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Field Sampling System for Determination of Cadmium and Nickel in Fresh Water by Flame Atomic Absorption Spectrometry

Walter N. L. dos Santos, Carla M. dos Santos and Sérgio L. C. Ferreira*

Instituto de Química, Universidade Federal da Bahia, 40170-290 Salvador- BA, Brazil

Um sistema contendo Amberlite XAD – 2 (estireno-divinilbenzeno) carregado com 2-(2-tiazolilazo)-5-dimetilaminfenol (TAM) é proposto para amostragem em campo, preconcentração e determinação de cádmio (II) e níquel (II) em amostras de águas naturais usando espectrometria de absorção atômica com chama (FAAS). O processo de otimização foi univariado e os seguintes parâmetros foram estudados: efeito de pH, efeito de vazão de amostragem, concentração da solução e vazão de eluente, efeito de outros ions, precisão e exatidão. Na etapa de amostragem, os ions metálicos são retidos na minicoluna sob a forma de TAM complexos. A amostra é percolada com vazão de 3,0 mL min^{-1} após filtração usando filtro de 0,45 μm. Posteriormente, a minicoluna é incorporada sobre um sistema em fluxo contínuo e os ions metálicos são eluídos com solução de ácido clorídrico de concentração 1,0 mol L^{-1} diretamente para o sistema de nebulização do espectrômetro. Para níquel, os limites de detecção (LOD) e quantificação (LOQ) foram 12 e 39 ng L^{-1}, respectivamente. A precisão expressa como desvio padrão relativo (RSD) para 10 determinações independentes foram 5,5% e 7,0% para concentrações de níquel de 10 e 1,0 μg L^{-1}, respectivamente. O fator de preconcentração, calculado como a relação entre as inclinações de curvas obtidas pelo presente procedimento e pela aspiração direta foi 637 para um volume de amostra de 150 mL. Para cádmio, os LOD e LOQ foram 22 e 72 ng L^{-1}, respectivamente. A precisão expressa como RSD, foi 6,0% e 6,8% para concentrações de cádmio de 10 e 1,0 μg L^{-1}, respectivamente. O fator de preconcentração experimental foi 548, também para um volume de amostra de 150 mL. O procedimento foi aplicado para determinação de cádmio e níquel em águas naturais de baixa salinidade, coletadas de lagoas da Cidade de Salvador, Bahia, Brasil.

A system containing Amberlite XAD – 2 (styrene-divinylbenzene copolymers) loaded with 2-(2thiazolylazo)-5-dimethylaminophenol (TAM) reagent is proposed for field sampling, preconcentration and determination of cadmium (II) and nickel (II) ions in fresh water using flame atomic absorption spectrometry (FAAS). The optimisation process was univariate and the followings parameters were studied: pH effect, effect of sample flow rate, eluent concentration and flow rate, effect of other ions, precision and accuracy as recovery tests. In the sampling step, metal ions are retained in a minicolumn as TAM complexes. The sample is pumped at 3.0 mL min^{-1} with on-line filtration using a 0.45 μm filter. Afterwards, the minicolumn is incorporated in a flow-injection system and the metal ions eluted with a solution of 1.0 mol L^{-1} hydrochloric acid into the nebuliser-burner system of the spectrometer. For nickel, the limits of detection (LOD) and quantification (LOQ) were 12 and 39 ng L^{-1}, respectively. The precision expressed as relative standard deviation (RSD) for ten independent determinations was 5.5% and 7.0% for nickel concentrations of 10 and 1.0 μg L^{-1}, respectively. The experimental preconcentration factor, calculated as the ratio of the slopes of the calibration curves obtained by the present procedure and manual direct aspiration was 637 for a sample volume of 150 mL. For cadmium, the LOD and LOQ are 22 ng L^{-1} and 72 ng L^{-1}, respectively. The precision, expressed as RSD was 6.0% and 6.8% for cadmium concentrations of 10 and 1.0 μg L^{-1}, respectively. The experimental preconcentration factor was 548 also for a sample volume of 150 mL. The procedure was applied for determination of cadmium and nickel in fresh water samples with low saline concentration, collected in lagoons from Salvador City, Bahia, Brazil.

Keywords: field sampling system, fresh water, cadmium, nickel, FAAS

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* e-mail: slcf@ufba.br

Introduction

Knowledge of metal content in natural aquatic environments is important for environmental assessment available nutritional resources for system's flora and fauna, as well as to characterize pollution levels. However determination of metal traces in natural water is not an easy task with regard to sensitivity of the most available analytical techniques, requiring previous preconcentration.[1] Furthermore, shifts in analytical results can occur due to sample contamination during sampling and storage related to contaminated preservants or storing flasks. Moreover preconcentration procedure often require buffers that can also contaminate samples. Thus, the development of field sampling systems (FSS) for sampling and preconcentration of trace metals in natural waters is desirable in order to minimize such problems.[2] Consequently field sampling systems have been used for trace metal determination in conjuction to inductively coupled plasma optical emission spectrometry (ICP OES),[3] graphite furnace atomic absorption spectrometry GFAAS,[4,5] flame atomic absorption spectrometry (FAAS),[6,7,8,9,10,-11] and X-ray fluorescence,[12] they have also been purposed to speciation studies [13-20] for mercuric,[14,15,16,-17] aluminium,[18] lead[19] and chromium [20,21, 22] and also separation processes for analysis by ICP-MS.[23] The Table 1 shows a comparison among FSS proposed for metal determination using spectroanalytical techniques.

FSS's are used in two steps: Sampling, when the metal ions are retained in minicolumns containing sorbents loaded with complexing reagents, and the desorption in which the metal ions are eluted by acid solutions and presented for determination. This second step can be carried out off-line or on-line, the metal ions are transported directly to a detection system. The requirements for field sampling systems (FSS) for metal determination in water samples may be summarized as follows: (*i*) the metal ion sorption must be quantitative (> 95%); (*ii*) the complexation pH must be in the range from 6.0 to 8.5, this avoids the use of buffer solution, considering the pH values normally found in natural waters; (*iii*) the sorption kinetic (as far as possible) should be fast, in order to allow the use of large sample volume within a feasible period; (*iv*) the desorption step should be fast (for on-line system) and complete in order to avoid memory effect; (*v*) the minicolumn should have a complexing capacity large enough to retain the metallic ion, without undergo interference of other ions present in water sample; (*vi*) the system should retain the metallic ion with stability to allow transport to laboratory and long term storage; (*vii*) the system must be re-usable with efficiency; (*viii*) the system must be reproducible.

In the present work, a field sampling system for the determination of cadmium and nickel in fresh water is proposed. It is based on the sorption of cadmium(II) and nickel(II) ions on minicolumn containing Amberlite XAD – 2 (styrene-divinylbenzene copolymers) loaded with 2-(2thiazolylazo)-5-dimethylaminophenol (TAM) reagent. This system was applied for determination of cadmium and nickel in fresh water with low saline concentration, collected in several lagoons from Salvador, City, Brazil.

Experimental

Reagents

Ultrapure water from an Easypure RF water purification system (Barnstead, Dubuque, USA) was used to prepare all solutions. The hydrochloric acid was Suprapure (Merck, Darmstadt, Germany). All other reagents were of analytical reagent grade. The laboratory glassware was kept overnight in a 5% v/v nitric acid solution. Afterwards, it was rinsed

Table 1. Analytical systems proposed for metal determination in water samples using FSS

Metal	Minicolumn	Sample	Analytical technique	LOD	PF/ SV/ ST	References
Cd, Co, Cu, Ni, Pb, Zn	Iminodiacetate Resin	Seawater and brines	ICP OES	0.4-7.6 μg L^{-1}	— / 90 mL/ 180 min	3
Mn	Silica C18	Natural water	GFAAS		10/ 50 mL/ —	4
Au	Thiol cotton fiber	Natural water	GFAAS	0.02 ng L^{-1}	— / 5000 mL/ 125 min	5
Pb	Polyaminophosphonic acid resin	Seawater	FAAS	2.8 ng L^{-1}	15632/ 2000 mL/ 571 min	7
Cu	A. XAD-4 PAN	Seawater	FAAS	60 ng L^{-1}	296/ 25 mL/ 50 min	6
Cd	A. XAD-2 PAN	Seawater	FAAS	3.8 ng L^{-1}	1059/ 90 mL/ 50 min	9
Cd	A. XAD-2 PAR	Seawater	FAAS	6 ng L^{-1}	1053/ 200 mL/ 57 min	10
Pb	A. XAD-2 PAN	Seawater	FAAS	5 ng L^{-1}	12000/ 1000 mL/ 285 min	11
Cd	A. XAD-2 TAM	Fresh water	FAAS	22 ng L^{-1}	548/ 150 mL/ 30 min	This work
Ni	A. XAD-2 TAM	Fresh water	FAAS	12 ng L^{-1}	637/ 150 mL/ 30 min	This work

A.- amberlite; LOD: Detection limit; PF: factor preconcentration; SV: sample volume; ST: sampling time.

thoroughly with ultrapure water and dried in a dust-free environment. The following solutions were used.

Nickel(II) solution (10.0 μg mL^{-1}). It was prepared by diluting a 1000 μg mL^{-1} nickel solution (atomic absorption Aldrich) with a 1.0 mol L^{-1} hydrochloric acid solution.

Cadmium(II) solution (10.0 μg mL^{-1}). It was prepared by diluting a 1000 μg mL^{-1} cadmium solution (atomic absorption Aldrich) with a 1.0 mol L^{-1} hydrochloric acid solution.

Hydrochloric acid (1.0 mol L^{-1}). It was prepared by direct dilution with deionized water from the concentrated suprapur solution.

TAM solution (0.05%). It was prepared by dissolving 0.10 g 2-(2-thiazolylazo)-5-dimethylaminophenol in 200 mL ethanol (Merck).

Instrumentation

The FSS was constituted of a Gilson Minipuls-3 peristaltic pump fitted with polyvinyl chloride (PVC) tubes, a Rheodyne 5041 model four-way manual valve, a 0.45 mm Milipore filter and laboratory-made PVC minicolumns (4.50 cm length and internal diameter of 4.0 mm) packed with 0.10 g of Amberlite XAD-2 loaded with TAM.

The FI elution system is constituted of an Alitea C-6 XV peristaltic pump fitted with Tygon tubes and a Rheodyne 5041 model four-way manual valve for the selection of the preconcentration/elution steps.[24]

A Varian Model SpectrAA 220 flame atomic absorption spectrometer was used for the analysis. Hollow Cd and Ni cathode lamps were operated at the current (4.0 mA) suggested by the manufacturer as well as the wavelengths (228.8 nm for cadmium and 232.0 nm for nickel), the slit (0.2 nm) and burner height (13.5 mm) had conventional values. The flame composition was 2.0 L min^{-1} acetylene and 13.5 L min^{-1} air. Nebulizer flow rate was 5.0 mL min^{-1}.

Column preparation

A 0.05% (m/v) TAM solution was percolated through the minicolumn containing about 0.10 g of Amberlite XAD-2 at a 5.0 mL min^{-1} flow rate, for fifteen minutes. In sequence, the column was washed with a 10% (m/v) sodium hydroxide solution until the purple effluent became colourless, to remove the TAM excess. Then, the column was washed with the 5% (v/v) hydrochloric acid solution and deionized water, respectively, using the same flow rate. Washing with nitric acid was necessary in order to prevent any metal contamination.[25,26] In this step, eight minicolumns were prepared at the same time (as many as the number of channels of the peristaltic pump). These minicolumns can be used several times (more than 100 cycles).

Field sampling system

The field sampling system (FSS) used is shown in Figure 1. The water sample (at its original pH) or an analytical solution at pH 7.0 is pumped at 3.0 mL min^{-1} through the minicolumn, the sampled total volume is controlled by time. If a real sample is considered, an on-line filtration with a 0.45 mm filter is necessary. The metal ions (Cd^{+2} and Ni^{+2}) are retained at the minicolumn and the sample matrix is sent to waste. After loading, the minicolumn is rinsed with ultrapure water for 5 min at a flow rate of 3.0 mL min^{-1}. The dry minicolumns are disconnected from the FSS, placed in a portable refrigerator and returned to the laboratory where they are stored in a refrigerator until analysis.[8]

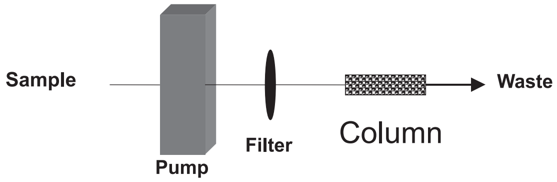

Figure 1. Field sampling system for determination of cadmium and nickel in fresh water samples.

On-line system for elution and determination of metal ions

The determination of the metal ions was performed by sequentially connecting each minicolumn to the system shown in Figure 2. Minicolumns are located immediately before the detector in order to avoid eluent dispersion. The desorption procedure is based in the elution of 1 mol L^{-1} hydrochloric acid solution at a flow rate of 5 mL min^{-1}. The metal ions (Cd^{+2} and Ni^{+2}) are released directly into the nebulizer of the spectrometer. Signals were measured as peak height in triplicate and averaged.

Analytical curves are the blanks were constructed by pumping through minicolumn the appropriate analytical solutions at pH 7.0.

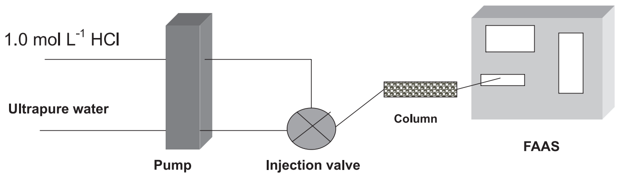

Figure 2. On-line elution system for determination of cadmium and nickel.

Results and Discussion

Determination of the experimental conditions

The optimisation process was univariate and the following experimental factors were studied: pH, sample flow rate (SFR), eluent concentration (EC) and eluent flow rate (EFR). All the experiments were carried out using cadmium and nickel solutions 10.0 μg L^{-1} and volumes of 10.0 mL.

The effect of sample pH on the metal ions sorption was studied in the pH range from 4.0 to 10.0 by adding to the diluted solutions ammonia or nitric acid as required. The results have shown that the analytical signals (absorbance) for both metal ions were maximum and constant in the pH range from 6.0 to 10.0. In this study, EC was set at 3.0 mol L^{-1}, while SRF and ERF were 0.5 and 5.0 mL min^{-1}, respectively.

The influence of the sample flow rate on the metal ions retention was carried out using solutions at pH 7.0, an EC of 3.0 mol L^{-1} and an ERF of 5.0 mL min^{-1}. The sample flow rate varied from 0.5 to 4.0 mL min^{-1}. The results demonstrated that for both metal ions, the analytical signal was maximum and constant for sample flow rate between 0.5 and 3.5 mL min^{-1}. A sample flow rate of 3.0 mL min^{-1} was then chosen for the next studies.

For evaluating of the effect of the eluent concentration on the metal ions desorption, hydrochloric acid solutions in the concentration range from 0.5 to 3.0 mol L^{-1} were investigated. For nickel, the desorption was constant in the all this concentration range; however, for cadmium the results demonstrated that the desorption is maximum for HCl concentrations higher than 0.75 mol L^{-1}. Then, hydrochloric acid concentration for the further studies was 1.0 mol L^{-1}. For these experiments the metal solutions were kept at pH 7.0 and SRF and ERF at 3.0 and 5.0 mL min^{-1}, respectively.

In the study of the hydrochloric acid flow rate influence, values between 3.5 and 5.5 mL min^{-1} were investigated using metal solutions at pH 7.0, SRF at 3.0 mL min^{-1} and EC of 1.0 mol L^{-1}. For nickel the analytical signal was constant in all this range, but for cadmium this maximum occurs in the range from 4.5 to 5.5 mL min^{-1}. This way, the eluent flow rate recommended for this system was 5.0 mL min^{-1}.

Analytical features

Analytical curves were performed using the proposed FSS with analytical solution volumes of 150 mL. The concentration ranged from 0.0 to 10.0 μg L^{-1}. The equations obtained were (A) = 0.00935 + 0.0751 [Cd] (R^2 = 0.9987) and (A) = 0.012 + 0.07841 [Ni] (R^2 = 0.9990), where [Cd] and [Ni] are the Cd and Ni concentration in μg L^{-1}. The equations obtained with direct aspiration (conventional FAAS) were (A) = 0.00409 + $1.37.10^{-4}$ [Cd] (R^2 = 0.9910) and (A) = 0.028 + $1.23.10^{-4}$ [Ni] (R^2 = 0.9982).

Experimental preconcentration factors (for sample volumes of 150 mL) were 548 and 637 for cadmium and nickel, respectively. They were calculated from the ratio between the slopes of the analytical curves obtained using this FSS and the direct aspiration of solutions of nickel and cadmium.[6] The theoretical preconcentration factors[6] were 535 for cadmium and 652 for nickel. They were calculated, considering the ratio between the sample volumes (150 mL) and elution volumes of 280 and 230 μL for cadmium and nickel, respectively. The comparison between the experimental preconcentration factors and the theoretical preconcentration factors indicate quantitative recoveries and the low dispersion of the FI system. The capacities of the minicolumns were also determinate. They were 0.19 mmol g^{-1} for nickel and 0.10 mmol g^{-1} for cadmium, respectively.

The FSS precisions for cadmium expressed as the relative standard deviation (RSD) were 6.0% and 6.8% for concentrations of 10.0 μg L^{-1} and 1.0μg L^{-1}, respectively. For nickel, it was 5.5% and 7.0% for concentrations of 10.0 μg L^{-1} and 1.0 μg L^{-1}, respectively.

The limits of detection (LOD) and quantification (LOQ), defined[27] as LOD = (3s/S) and LOQ = (10s/S), where (S) is the slope of the analytical curve using the FSS, and s is the standard deviation of ten consecutive measurements of the blank. Were for cadmium 22 and 72 ng L^{-1}, respectively, while for nickel they were 12 and 39 ng L^{-1}, respectively. The LOD values achieved demonstrated that this system is perfectly compatible for determination of cadmium and nickel in fresh water samples.

Effect of other ions

In order to check the effect of other metal ions on the proposed system, solution volumes of 150 mL containing cadmium, nickel and other metal ions (all at 10.00 μg L^{-1}) were prepared and the FSS was used for the determination of cadmium and nickel. The achieved average recoveries were 99.1 and 98.1 for cadmium and nickel (n=3), respectively. This experiment was carried out using a multielemental ICP OES solution Quality Control Standards (QCS-19), which has arsenic, antimony, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, molybdenum, nickel, thallium, titanium, zinc, lead, magnesium, manganese and selenium at the concentration of 100 μg mL^{-1} each one. These results have shown that

Table 2. Determination of cadmium in fresh water samples collected in Salvador, Brazil

Sample	Cd added (μg L^{-1})	Cd achieved (μg L^{-1})	Recovery (%)	Ni added (μg L^{-1})	Ni achieved (μg L^{-1})	Recovery (%)
Abaeté Lagoon	0.00	0.30 ± 0.01	—	0.0	0.19 ± 0.05	—
	0.50	0.73 ± 0.04	86	0.5	0.74 ± 0.04	110
Tororó Lagoon	0.00	0.33 ± 0.07	—	0.0	0.66 ± 0.07	—
	0.50	0.88 ± 0.06	110	1.0	1.64 ± 0.10	98
Pituaçu Lagoon	0.00	0.48 ± 0.05	—	0.0	1.53 ± 0.06	—
	0.50	1.02 ± 0.07	108	1.0	2.43 ± 0.09	90

these other metal ions at the studied concentration did not demonstrate any potential of effecting in the determination of cadmium and nickel in freshwater samples. Addition/recovery tests of cadmium and nickel for synthetic seawater solution demonstrated also that this FSS could not be applied for determination of cadmium and nickel ion diluted in seawater samples. In these samples, cadmium(II) and nickel(II) ions are not retained in the minicolumn.

Application

The proposed system was used for determination of cadmium and nickel in fresh water samples collected in Salvador, City, Bahia, Brazil. The results are described in Table 2. For cadmium the concentration ranged from 0.30 to 0.48 μg L^{-1} and for nickel from 0.19 to 1.53 μg L^{-1}. The addition/recovery experiments (Table 2) in the analysed samples demonstrated the accuracy and applicability of the system developed for determination of nickel and cadmium in fresh water.

Conclusions

The FSS has advantages over other systems previously proposed for metal determination using FAAS,[6-11] considering that: The FSS allows the determination of two metal ions (cadmium and nickel); The sampling flow rate is relatively higher (3.0 mL min^{-1}) compared to ones, which use sampling flow rate of 0.50 mL min^{-1}. The disadvantages are: the FSS can not be used for metal determination in seawater samples and the detection limit for cadmium is lower than others FSS´s proposed by Yebra *et al.*,[9,10] although it does not limits its application for cadmium determination in fresh water.

The proposed system allows the metal determination with the followings advantages: lowers contamination of the sample, avoids addition of acid in the conservation step, avoids use of buffer solution in preconcentration step, avoids transport and storage of the sample, in-situ preconcentration with matrix separation and the minicolumns can be used several times (more than 100 cycles).

The achieved results for cadmium and nickel in the analysed samples are agreeing with other data reported in the literature.

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