

Speciation determination of chromium(III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry (FAAS)

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Abstract

bis-[2-Hydroxy-1-naphthaldehyde] thiourea was synthesized and preconcentration cloud point extraction (CPE) for speciation determination of chromium(III) and (VI) in various environmental samples with flame atomic absorption spectrometry (FAAS) has been developed. Chromium(III) complexes with bis-[2-hydroxynaphthaldehyde] thiourea is subsequently entrapped in the surfactant micelles. After complexation of chromium(III) with reagent, the analyte was quantitatively extracted to the surfactant-rich phase in the non-ionic surfactant Triton X-100 after centrifugation. The effect of pH, concentration of chelating agent, surfactant, equilibration temperature and time on CPE was studied. The relative standard deviation was 2.13% and the limits of detection were around $0.18 \mu\text{g L}^{-1}$.

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1. Introduction

Many years ago, the applications of micellar systems or other organized molecular assemblies were already recognized, and in the last decade they have been exploited in different fields of analytical chemistry, mainly those focusing the improvement of the analytical performance of already existing methods, or even for the purpose of developing new methods [1]. Speciation of procedures based on the peculiar properties of aqueous non-ionic and zwitterionic surfactant solution has also been proposed as an alternative to the use of traditional organic solvents.

Separation and preconcentration based on cloud point extraction (CPE) is becoming an important and practical application of surfactants in analytical chemistry. The technique is based on the property of most non-ionic surfactants in aqueous solutions

to form micelles and become turbid when heated to a temperature known as the cloud point temperature. Above the cloud point, the micellar solution separates into a small volume of surfactant-rich phase and a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC) thus being considered the poor phase [2]. Any analyte solubilized in the hydrophobic core of the micelles will separate and become concentrated in the small volume of the surfactant-rich phase. The use of preconcentration steps based on phase separation by cloud point extraction offers a convenient alternative to more conventional extraction systems. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, fast and of lower toxicity to the environment than extractions that use organic solvents. CPE also provides results comparable to those obtained with other separation techniques. Accordingly, any species that interacts with the micellar system, either directly (generally hydrophobic organic compounds) or after a prerequisite derivatization reaction (e.g. metal ions after reaction with a suitable hydrophobic

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ligand) may be extracted from the initial solution and also be preconcentrated.

The analytical potential of the CPE has been discussed by several authors [3–11]. Cloud point procedures have been proposed using anionic surfactants, where the phase separation is carried out by increasing the acid concentration of the medium [12]. Cloud point extraction offers some advantages over conventional liquid–liquid extraction, including experimental convenience, low cost, ease of waste disposal and the use of non-toxic and less dangerous reagents [13,2].

Chromium is widely used in various industries, such as plating, tanning, paint and pigment production and metallurgy, which possibly contaminate the environment. Speciation analysis of trace amounts of chromium(III) and chromium(VI) ions has become an important topic in environmental and biological sciences [14,15]. It is well known that the toxicological and biological properties of most elements depend on their chemical forms. Therefore, the knowledge on the speciation of chromium is of particular necessity [16–18].

Chromium(III) compounds play an important role in the metabolism of glucose and certain lipids, whereas chromium(VI) compounds are toxic and carcinogenic [19–21]. World Health Organization (WHO) thought that the guideline value of 0.05 mg L^{-1} of Cr(VI) is too high, compared with its high risk of carcinogenicity. Consequently, the development of sensitive method, as well as the speciation method of chromium in environment is absolutely required.

In the present work, bis-(2-hydroxy-1-naphthaldehyde) thiourea, a novel reagent was used for cloud point extraction method for the estimation of chromium species in different environmental samples. The developed method was applied to the speciation of Cr in industrial wastewater, natural water and spiked water samples and also certified materials with satisfactory results.

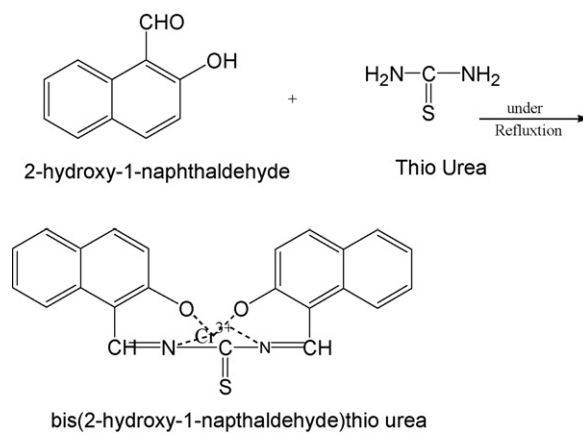
2. Experimental

2.1. Instrumentation

Flame atomic absorption spectrometer (Perkin-Elmer Model AAnalyst 2380) was used to determine metal concentration using an air/acetylene flame and a chromium hollow cathode lamp, as the radiation source, was those recommended by the manufacturer. A digital pH meter (Elico Li 129 model) was used for all pH measurements. A thermo stated bath maintained as the desired temperature was used for the cloud point extraction experiments, and phase separation was assisted using a centrifuge.

2.2. Synthesis of bis-[2-hydroxy-1-naphthaldehyde] thiourea

2-Hydroxy-1-naphthaldehyde (0.138 g, 2 mmol) is dissolved in 40% methanol and thiourea (0.137 g, 1 mmol) which is further dissolved in water and the mixture was refluxed at room temperature for 3 h and the flask was kept in ice-cold condition for 2 days. Light yellow color crystals were obtained. These crystals



Scheme 1. Reaction mechanism of bis-[2-hydroxy-1-naphthaldehyde] thiourea (2-HNAT).

were washed with doubly distilled water and recrystallized from methanol. This reaction mechanism is shown in Scheme 1.

2.3. Reagents and solutions

All of the chemicals used were of analytical reagent grade, free from chromium traces. Stock solutions of Cr(III) and Cr(VI) were prepared by dissolving appropriate amounts of $\text{Cr}(\text{NO}_3)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$ in doubly distilled water. The non-ionic surfactant, Triton X-100 was used without further purification. A 0.1 M solution of bis-[2-hydroxy-1-naphthaldehyde] thiourea was prepared by dissolving appropriate amounts of this reagent in methanol. Doubly distilled water was used throughout the entire study. The pipettes and vessels used for trace analysis were kept in 5% nitric acid for at least 12 h and subsequently washed three times with doubly distilled water.

2.4. Cloud point extraction procedure

For the CPE, aliquots of 10 mL of a solution containing the analytes, Triton X-100 and bis-(2-hydroxy-1-naphthaldehyde) thiourea buffered at a suitable pH was kept in the thermostatic bath maintained at 45°C for 20 min. Since the surfactant density was 1.07 g mL^{-1} , the surfactant-rich phase can settle through the aqueous phase. Centrifuging for 15 min at 2500 rpm accelerated the phase separation. After cooling in an ice bath, the surfactant-rich phase became viscous and was retained at the bottom of the tube. Simply a syringe centered in the tube can readily discard the aqueous phases. In order to decrease the viscosity and facilitate sample handling prior to the FAAS assay, 300 mL of methanol solution containing 0.1 M HNO_3 was added to the surfactant-rich phase. The final solution was introduced into the nebulizer of the spectrometer by conventional aspiration.

2.5. Sample collection and preparation

Wastewater samples from small-scale industrial facilities (Gajulamanyam, Renigunta) were collected and filtered through 0.45 mm pore size membrane filters immediately after sampling

Table 1
Instrumental operating conditions for proposed method

Lamp current	15
Wave length (nm)	357.9
Slit (nm)	0.7
Cuvette coated material	Zr
Gas flow (mL min ⁻¹)	35
Sample volume (mL)	500

and stored at 4 °C in dark. Natural and tap water samples were collected in and around Tirupati.

3. Results and discussion

Under optimum experimental conditions which are represented in Table 1. Cr(III) reacts with bis-(2-hydroxy-1-naphthaldehyde) thiourea to form hydrophobic complex, which is subsequently trapped in surfactant micelles. The total chromium was determined as Cr(III) by the described method after reducing Cr(VI) to Cr(III). Then the concentration of Cr(VI) was calculated by subtracting the concentration of Cr(III) from the total chromium concentration.

3.1. Effect of pH

Cloud point extraction of chromium species were performed in different pH buffer solutions. The separation of metal ions by CPE involves prior formation of a complex with sufficient hydrophobic chelating agent to be extracted into the small volume of the surfactant-rich phase, thus yielding the desired preconcentration. The extraction yield depends on the pH at which complex formation occurs. In Fig. 1, the highest recoveries for Cr(III) were obtained in the pH range 7.5–8.5. While the recovery of Cr(III) was quantitative at pH 8.0, the recovery of Cr(VI) was facilitating low. Hence at pH 8.0, Cr(III) was determined and chosen for subsequent work.

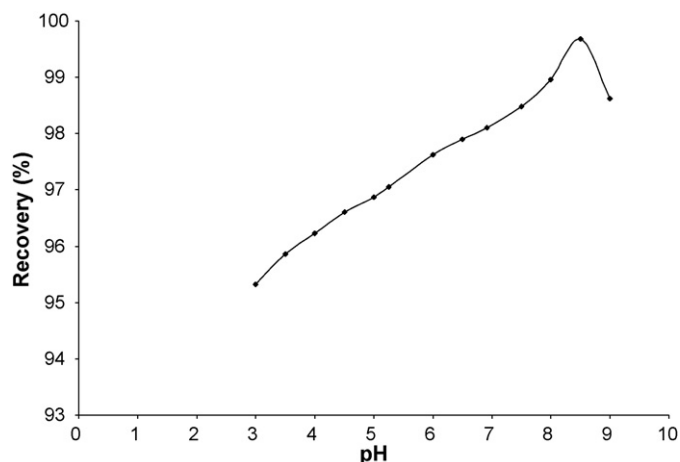


Fig. 1. Effect of pH on recovery of metal ion.

3.2. Effect of buffer concentration

The influence of buffer amount was carried out in which the other experimental variables remaining constant. The results have shown that above 0.5 mL of buffer solution added in 5 mL of solution shows no variation in the extraction yield. A 0.5 mL aliquot of buffer solution was added in all subsequent experiments.

3.3. Effect of reagent concentration on the cloud point extraction

The effect of bis-(2-hydroxy-1-naphthaldehyde) thiourea concentration on the determination of chromium was investigated in the range of 0.01–0.09 M. The chelating concentration increased up to certain values, which were sufficient for total complexation and leveled off there after. The signal increased up to a bis-(2-hydroxy-1-naphthaldehyde) thiourea concentration of 0.06 M reached near quantitative extraction efficiency. A concentration of 0.06 M was therefore chosen as the optimum concentration for the subsequent studies.

3.4. Effect of Triton X-100 concentration

A successful CPE would be that which maximizes the extraction efficiency through minimizing the phase volume ratio, thus maximizing its concentrating factor. Triton X-100 was chosen for the formation of the surfactant-rich phase due to its low cloud point temperature and high density of the surfactant-rich phase by which phase separation will be facilitated by centrifugation. Extraction of chromium with the TritonX-100 concentration was investigated within the range of 0.1–6.0 g L⁻¹ which is shown in Fig. 2. The optimum surfactant concentration used for the Cr(III) was 3.0 g L⁻¹. So, the concentration of TritonX-100 was chosen as 3.0 g L⁻¹ in order to achieve the optimal surfactant concentration in conjunction with the highest possible extraction efficiency.

3.5. Effect of the equilibrium temperature and time

Optimal equilibration temperature and shortest time are necessary to complete reactions, and to achieve easy phase sep-

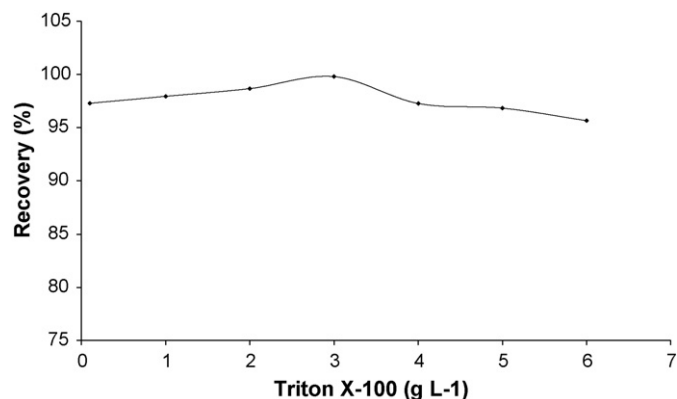


Fig. 2. Effect of Triton X-100 on recovery of metal ion.

Table 2
Influence of foreign ions

Foreign ion	Concentration ($\mu\text{g mL}^{-1}$)	Recovery (%)
Na ⁺	25×10^3	100.3
K ⁺	25×10^3	101.7
Ca ²⁺	100	97.6
Mg ²⁺	100	99.8
Ba ²⁺	5	99.7
Al ³⁺	5	100.2
Mn ²⁺	5	98.0
Co ²⁺	5	99.6
Cu ²⁺	5	102.3
Ag ⁺	5	96.7
Cd ²⁺	2	98.5
Pb ²⁺	2	99.9

ation and preconcentration as efficiently as possible. It was found that 55 °C was adequate for these analyses. The dependence of the extraction efficiency upon the time was studied for a time span of 5–30 min, respectively. The extraction time of 20 min was suitable for the separation process.

3.6. Effect of viscosity

In order to decrease the viscosity of the surfactant-rich phase and facilitate its handling and introduction into the nebulizer of the spectrometer, a methanol solution containing 0.1 M nitric acid was added to the surfactant-rich phase after the separation of the two phases. It was found that an optimum volume of methanol (150–250 mL) was necessary for a good absorbance signal. For smaller added volumes of acidified methanol, the signal was lower because of the inappropriate properties of the solution for aspiration and nebulization, whereas for greater volumes, there was a decrease in the signal due to dilution. An optimal volume of 200 mL of acidified methanol was chosen in order to ensure good absorbance signal.

3.7. Interferences

In view of the high selectivity provided by FAAS, the only interferences studied were those relating to the preconcentration step. The results are shown in Table 2. The recoveries of Cr(III) are almost quantitative in presence of interfering cations. However, Al³⁺ interferes with the preconcentration of the Cr(III) ion. By masking Al³⁺ with fluoride, its interference was eliminated, with the reaction between Cr(III) and the ligand.

Table 3
Optimum conditions

Preconcentration factor	58
Regression equation ($\mu\text{g L}^{-1}$)	$Y = 12 \times 10^{-3}C + 0.009$
Correlation coefficient (<i>r</i>)	0.9963
R.S.D. (%)	2.3
LOD ^a ($\mu\text{g L}^{-1}$)	0.18
Linear range ^b ($\mu\text{g L}^{-1}$)	0.18–150

^a Limit of detection as five time the signal-to-noise ratio.

^b For surfactant concentration.

Table 4
Determination of Cr(III) and Cr(VI) in water samples

Sample	Proposed method		Reported method ²²				F-test and <i>t</i> -test	
	Added ($\mu\text{g mL}^{-1}$)	Cr(VI)	Found ($\mu\text{g mL}^{-1}$)	Cr(III)	Cr(VI) ^a	Recovery (%)	Cr(III)	Cr(VI)
Tap water ^b	–	–	0.3	–	–	–	–	–
	5	5	5.20	4	4	101.7	102.3 ± 0.11	102.3 ± 0.11
	10	10	10.39	10	10	99.07	100 ± 0.31	99.0 ± 0.08
River water ^c	–	–	13.7	–	–	–	–	–
	5	5	18.87	4	4	100.94	100.6 ± 0.06	101.6 ± 0.09
	10	10	24.06	10	10	101.52	103.4 ± 0.07	99.3 ± 0.07

^a Calculated by subtracting Cr(III) from total Cr.

^b Collected tap water from Chandragiri town area.

^c River water collected near Rengunta industrial area.

Table 5
Application of the proposed method to the speciation of Cr in a reference material

Element	Certified value ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)
Cr(III)	26.8 ± 1.0	25.9 ± 0.5
Cr(VI)	22.8 ± 1.0	22.2 ± 0.4

3.8. Detection limit and precision

Under the optimum experimental conditions, the relative standard deviation (R.S.D.) was 2.3% for both species, i.e. Cr(III) and Cr(VI). The preconcentration factor, calculated as the ratio of the concentration of analyte after preconcentration to that prior to preconcentration, which gives the same absorbance peak area, is 58. The detection limit is sufficiently low and lies around $0.18 \mu\text{g L}^{-1}$. The results are shown in Table 3.

4. Applications

The proposed method was applied to the speciation of Cr(III) and Cr(VI) in tap water and river water. The proposed method could be successfully applied for the preconcentration and speciation of trace amounts of chromium in tap water, river water and spiked water samples, and the results are shown in Table 4. The relative error was lower than 2.1% for Cr(III), Cr(VI) and the total chromium. Validation of the method was performed using certified reference material, BCR 544, which is synthetic water certified for both species. The agreement of the certified values with those obtained using the proposed method is acceptable, as can be seen from Table 5.

5. Conclusion

The proposed method was employed for the determination of Cr(III) in water samples collected from the industrial areas (Gajulamanyam) and Gram Panchayat taps (Chandragiri), followed by their determination with FAAS. The recoveries for Cr(III) spiked in the natural water samples indicate no interference encountered from these sample matrices. The concentrations of Cr(III) in the natural water and industrial water by the present method were in good agreement with those of existed methods [22]. The proposed method was successfully employed for the determination of chromium species in environmental samples with low detection limit, accuracy and precision.

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