

Speciation of Cr (III) and Cr (VI) in Water Sample by Spectrophotometry with Cloud Point Extraction

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Abstract

The use of CPE techniques for metal speciation has become more important. A study has been carried out to determination of Cr(VI) and Cr(III) in water sample after cloud point extraction. The method is based complexation of Cr (VI) with 1,5-Diphenylcarbaid, Cr(II) is convert to Cr(VI) by reduction agent and forms complexation then in the optimum condition is measured with specterophotometric method in 540 nm. The cloud point extraction was used by surfactant of Triton-x-114 for preconcentration and determination of Cr(VI). The determination of Cr(III) in the sample was achieved by absorbance difference total cromium and Cr(VI). The effective parrameter such as ,pH solution ,organic solvent, surfactant concentration, ligand concentration, extraction time temperature were investigated and optimized. Under the optimum condition the enrichment factor obtained 10. The calibration curve was linear over the range 2-200 ng m l⁻¹ with relative standard deviation(RSD)0.3%(n=10 at 100 ng m l⁻¹). The interference effects of some cations were studied. The performance of the proposed technique was evaluated for the determination of Cr (VI) and Cr (III) in the water sample (tap water and waste water).

Introduction

Chromium is one of the most abundant elements on Earth. The amount of chromium in the environment has gradually been increased predominantly by industrial activities especially from tanneries, mines and incinerators [1]. Chromium exists in Cr(III) and Cr(VI) oxidation states in aqueous solutions [2], [3] and [4]. The properties of these species are different [1]. Trivalent chromium, the main chemical form found in foods, is essential for maintaining normal glucose metabolism [4] and [5]. Cr (VI) oxidation state is detrimental to health as it may be involved in the pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers. Industrial processes such as plating, tanning, paint production, pigment production and metallurgy involve the use of Cr(VI) compounds and are therefore the most frequent source of hexavalent chromium [5] and [6]. The importance of chromium speciation is governed by the fact that the toxicity and reactivity depend on the chemical form or oxidation state of chromium [7-9].

Separation and preconcentration based on cloud point extraction (CPE) are 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 cloud point temperature. Above cloud point temperature, the micellar solution separates into a surfactant-rich phase of a small volume and a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). 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 aim of the present work was to apply CPE as a separation and preconcentration step combined with spectrophotometry for the speciation of chromium. The experimental parameters affecting the CPE efficiency were investigated in detail. The proposed method has been applied to the speciation of chromium in tap and lake water samples with satisfactory results

Experimental

Instrumentation

A UV-Vis spectrophotometer-6405 (JENWAY) was used. The pH values were measured with a pH meter Sartorius pp-15 Model glass-electrode. A thermostated bath maintained at the desired temperatures was used for the cloud point experiments. An 80-2 centrifuge (Changzhou Guohua Electric Appliance CO. LTD. , PR China) was used to accelerate the phase separation.

Standard solution and reagents

All chemicals used were of analytical grade. Stock solution (1.000 g L^{-1}) of Cr (III) was prepared by dissolving of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.1 mol L^{-1} hydrochloric acid. Stock solutions (1.000 g L^{-1}) of Cr (VI) were prepared by dissolving of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.1 mol L^{-1} nitric acid. The non-ionic surfactant Triton X-114 was obtained from Sigma (St. Louis, MO, USA) and was used without further purification. A $1.0 \times 10^{-2} \text{ mol L}^{-1}$ solution of 1, 5-Diphenylcarbaid was prepared by dissolving appropriate amounts of this reagent in absolute methanol from the commercially available product. Doubly distilled water was used throughout the entire experiment. The pipettes and vessels used were kept in 10% nitric acid for at least 24 h and subsequently washed four times with doubly distilled water.

Cloud point extraction procedure

For CPE, 10 mL aliquots of a solution containing the Cr (VI) buffered at a suitable pH, Triton X-114 and 1, and 5-Diphenylcarbaid solution were kept in the thermostatic bath maintained at 60°C for 20 min. The solution separated into two phases, and the surfactant-rich phase could settle through the aqueous phase. Phase separation was accelerated by centrifuging the solution at 4000 rpm for 10 min. After cooling in an ice-bath, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The aqueous phases can readily be discarded simply by inverting the tubes. To decrease the viscosity of the surfactant-rich phase and allow its pipetting, 1 ml of $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ was added to it and diluted with methanol to 5 ml then determine chromium at 540 nm. Calibration was performed against aqueous standards submitted to CPE procedure. A blank submitted to the same procedure was measured parallel to the samples and calibration solutions. Oxidation of Cr(III) to Cr(VI) has been performed. After oxidation of Cr(III) to Cr(VI) by using H_2O_2 in basic media, the method was applied to the determination of Cr(VI)

Sample analysis

Tap water samples were taken from our laboratory and region located in Korasan Razave were collected in pre-washed polyethylene bottles and then the samples were filtered through a Millipore cellulose membrane filter with $0.45 \mu\text{m}$ of pore size and analysed as soon as possible after sampling. The water samples must not be acidified before storage, because this

would change the chemical species. The analysis of chromium species in water samples was made as described above. Total chromium in natural water samples was determined as chromium (VI) after oxidation of Cr (III) to Cr (VI) by using H₂O₂. The concentration of Cr (III) was calculated by subtracting the concentration of Cr (VI) from total chromium concentration.

Results and discussion

Effect of pH on CPE of Cr (III) and Cr (VI)

The formation of hydrophobic metal complex and its chemical stability are the two important factors influencing CPE efficiency. The pH plays a unique role on the metal complex formation and subsequent extraction. The effect of pH on the CPE efficiency of Cr (VI) was studied and the results are shown that extraction was quantitative (recovery > 95%) for Cr (VI) in the pH range 5.0–7.0.

Effect of 1, 5-Diphenylcarbazid concentration

A 10 mL solution containing 100 ng of Cr (VI) in 1.0 g L⁻¹ Triton X-114, at a medium buffer of pH 5-7 containing various amounts of 1, 5-Diphenylcarbazid was subjected to the CPE process. The extraction recovery for Cr (VI) increased up to a 1, 5-Diphenylcarbazid concentration of 7.5×10^{-4} mol L⁻¹ and reaches near 100%. A 1, 5-Diphenylcarbazid concentration of 1.0×10^{-3} mol L⁻¹ was chosen to account for other extractable species that might potentially interfere with the extraction of Cr (VI).

Effect of Triton X-114 concentration

A successful CPE would be that maximizes the enrichment factor through minimizing the phase volume ratio. The variation in extraction efficiency of chromium within the Triton X-114 concentration range of 0.1–2.0 g L⁻¹ was examined. Quantitative extraction was observed when Triton X-114 concentration above 0.9 g L⁻¹. So a concentration of 1.0 g L⁻¹ was chosen as the optimum surfactant concentration in order to achieve the highest possible enrichment factor.

Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon equilibration temperature and time was studied with a range of 25–80°C and 5–30 min, respectively. The results showed that an equilibration temperature of 60 °C and a time of 10 min were adequate to achieve quantitative extraction.

Interferences

The effect of various interfering ions found in water samples, on the determination of Cr (VI) was studied. Cations that may react with 1, 5-Diphenylcarbazid and are extracted to the micelle phase were studied. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Cr (VI) less than 90%, are given in Table 1. It can be seen that the major cations in the water samples have no obvious influence on the extraction of Cr (VI) under the selected conditions.

Characteristics of the method

Under the optimal experimental conditions, the calibration curve for Cr (VI) is linear up to 200 ng mL^{-1} with a correlation coefficient (r) of 0.9990. The relative standard deviation (R.S.D.) for 10 samples of 100 ng mL^{-1} of Cr (VI) subjected to the CPE procedure is 0.3%. The detection limit (LOD) of this method, calculated as three times the standard deviation of the blank signals, is 1.5 ng mL^{-1} . The enrichment factor, calculated as the ratio of the absorbance of the preconcentrated sample to that obtained without preconcentration, is 10.

Sample analysis

The proposed method has been applied to the determination of Cr (III) and Cr (VI) in tap and lake water samples collected in Mashhad. In addition, the recovery experiments of different amounts of Cr (III) and Cr (VI) were carried out, and the results are shown in Table 2. The results indicated that the recoveries were reasonable for trace analysis, ranging from 98 to 101%.

Conclusion

The feasibility of chromium speciation in water has been demonstrated based on cloud point extraction of Cr (VI) with 1, 5-Diphenylcarbazid in the presence of the surfactant Triton X-114 and sequential determination by spectrophotometry. The developed method is definitely simple, reproducible, and highly sensitive, because of the distinct and advantageous features of CPE (in situ and single-step extraction). The method has been successfully applied to the speciation of chromium in tap and lake water samples, and the precision and accuracy of the method are satisfactory. The method may also be used for the speciation of chromium in various matrices other than water.

References

- [1] A. Manova, S. Humenikova, M. Strelec and E. Beinrohr, Determination of chromium(VI) and total chromium in water by in-electrode coulometric titration in a porous glassy carbon electrode, *Microchim. Acta* 159 (2007), pp. 41–47.
- [2] S. Yalçın and R. Apak, Chromium (III, VI) speciation analysis with preconcentration on a maleic acid-functionalized XAD sorbent, *Anal. Chim. Acta* 505 (2004), pp. 25–35.
- [3] M. Ghaedi, E. Asadpour and A. Vafaie, Sensitized spectrophotometric determination of Cr(III) ion for speciation of chromium ion in surfactant media using alpha-benzoin oxime, *Spectrochim. Acta* 63A (2006), pp. 182–188.
- [4] N. Rajesh, B.G. Mishra, P.K. Pareek, Solid phase extraction of chromium(VI) from aqueous solutions by adsorption of its diphenylcarbazide complex on a mixed bed adsorbent (Acid Activated Montmorillonite -Silica gel) column, *Spectrochim. Acta Part A*, in press.
- [5] M.J. Marqués, A. Salvador, A. Morales-Rubio and M. de la Guardia, Chromium speciation in liquid matrices: a survey of the literature, *Fresen. J. Anal. Chem.* 367 (2000), pp. 601–613.
- [6] B. Preetha and T. Viruthagiri, Bioaccumulation of chromium (VI), copper(II) and nickel(II) ions by growing *Rhizopus arrhizus*, *Biochem. Eng. J.* 34 (2) (2007), pp. 131–135.

- [7] S. Pramanik, S. Dey and P. Chattopadhyay, A new chelating resin containing azophenol-carboxylate functionality: synthesis, characterization and application to chromium speciation in wastewater, *Anal. Chim. Acta* 584 (2007), pp. 469–476.
- [8] F. Shemirani and M. Rajabi, Preconcentration of chromium (III) and speciation of chromium by electrothermal atomic absorption spectrometry using cellulose adsorbent, *Fresen. J. Anal. Chem.* 371 (2001), pp. 1037–1040.
- [9] L. Shen, J.L. Xia, H. He, Z.Y. Nie and G.Z. Qiu, Biosorption mechanism of Cr(VI) onto cells of *Synechococcus* sp, *J. Cent. South Univ. Technol.* 14 (2) (2007), pp. 157–162.

Table 1 Tolerance limits of coexisting ions Cr (VI): 100 ng mL⁻¹.
CPE conditions: 1 × 10⁻³ mol L⁻¹, 5-Diphenylcarbazid, 1.0 g L⁻¹ Triton X-114, pH 5.0-7.0.

Coexisting ions	Foreign ion to analyte ratio
K ⁺ , Na ⁺	1000
Ca ²⁺ , Mg ²⁺ , Ba ²⁺ ,	500
Cu ²⁺ , Mn ²⁺ , Zn ²⁺ , Cd ²⁺ , Ni ²⁺ , Pb ²⁺	10
Al ³⁺ , Fe ³⁺ , Cr(VI)	50

Table 2 Determination of chromium species in natural water samples

^a Mean of five determinations.

^b Calculated value.

Samples	Added (ng mL ⁻¹)		Found ^a (ng mL ⁻¹)			Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI) ^b	Total	Cr(III)	Cr(VI)
Tap water	0	0	3.3 ± 0.1	2.4 ± 0.1	5.8 ± 0.1	–	–
	2.0	2.0	5.2 ± 0.1	4.4 ± 0.1	9.6 ± 0.2	98	100
	5.0	5.0	8.4 ± 0.2	7.3 ± 0.2	14.7 ± 0.3	101	98
Lake water	0	0	5.5 ± 0.2	4.1 ± 0.1	9.7 ± 0.3	–	–
	5.0	5.0	10.5 ± 0.3	9.0 ± 0.1	19.5 ± 0.4	100	98
	10.0	10.0	15.3 ± 0.3	14.3 ± 0.3	29.6 ± 0.5	99	101