sup>-1</sup>. Therefore, a TAN concentration of 0.2 mmolL<sup>-1</sup> was selected for further experiments.

### 3.4. Effect of temperature and time on CPE

To achieve easy phase separation and preconcentration as efficient as possible, several other conditions which could affect the efficiency of the CPE procedure, e.g. equilibration temperature, incubation and centrifugation time were subsequently investigated. Temperature can effect complexation reactions and micelle formation. The effect of the equilibration temperature was investigated from 20 to 60 °C. It was found that the CPE efficiency increased with increase in equilibration temperature from 20 to 35 °C, and reach a maximum in the range of 35–40 °C. Over 40 °C, the CPE efficiency decreased probably due to the stability problems for chelates and chelating agents [24]. As a result, an equilibration temperature of 40 °C was applied throughout the experiment, enabling the in situ application of the method which is important for maintenance of the speciation occurring in the sample.

Studies on the effect of incubation time showed that the maximum extraction efficiency was observed at 20 min for Cr(III) and Cr(VI), and further increase in the incubation time resulted in a constant value in the efficiency. The results showed that an incubation time of 20 min is adequate for quantitative complexation of

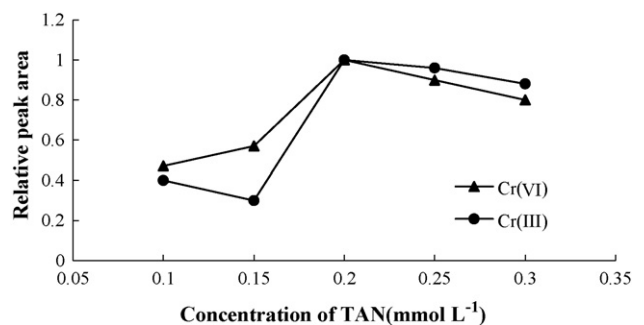


Fig. 4. Effect of TAN on CPE. Other conditions: 1.25% (v/v) Triton X-114, pH 5.5, equilibration temperature 40 °C. HPLC conditions as in Fig. 2.

both species in a single step without the need for an extra cloud point extraction experiment. Centrifugation time had no effect on the analytical characteristics. A centrifugation time of 15 min was selected for the entire procedure, because for this time period analyte extraction was almost quantitative.

### 3.5. HPLC speciation of chromium

A major disadvantage of using Triton X-series surfactants as CPE agents is that high background absorbance shown by surfactants in UV region could severely interfere with the determination of the analytes. In addition, injection of viscous surfactant-rich phase into the HPLC column may impair the precision for Cr speciation due to deterioration of column efficiency caused by the adsorption of viscous surfactant onto the column. Considering the above important issues, the composition of mobile phase should avoid such potential interference as well as facilitate the removal of the injected surfactant from HPLC column. Therefore, a mixture of methanol, water and CTMAB was used as the mobile phase and the composition of the mobile phase was optimized for baseline separation of the TAN, the TAN complexes of Cr(III) and Cr(VI) and Triton X-114 with good precision for Cr species. Using the buffer solution containing methanol/water and without CTMAB as mobile phase, the analytes got partly resolved. However, when CTMAB was simultaneously present in mobile phase, the resolution was greatly improved. This shows clearly that the adoption of CTMAB as a component of mobile phase was found to be essential to minimize the strong interaction of the analytes with the silanol groups of column packing, which can also make the peaks symmetric and sharper. Under careful optimization, a mixture of methanol–water (69:31, v/v) and 4.5 mM CTMAB buffered with 0.03 M NaAc–HAc (pH 5.5) as the mobile phase at a flow rate of 0.8 mL min<sup>-1</sup> was preferred in all subsequent experiments.

### 3.6. Interference studies

Under the optimized conditions for CPE, interference studies were carried out by individually spiking gradually increased amounts of foreign metal ions into the test standard solutions containing two chromium species (each at 100 µg L<sup>-1</sup> level) before subjected to the cloud point extraction, and a deviation greater than ±5% from the signals observed in absence of any foreign metals which was used as the criterion of interference occurring. It was found that the tolerable concentration ratio of foreign ions to 100 µg L<sup>-1</sup> Cr(III) was 500 for Mg(II) and Ca(II); 50 for Cd(II) and Fe(III); 20 for Zn(II), Cu(II), Pb(II) and Mn(II) and to 100 µg L<sup>-1</sup> Cr(VI) was 500 for Mg(II) and Ca(II); 20 for Cu(II) and Mn(II); 10 for Zn(II), Cd(II), Fe(III) and Pb(II). It demonstrates that the common coexisting ions did not have significant effect on the separation and determination of Cr(III) and Cr(VI) and the developed method is fairly free from interferences. The influence of ionic strength was examined by studying the signal in the presence of known concentration of NaCl. It was proved that an increase in the ionic strength has no effect on the efficiency of extraction of Cr species. This is in agreement with the results reported in the literature [22].

### 3.7. Analytical characteristics

Analytical characteristic data of the proposed CPE–HPLC for Cr(III) and Cr(VI) speciation were summarized in Table 1. The relative standard deviation (R.S.D.) for seven replicate injections of a mixture of 100 µg L<sup>-1</sup> of Cr(III) and Cr(VI) were 1.2 and 0.9% for the retention time, 4.7 and 2.7% for the peak area, respectively. The concentration factor, which is defined as the concentration

**Table 1**  
Analytical characteristics of the method (N:7).

Parameters	Cr(III)	Cr(VI)
Retention time (R.S.D.) (%)	1.2	0.9
Peak area (R.S.D.) (%)	4.7	2.7
Preconcentration factor	45	40
Linear range (µg L <sup>-1</sup> )	50–5000	50–5000
LOD (µg L <sup>-1</sup> )	7.5	3.5

ratio of analyte in the final diluted surfactant-rich extract ready for HPLC separation to that obtained in the initial solution, was 45 for Cr(III) and 40 for Cr(VI). The detection limit (LOD) of this method, calculated as three times the standard deviation of the blank signals was 7.5 µg L<sup>-1</sup> for Cr(III) and 3.5 µg L<sup>-1</sup> for Cr(VI), respectively. Under the optimal experimental conditions, the linear concentration range was from 50 to 5000 µg L<sup>-1</sup> for both Cr ions.

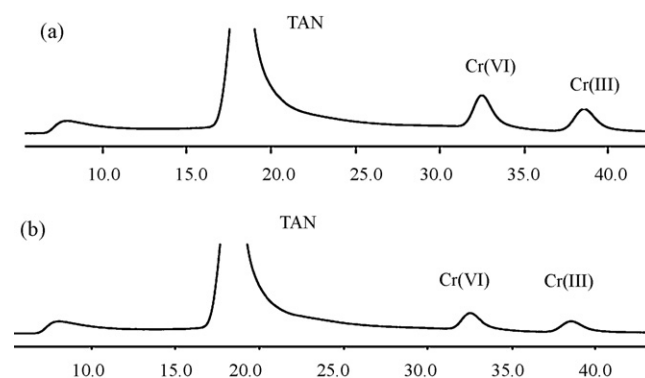
### 3.8. Application to chromium speciation in the sediments of Chaohu Lake

Fig. 5 compares the chromatograms of a standard solution of 100 µg L<sup>-1</sup> Cr(III) and Cr(VI), and sampling site 1 under the optimal conditions. As can be seen from Fig. 5, no difference of the retention times for Cr(III) and Cr(VI) was observed in the standard mixture, and lake sediment sample. The proposed method was applied to the separation and determination of Cr(III) and Cr(VI) in different sediment samples of Chaohu Lake and the results are presented in Table 2. The recoveries in the range of 96.4–104% were obtained by analysis of spiked real samples. The major input of chromium from factories is located upstream of Nanfei river from site 1.

Concentrations of chromium forms varied in the ranges 26.2–60 mg kg<sup>-1</sup> for Cr(III) and 17.8–53.2 mg kg<sup>-1</sup> for Cr(VI). In all sampling series, the highest Cr(III) and Cr(VI) concentrations were found at site 1, located very close to the main chromium input. With increasing distance from the chromium pollution source a distinct decrease of Cr(III) concentration is observed. Cr(VI) concentrations follow the same trend. The Cr(VI)/Cr(III) ratios are always the highest in site 5.

These observations can be explained as being due to sedimentation of colloid-bound Cr(III) in lake, and a long distance transport of soluble Cr(VI). Moreover, the oxidation of Cr(III) to Cr(VI) during the transport can not be excluded.

For the validation of the proposed method, a certificated reference material (CRM) of GBW08304 river sediment sample was analyzed and the analytical results were in good agreement with the certified values (Table 3).



**Fig. 5.** Chromatograms of (a) a standard solution of 100 µg L<sup>-1</sup> Cr(III) and Cr(VI) and (b) sediment sample 1 under the optimal conditions. Cloud point extraction conditions: 0.2 mmol L<sup>-1</sup> TAN, 1.25% (v/v) Triton X-114, pH 5.5, equilibration temperature 40 °C. HPLC condition as in Fig. 2.



**Table 2**

Analytical results for speciation of Cr(III) and Cr(VI) in sediments of Chaohu Lake (N:3).

Samples	Concentration (mg kg <sup>-1</sup> )		Added (mg kg <sup>-1</sup> )		Found (mg kg <sup>-1</sup> )		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1#	60 ± 1.2	53.2 ± 0.8	10	10	69.23	64.0	98.9	101.3
2#	50.8 ± 1.1	42.5 ± 0.9	10	10	62.2	51.4	102.3	97.9
3#	41.8 ± 0.7	40.5 ± 0.8	10	10	51.3	49.5	99.1	98.0
4#	41.5 ± 0.8	45 ± 1.1	10	10	53.6	55.7	104.0	101.2
5#	27.5 ± 0.6	40.2 ± 1.8	10	10	36.2	49.6	96.4	98.8
6#	26.2 ± 1.0	17.8 ± 1.6	10	10	36.4	27.6	100.5	99.3

**Table 3**

Analytical results for chromium speciation in the certified reference materials after application of the presented procedure (N: 3).

Samples	Measured (mg kg <sup>-1</sup> )		Certified (mg kg <sup>-1</sup> )	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
GBW08304 <sup>a</sup>	Not detected	84 ± 2	Not detected	86 ± 5
GBW08304	62 ± 2 <sup>b</sup>	84 ± 2	67 ± 4 <sup>b</sup>	86 ± 5

<sup>a</sup> National reference materials (China).<sup>b</sup> Spiked river sediment reference material.

#### 4. Conclusion

The feasibility of chromium speciation in lake sediments has been demonstrated based on cloud point extraction of Cr(III) and Cr(VI) with TAN in the presence of the surfactant Triton X-114 and sequential determination by HPLC. The developed method is characterized with 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 species in sediment samples collected from the Chaohu Lake with low detection limit, good accuracy and precision.

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#### References

- [1] J.O. Nriagu, E. Nieboer (Eds.), *Chromium in the Natural and Human Environment*, Wiley, New York, 1998.
- [2] I. Narin, A. Kars, M. Soylak, A novel solid phase extraction procedure on amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples, *J. Hazard. Mater.* 150 (2008) 453–458.
- [3] K. Kiran, K.S. Kumar, B. Prasad, K. Suvardhan, L.R. Babu, K. Janardhanam, Speciation determination of chromium(III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry (FAAS), *J. Hazard. Mater.* 150 (2008) 582–586.
- [4] P. Liang, Q. Ding, Y. Liu, Speciation of chromium by selective separation and preconcentration of Cr(III) on an immobilized nanometer titanium dioxide microcolumn, *J. Sep. Sci.* 29 (2006) 242–247.
- [5] A.A. Menegario, P. Smichowski, G. Polla, On-line preconcentration and speciation analysis of Cr(III) and Cr(VI) using baker's yeast cells immobilized on controlled pore glass, *Anal. Chim. Acta* 546 (2005) 244–250.
- [6] M.F. Sawalha, J.L. Gardea-Torresdey, J.G. Parsons, J.R. Peralta-Videa, Determination of adsorption and speciation of chromium species by saltbush (*Atriplex canescens*) biomass using a combination of XAS and ICP-OES, *Microchem. J.* 81 (2005) 122–132.
- [7] G.M.M. Rahman, H.M.S. Kingston, T.G. Towns, R.J. Vitale, K.R. Clay, Determination of hexavalent chromium by using speciated isotope-dilution mass spectrometry after microwave speciated extraction of environmental and other solid materials, *Anal. Bioanal. Chem.* 382 (2005) 1111–1120.
- [8] X. Zhu, B. Hu, Z. Jiang, M. Li, Cloud point extraction for speciation of chromium in water samples by electrothermal atomic absorption spectrometry, *Water Res.* 39 (2005) 589–595.
- [9] P. Kubň, P. Kubň, V. Kubň, Speciation of chromium (III) and chromium (VI) by capillary electrophoresis with contactless conductometric detection and dual opposite end injection, *Electrophoresis* 24 (2003) 1397–1403.
- [10] M.S. Hosseini, F. Belador, Cr(III)/Cr(VI) speciation determination of chromium in water samples by luminescence quenching of quercetin, *J. Hazard. Mater.* 165 (2009) 1062–1067.
- [11] A. Massumi, N.M. Najafi, H. Barzegari, Speciation of Cr(VI)/Cr(III) in environmental waters by fluorimetric method using central composite, full and fractional factorial design, *Microchem. J.* 72 (2002) 93–101.
- [12] W. Yang, Z. Zhang, W. Deng, Speciation of chromium by in-capillary reaction and capillary electrophoresis with chemiluminescence detection, *J. Chromatogr. A* 1014 (2003) 203–214.
- [13] M. Tuzen, M. Soylak, Chromium speciation in environmental samples by solid phase extraction on chromosorb 108, *J. Hazard. Mater.* 129 (2006) 266–273.
- [14] M. Tuzen, M. Soylak, Multiwalled carbon nanotubes for speciation of chromium in environmental samples, *J. Hazard. Mater.* 147 (2007) 219–225.
- [15] K. Goto, Y. Fukue, H. Watanabe, Spectrophotometric determination of manganese with 1-(2-pyridylazo)-2-naphthol and a non-ionic surfactant, *Talanta* 24 (1977) 752–753.
- [16] T. Saitoh, Y. Kimura, T. Kamidata, H. Watanabe, K. Haragichi, Distribution equilibria of metal chelates with thiazolylazo dyes between two phases formed from an aqueous micellar solution of a nonionic surfactant, *Anal. Sci.* 5 (1989) 577–581.
- [17] E.K. Paleologos, C.D. Stalikas, S.M. Tzouwara-Karayanni, M.I. Karayannis, Selective speciation of trace chromium through micelle-mediated preconcentration, coupled with micellar flow injection analysis-spectrofluorimetry, *Anal. Chim. Acta* 436 (2001) 49–57.
- [18] D.L. Giokas, E.K. Paleologos, M.I. Karayannis, Speciation of Fe(II) and Fe(III) by the modified ferrozine method, FIA-spectrophotometry, and flame AAS after cloud-point extraction, *Anal. Bioanal. Chem.* 373 (2002) 237–243.
- [19] Z. Fan, Speciation analysis of antimony (III) and antimony (V) by flame atomic absorption spectrometry after separation/preconcentration with cloud point extraction, *Microchim. Acta* 152 (2005) 29–33.
- [20] F. Shemirania, M. Baghdadia, M. Ramezanib, Preconcentration and determination of ultra trace amounts of arsenic(III) and arsenic(V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry, *Talanta* 65 (2005) 882–887.
- [21] X. Zhu, X. Zhu, B. Wang, Cloud point extraction for speciation analysis of inorganic tin in water samples by graphite furnace atomic absorption spectrometry, *J. Anal. At. Spectrom.* 21 (2006) 69–73.
- [22] A.N. Tang, D.Q. Jiang, Y. Jiang, S.W. Wang, X.P. Yan, Cloud point extraction for high-performance liquid chromatographic speciation of Cr(III) and Cr(VI) in aqueous solutions, *J. Chromatogr. A* 1036 (2004) 183–188.
- [23] Z. Chen, R. Naidu, A. Subramanian, Separation of chromium (III) and chromium (VI) by capillary electrophoresis using 2,6-pyridinedicarboxylic acid as a pre-column complexation agent, *J. Chromatogr. A* 927 (2001) 219–227.
- [24] C.D. Stalikas, Micelle-mediated extraction as a tool for separation and preconcentration in metal analysis, *Trends Anal. Chem.* 21 (2002) 343–355.