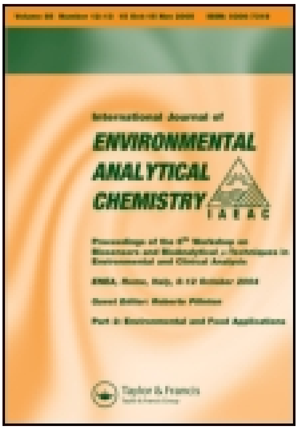

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Cloud point extraction for the determination of cadmium and lead employing sequential multi-element flame atomic absorption spectrometry

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Cloud point extraction for the determination of cadmium and lead employing sequential multi-element flame atomic absorption spectrometry

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A cloud point extraction procedure for pre-concentration and determination of cadmium and lead in drinking water using sequential multi-element flame atomic absorption spectrometry is described. *4-(2-thiazolylazo)-orcinol* (TAO) has been used as complexing agent and the micellar phase was obtained using the non-ionic surfactant *octylphenoxypolyethoxyethanol* (Triton X-114) and centrifugation. The conditions for reaction and extraction (surfactant concentration, reagent concentration, effect of incubation time, etc) were studied and the analytical characteristics of the method were determined. The method allows the determination of cadmium and lead with quantification limits of 0.30 $\mu g\,L^{-1}$ and 2.6 $\mu g\,L^{-1}$, respectively. A precision expressed as relative standard deviation (RSD, $n = 10$) of 2.3% and 2.6% has been obtained for cadmium concentrations of 10 $\mu g\,L^{-1}$ and 30 $\mu g\,L^{-1}$, respectively, and RSD of 1.3% and 1.7% for lead concentrations of 10 $\mu g\,L^{-1}$ and 30 $\mu g\,L^{-1}$, respectively. The accuracy was confirmed by analysis of a natural water certified reference material. The method has been applied for the determination of cadmium and lead in drinking water samples collected in the cities of Ilhéus and Itabuna, Brazil. Recovery tests have also been performed for some samples, and results varied from 96 to 105% for cadmium and 97 to 106% for lead. The cadmium and lead concentrations found in these samples were always lower than the permissible maximum levels stipulated by World Health Organization and the Brazilian Government.

Keywords: cloud point extraction; cadmium; lead; sequential multi-element flame atomic absorption spectrometry

1. Introduction

It is well known that the quantification of lead and cadmium in drinking water is very important considering the toxicity of these metals and their adverse effects on human health [1,2]. Important anthropogenic sources of these elements are emissions from industrial plants and automotive fuel [3]. Due the low concentration of these metals their determination is difficult considering that some of the conventional analytical techniques do not offer sufficient sensitivity for that purpose. Several pre-concentration techniques were therefore proposed for the determination of cadmium and lead in water [4–7].

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More sophisticated techniques, such as inductively coupled plasma optical emission spectrometry [8,9], inductively coupled plasma mass spectrometry [10] and electrothermal atomic absorption spectrometry [11] have been employed for the direct determination of Cd and Pb in water. Flame atomic absorption spectrometry (FAAS) requires a pre-concentration step [12–14] but it combines simplicity, speed of analysis and lower cost. Methods using FAAS as sequential multi-element technique have been proposed in recent years [9,15]. Amorim and Ferreira proposed the sequential determination of Cd and Pb in table salt using FAAS [16]. A method using on-line separation and enrichment was also proposed for fast sequential determination of Cu, Pb, Cd, Co, Ni and Mn in environmental samples by FAAS [17]. Projahn *et al.* described a sequential determination of Cu, Mn, Fe, Zn and Mg in mineral sample and a scrap wood digest [18]. Other alternative is GF AAS using *in situ* trapping hydride as Sun and Suo [19] for the determination of cadmium in environmental waters.

In the last decade, separation methods based on cloud point extraction (CPE) were frequently applied in pre-concentration procedures [20,21]. This technique is based on the formation of metallic chelates in the surfactant aggregate. The CPE has been applied in pre-concentration procedures for the determination of metal ions [22–26] and other species [27–29]. Advantages and limitations of this technique have been summarised in recent reviews [30–32].

An important factor that controls the extraction efficiency in CPE is the hydrophobicity of ligands and complexes. Reagents with different functional groups, such as pyridylazo and thiazolylazo, have been widely employed for that purpose due their low solubility in water and capacity of forming complexes with several metallic ions. The reagent *4-(2-thiazolylazo)-orcinol* (TAO) was first synthesised by Jensen in 1960 and applied as indicator in several complexing reactions [33].

The goal of the present paper has been to investigate the application of TAO as complexing agent in the CPE of Cd and Pb from water samples. Two metal ions were pre-concentrated after complex formation with TAO. The micellar phase has been obtained using the non-ionic surfactant *octylphenoxypolyethoxyethanol* (Triton X-114) and the determination was made using fast sequential flame atomic absorption spectrometry (FS-FAAS). The method has been applied for the determination of Cd and Pb in drinking water samples collected in the cities of Ilhéus and Itabuna (Bahia-Brazil).

2. Experimental

2.1 *Instrumentation*

A Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer with fast sequential module (FS-FAAS) was used for the analysis. A multi-element silver, cadmium, lead and zinc hollow cathode lamp was operated with a current of 10.0 mA. The most sensitive wavelengths for Cd at 228.8 nm and Pb at 217.0 nm were used with bandwidths of 0.5 nm for Cd and 1.0 nm for Pb. The gas flow rates have been 2.0 L min^{-1} for acetylene and 13.5 L min^{-1} for air, and the burner height was 13.5 mm. The nebuliser aspiration rate was kept between 5.5 and 6.0 mL min^{-1}. A Fanem (São Paulo, Brazil) thermostatic bath has been used to reach the cloud point temperature. A Janetzki T 32 C (Berlin, Germany) centrifuge was used to accelerate phase separation.

2.2 *Reagents*

The non-ionic surfactant Triton X-114 (Aldrich) was used without further purification. A 0.04% (w/v) *4-(2-thiazolylazo)-orcinol* (TAO) (Aldrich) solution was prepared by dissolving 0.04 g of the reagent in 10 mL of ethanol and diluting to 100 mL with ethanol.

Stock standard solutions of cadmium and lead (Merck) at a concentration 1000 mg L^{-1} have been used to prepare a mixed working standard solution of 50.0 μg L^{-1} Cd and Pb by diluting appropriate dilution volumes of the stock standard solutions with 1% (v/v) nitric acid.

A 0.1 mol L^{-1} stock buffer solution has been prepared by dissolving appropriate amounts of sodium tetraborate (Merck).

All other reagents were of analytical grade and all solutions were prepared in ultrapure water obtained from an EASY pure RF purification system (Barnstedt, Dubuque, IA, USA).

2.3 *General procedure*

For the cloud point extraction, an aliquot of 50 mL of sample volume was transferred to a 100-mL centrifuge tube. A 0.04% w/v TAO solution (300 μL), 0.32 mg mL Triton X-114 (500 μL) and a pH 10 buffer solution (500 μL) were added.

The resultant solution was kept in a thermostatic bath at 40°C for 15 min. Phase separation was accomplished by centrifugation at 2500 rev min^{-1} for 10 min. On cooling in an ice-bath for 10 min, the surfactant-rich phase became viscous and the aqueous phase could be separated by inverting the tubes. To reduce the viscosity of the surfactant-rich phase and facilitate sample handling, 300 μL of ethanol solution containing 1% HNO_3 was added. This final solution was introduced into the flame by conventional aspiration.

2.4 *Sample preparation*

The samples were filtered through a 0.45 μm membrane immediately after collection, acidified to pH 2.0 with nitric acid and stored at 6°C. The bottles were previously washed with a 10% (v/v) nitric acid–water solution and afterward with ultrapure water. The general procedure described above has been applied in the same way.

2.5 *Optimisation of the extraction step*

For determination of the best conditions for simultaneous pre-concentration the variables pH and concentration of buffer, concentration of TAO, surfactant, and incubation time were investigated. A 50.0 μg L^{-1} working solution containing the analytes Cd(II) and Pb(II) and maximum absorbance have been used to find best conditions.

3. Results and discussion

3.1 *Effect of experimental conditions*

The cloud point extraction of Cd and Pb has been performed at different pH values. The extraction involves complex formation of the analytes with a sufficiently hydrophobic reagent at an appropriate pH value. Hence, the effect of pH on the complexing reaction has been studied in the range of 4 to 11. The results show that the highest absorbance is obtained for pH values above 10 for both analytes; a pH value of 10 has therefore been chosen for all subsequent investigations.

The buffer concentration has been studied in the range of 0.5 to 3.0 mmol L^{-1}. The absorbance signal was highest for a buffer concentration of 2.0 mmol L^{-1}, which has been adopted for all subsequent experiments.

The effect of the TAO concentration on the extraction yield of Cd and Pb has been studied in the range 3.404×10^{-6} to 1.702×10^{-5} mol L^{-1}. The extraction yield increased with increasing TAO concentration, reaching maximum absorbance values at a TAO concentration of 1.02×10^{-5} mol L^{-1}.

The effect of the concentration of Triton X-114 in the range 0.064 mg mL^{-1} to 0.64 mg mL^{-1} on the analyte absorbance as studied. The highest absorbance signals were obtained for 0.32 mg mL^{-1} Triton X-114; hence, this concentration was used for all further experiments.

The effect of incubation time on the analytical signal has been studied in the range of 10–50 min with the temperature being fixed at 40°C. An extraction time of 15 min was found to be sufficient for the separation process.

3.2 *Validation studies*

The figures of merit have been determined using the optimised conditions and 50 mL of sample volume for pre-concentration. The enrichment factors, EF, calculated as the ratio of the slopes of calibration curves with and without pre-concentration, were 56 and 85 for Cd and Pb, respectively.

The limits of quantification (LOQ, $10\sigma/S$, $n = 10$), where σ is the standard deviation of the blank and S is the slope of analytical curve, were 0.3 and 2.7 μg L^{-1}, respectively calculated as IUPAC recommendation [34]. The precision, expressed as relative standard deviation (RSD, $n = 10$), was 2.3% and 1.3% for concentrations of 10 μg L^{-1} Cd and 30 μg L^{-1} Cd, respectively, and 2.6% and 1.7% for concentrations of 10 μg L^{-1} Pb and 30 μg L^{-1} Pb, respectively. The calibration equations using the pre-concentration procedure were $A = 0.0046$ [Cd, μg L^{-1}] + 0.0009 and $A = 0.0021$ [Pb, μg L^{-1}] + 0.0005 with a correlation coefficient (R) of 0.9996 for both metals.

To confirm the accuracy of the procedure Cd and Pb have been determined in the certified reference material NIST SRM 1643d (trace elements in water) using the proposed procedure. The NIST 1643d simulates the elemental composition of fresh water. The results obtained for accuracy were for Cd 6.5 ± 0.8 μg L^{-1} using the proposed method being 6.47 ± 0.37 μg L^{-1} the certified value and for Pb 17.9 ± 1.1 μg L^{-1} using the proposed method with the certified value 18.15 ± 0.64 μg L^{-1}.

3.2.1 *Effect of interfering ions*

The effect of other metal ions was studied using 50 mL of a solution containing 10 μg L^{-1}, each, of cadmium and lead in the presence of 100 μg L^{-1}, each, of nickel, chromium cobalt, zinc, aluminum, iron, manganese, mercury, molybdenum and vanadium. The results showed that at these concentrations the other metal ions did not interfere in the proposed procedure.

Table 1. Determination of cadmium and lead in water samples ($n=3$).

	Cd ($\mu g\,L^{-1}$)			Pb ($\mu g\,L^{-1}$)		
Sample	Added	Found	Rec%	Added	Found	Rec%
1	0	< LOQ[a]	–	0	< LOQ[a]	
	1.0	1.01 ± 0.07	101	2.0	4.4 ± 1.0	97
2	0	1.10 ± 0.08		0	4.5 ± 1.8	
	1.0	2.06 ± 0.10	96	5.0	9.8 ± 0.5	106
3	0	1.74 ± 0.03		0	7.3 ± 1.7	
	2.0	3.80 ± 0.05	103	7.0	14.5 ± 0.5	103
4	0	2.60 ± 0.40		0	5.7 ± 1.0	
	3.0	5.76 ± 0.90	105	6.0	11.9 ± 0.9	102
5	0	2.55 ± 0.19		0	5.7 ± 0.5	
	3.0	5.47 ± 0.60	97	5.0	10.9 ± 1.3	104
6	–	0.95 ± 0.06	–	–	6.2 ± 1.4	–
7	–	0.71 ± 0.09	–	–	8.2 ± 0.7	–
8	–	0.80 ± 0.10	–	–	5.0 ± 1.7	–
9	–	0.77 ± 0.27	–	–	8.4 ± 1.4	–
10	–	1.06 ± 0.05	–	–	7.5 ± 1.2	–

[a] Below limits of quantification.

3.3 *Application*

The proposed method was applied for cadmium and lead determination in drinking water samples collected in the cities of Ilhéus and Itabuna, Brazil. Ten samples were analyzed and the concentrations of cadmium and lead varied from 0.7 to 2.6 $\mu g\,L^{-1}$ Cd and 4.5 to 8.4 $\mu g\,L^{-1}$ Pb, respectively. Addition/recovery test were performed for five samples and recovery values were in the range from 96 to 105% for cadmium and 97 to 106% for lead. These results demonstrate the applicability of this method for the analysis of water samples. All results are summarised in Table 1. The concentration of both elements in all the investigated water samples was lower than the permissible maximum levels of 5 $\mu g\,L^{-1}$ (Cd) and 10 $\mu g\,L^{-1}$ (Pb) established by the Health Organization of the Brazilian Government [35] and the World Health Organization.

4. Conclusions

Cloud point extraction is a good alternative to conventional techniques for pre-concentration of trace quantities of cadmium and lead from water samples because it offers simplicity and speed, and it does not require toxic organic solvents. TAO is a very stable and fairly selective complexing reagent.

The limits of quantification allow the determination of cadmium and lead in drinking water and concentrations of lead and cadmium in the samples analysed are according to national and international regulations. The fast sequential mode is well suited for routine determinations using flame atomic absorption spectrometry.

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