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Preliminary evaluation of the cadmium concentration in seawater of the Salvador City, Brazil

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Abstract

A method for preconcentration and determination of trace amounts of cadmium in high saline samples is described. It is based on the adsorption of the metal in the activated carbon as complex cadmium(II)–4-(2-pyridylazo-resorcinol) (PAR). The final determination was carried by flame atomic absorption spectrometry (FAAS). The optimization of extraction parameters such as the pH effect, PAR mass, activated carbon mass and shaking time was carried out using a two-level full factorial design (2^4) and two Doehlert matrix designs. The results of the factorial design, considering the analysis of variance (ANOVA), demonstrate that all these factors are statistically significant, as well as the interactions (pH×PAR mass), (pH×activated carbon mass) and (activated carbon mass×shaking time). The final optimization was carried out using Doehlert matrix designs considering the results of the factorial design. The recoveries were quantitative (96.0–106.7%) for seawater samples spiked with Cd at concentrations of 0.125 and 0.625 μg l^{-1}. A preconcentration factor of 149 was obtained. The effect of diverse metallic ions on the proposed procedure was investigated too. The procedure was used for cadmium determination in surface seawater samples collected in Salvador City, Brazil. The cadmium content in the analysed samples varies from 0.035 to 0.17 μg l^{-1}. These results are agreement with other data reported in the literature.

1. Introduction

The determination of heavy metals, especially some toxic metals which play important roles in biological metabolism, has received particular attention [1]. Cadmium is a toxic metal and its concentration in unpolluted environmental water is sometimes at the ng ml^{-1} level or below. Several techniques, including flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS), have been widely used for the determination of trace elements in different samples because the available data are highly precise and accurate; however, with seawater, some, such FAAS, do not present detection limit sufficient for this analytical measure [2]. Also, ICP OES methods sometimes suffer from problems with signal sup-

pression and clogging of the sample introduction system when the sample contains dissolved solids at concentrations >0.2% m v^{-1}. It is obvious, therefore, the need to preconcentrate those analyte before their final analytical quantification. For this, several methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the concentrations of the analytes and the measurement techniques. They include ion exchange [3], coprecipitation [4,5], solvent extraction [6,7] and adsorption [8]. Among the various preconcentration methods, solid-phase extraction (SPE) is one of the most effective multielement preconcentration methods because of simplicity, rapidity and ability to attain a high concentration factor. Table 1 shows the achieved cadmium concentration in seawater samples collected around the world [9–15].

Several chelating agents are used for cadmium preconcentration: ammonium diethyldithiophosphate (DDTP) [16], 1-(2-pyridylazo)-2-naphthol (PAN) [17], pyrrolidine dithiocarbamate [10,18], piperidine dithiocarbamate (pipDTC) [19], EDTA and 8-hydroxyquinoline-5-sulphonic acid

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Table 1
Results for cadmium determination in several seawater samples

Sampling place/year	Achieved results (μg l^{-1})	Analytical technique	Preconcentration process	Reference
Japan Inland sea, 1987	0.05–0.06	ICP OES	Chelex-100 resin	[9]
Iskenderun Bay, Turkey, 2002	3.63	FAAS	Chromosorb-102 resin column	[10]
Iskenderun Bay, Turkey, 1999	5.38	FAAS	Coprecipitation with cerium(IV) hydroxide	[11]
North Atlantic ocean, 1985	0.016–0.047	GFAAS	Dithiocarbamate/Freon TF extraction	[12]
Mersin Bay, Mediterranean sea, 1997	0.37	FAAS	Coprecipitation with cobalt-diethyldithiocarbamate	[13]
Atlantic ocean, Galician cost, 2002	0.024–0.034	FAAS	Amberlite XAD-2 impregnated with PAN	[14]
Atlantic ocean, Galician cost, 2002	0.010–0.25	FAAS	Amberlite XAD-2 impregnated with PAR	[15]

FAAS: flame atomic absorption spectrometry; GFAAS: graphite furnace atomic absorption spectrometry; ICP OES: inductively coupled plasma optical emission spectrometry.

[20]. However, the advantages of other chelating reagents have been studied. Among them, 4-(2-pyridylazo-resorcinol) (PAR) has been used because it forms stable complex with cadmium, which is a real advantage in many analytical applications, and because several components of natural samples are not complexed. In view of the complex nature of seawater, selection of the proper solid phase for a specific suite of trace metals is most important. A disadvantage of some resins is the affinity they exhibit for the alkali and alkaline earth metals, as well as the presence of these metals decreases the collection efficiency of the resin for several trace metals. The activated carbon was chosen in this work, because it is effective, inexpensive, readily available and has high sorption capacity for metal ions.

The main objective of this work was develop and evaluate a reliable method for the determination of cadmium in surface seawater samples collected in several beaches of the Salvador City, Brazil. The cadmium was pre-complexed with a PAR ligand and retained on activated carbon using a batch procedure; after separation, the elution was made in proper medium and the metal analyzed by FAAS. Doehlert matrix was used for optimization of the experimental variables.

Factorial design is a optimization process [21,22], which has been used for a preliminary evaluation of the experimental variables of a system. It allows the determination the effects and significances of these variables. Doehlert matrix [23,24] is included in the response surface methodology, being a design of the second-order type. It is easily applied to optimise experimental variables and offers advantages in relation to more frequently used designs such as central composite or Box–Behnken [25].

In our laboratory, Doehlert designs were used in the optimization step of the variables of the preconcentration procedures for determination of molybdenum [26], zinc [27] and copper and vanadium [28] in seawater using ICP OES.

2. Experimental

2.1. Instrumentation

A Varian model Spectra 220 flame atomic absorption spectrometer equipped with cadmium hollow cathode lamp and an air-acetylene burner was used. The instrumental parameters were those recommended by the manufacturer. The wavelength selected for the determination was Cd 228.8 nm.

A DIGIMED pH meter (Santo Amaro, Brazil) was used to measure pH values. An Ética mechanical shaker (São Paulo, Brazil) at 100 counts min^{-1} was also used.

The calibration curve (0–1.25 μg l^{-1}) for cadmium was plotted with solutions prepared from a 1.0 μg ml^{-1} stock solution.

2.2. Reagents

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from a EASYpure RF (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of Suprapur quality (Merck). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust-free environment.

Cadmium solution (1.0 μg ml^{-1}) was prepared by diluting a 1000 μg ml^{-1} cadmium solution (Merck) with a 1% (v v^{-1}) hydrochloric acid solution.

PAR solution 0.25% (w v^{-1}) was prepared by dissolution of 1.25 g of 4-(2-pyridylazo)-resorcinol (Aldrich) in 500 ml of ethanol p.a. (Merck).

Acetate buffer (pH 5.75) was prepared by mixing 149.2 g of sodium acetate and 10.3 ml of concentrated acetic acid with dilution to 1000 ml with ultrapure water.

Tris buffer (pH 8.00) was prepared by mixing 3.0 g of tris(hydroxymethyl)aminomethane and 1.1 ml of concentrated hydrochloric acid with dilution to 500 ml with ultrapure water.

Tris buffer (pH 9.10) was prepared by mixing 3.0 g of tris(hydroxymethyl)aminomethane and 0.2 ml of concentrated hydrochloric acid with dilution to 500 ml with ultrapure water.

Glycine/sodium hydroxide buffer (pH 10.00) was prepared by mixing 50 ml of 0.2 mol l^{-1} glycine and 32. 0 ml of 0.2 mol l^{-1} sodium hydroxide with dilution to 200 ml with ultrapure water.

Nitric acid solution (3.0 mol l^{-1}) was prepared by diluting a 189.9 ml concentrated nitric acid p.a. (Merck) to 1000 ml with ultrapure water.

Synthetic seawater was prepared with the composition of (in g l^{-1}): 27.9 of NaCl, 1.4 of KCl, 2.8 of MgCl$_2$, 0.5 of NaBr, 2.0 of MgSO$_4$ and 0.2 of NaHCO$_3$.

2.3. Surface seawater samples

Seawater samples were collected in polypropylene bottles previously cleaned by soaking in 2.0 mol l^{-1} nitric acid. Samples were filtered through a membrane of 0.45-μm pore size, acidified to 1% (v v^{-1}) with concentrated nitric acid and stored frozen until analysis. Sampling stations were beaches of the Atlantic Ocean in Salvador, City, Brazil. Salvador is in the eastern region of Brazilian coast.

2.4. General procedure

Into a stoppered flask was added a sample volume of 800 ml containing cadmium(II) ions. Afterwards, 10 ml of buffer solution and a volume of PAR solution (0.25%) were added. After fast shaking, it was added a mass of active carbon and the mixture was shaken for a time. The system was then filtered under vacuum through a 2.5-cm-diameter cellulose membrane. The filtered residue of activated carbon was transferred to an erlenmeyer and digested with 4.00 ml of concentrated nitric acid solution at 120 °C until dry. The residue was treated with 5.0 ml of 3 mol l^{-1} nitric acid solution, filtered in paper filter (Whattman no. 40). The filtrate was collected and used for cadmium determination by FAAS.

2.5. Optimization strategy

The optimization process was carried out using two-level full factorial and Doehlert matrix designs. All the experiments were done in duplicates, with a random order, using 800 ml of synthetic seawater containing 10.0 μg of cadmium. Four variables (pH, PAR mass, activated carbon mass and shaking time) were regarded as factors and the experimental data were processed by using the STATISTIC computer program [29].

2.6. Procedure used in the factorial design

This experiment was carried out using the general procedure and the experimental conditions of pH, PAR mass, activated carbon mass and shaking time are described in Table 2. Maximum and minimum levels of each factor

were established considering previous experiments performed in ours laboratory.

2.7. Procedures used in the Doehlert matrix

These experiments were performed in agreement with the results achieved in the factorial design and were carried out using the general procedure. The experimental conditions of pH, PAR mass, activated carbon mass and shaking time were established considering the values required as the Doehlert matrix.

2.8. Lagrange's criterium

Lagrange's criterium was used for the determination of the critical point of the second-order equation and is based on the calculation of the Hessian determination of Y.

$$H(A, B) = (\delta^2 Y/\delta A^2)(\delta^2 Y/\delta B^2) - (\delta^2 Y/\delta A\delta B)^2 \qquad (1)$$

The critical point (a_o, b_o) is maximum if $H(a_o, b_o) > 0$ and $\delta^2 Y/\delta A^2(a_o, b_o) < 0$, and it is minimum if $H(a_o, b_o) > 0$ and $\delta^2 Y/\delta A^2(a_o, b_o) > 0$. A saddle point exists, if $H(a_o, b_o) < 0$. If the response surface has a maximum, this point is calculated by solving the equation systems: $\delta^2 Y/\delta A^2 = 0$ and $\delta^2 Y/\delta B^2 = 0$.

3. Results and discussion

3.1. Factorial design

In the method of solid phase extraction developed, cadmium(II) ions form complexes with PAR that is retained on the active carbon. All parameters such as pH, PAR mass, activated carbon mass and shaking time were regarded in the multivariate optimization step. For this, a two-level full factorial design (2^4) in duplicate was carried. Table 3 shows the experimental design matrix and the results obtained from each run in duplicate for cadmium extraction. All four factors, as well as the interactions (pH×PAR mass) and (PAR mass×activated carbon mass) are statistically significant, based on the analysis of variance (ANOVA). The parameters pH, PAR mass and shaking time provide the most significant effects for cadmium extraction and activated carbon mass produces the less significant effect evaluating the Pareto chart (Fig. 1). The interactions (pH×PAR mass) and (activated carbon mass×PAR mass) have also a high effect on extraction.

3.2. Final optimization by Doehlert design

The results found in the factorial design demonstrated that the variables in the studied levels need a final optimization. Two Doehlert designs were used for it. Firstly, was performed a optimization of the variables

Table 2
Factors and levels used in the factorial design for extraction of cadmium

Factor	Low (−)	High (+)
pH	5.75	10.00
PAR mass (μg)	2500	15000
Activated carbon mass (mg)	50	200
Shaking time (min)	10	50

Table 3
Design matrix and the results of cadmium extraction (%)

No	PAR mass	pH	Activated carbon mass	Shaking time	Cadmium extraction (%)
1	+	+	+	+	95.6/93.8
2	+	+	+	−	91.9/91.7
3	+	+	−	+	75.6/77.3
4	+	+	−	−	60.4/63.3
5	+	−	+	+	86.4/88.1
6	+	−	+	−	63.5/87.3
7	+	−	−	+	86.2/84.3
8	+	−	−	−	79.2/75.5
9	−	+	+	+	89.4/89.6
10	−	+	+	−	66.0/64.5
11	−	+	−	+	91.1/92.7
12	−	+	−	−	80.1/83.6
13	−	−	+	+	64.9/65.0
14	−	−	+	−	60.7/61.1
15	−	−	−	+	64.2/58.4
16	−	−	−	−	58.4/56.3

involved in the complexation reaction (pH and PAR mass) using a Doehlert design. Afterward, a second design was carried out for optimization of the variables involved in the extraction step (shaking time and activated carbon mass).

3.2.1. Design 1—experimental conditions of pH and PAR mass for cadmium extraction

The optimized variables in this design were PAR mass and pH, setting activated carbon mass and shaking time at 200 mg and 50 min, respectively. The seven experiments required by Doehlert design are described in Table 4. PAR mass and pH varied from 2550 to 15000 μg and from 6.0 to 10.0, respectively.

The obtained data were used in the Doehlert matrix and the equation below illustrates the relationship among PAR mass, pH and cadmium extraction (%).

$$\% \text{ Cd extraction} = 22.626 + 0.004\text{PAR} + 11.227\text{pH}$$
$$- 9.806 \times 10^{-8}\text{PAR}^2$$
$$- 2.329 \times 10^{-4}\text{PAR} \cdot \text{pH} - 0.45\text{pH}^2 \quad (2)$$

Fig. 2 shows the corresponding surface response. The values of cadmium extraction (%) experimental and predicted offer a coefficient for correlation (R) of 0.979, indicating a good fit for the model.

The application of Lagrange's criterium in this equation demonstrates that:

$$H(a_o, b_o) = 1.20 \times 10^{-7}$$

$$\delta^2 Y/\delta \text{pH}^2 = -0.90$$

$$\delta^2 Y/\delta m_{\text{PAR}}^2 = -1.96 \times 10^{-7}$$

These results indicated that there was a maximum on the surface response, and it was calculated by the following equations:

$$\delta \text{Cd extraction}/\delta m_{\text{PAR}} = 0 = 0.004 - 19.612 \times 10^{-8}\text{PAR}$$
$$- 2.369 \times 10^{-4}\text{pH} \quad (2')$$

$$\delta \text{Cd extraction}/\delta \text{pH} = 0 = 11.227 - 2.369 \times 10^{-4}\text{PAR}$$
$$- 0.90\text{pH} \quad (2'')$$
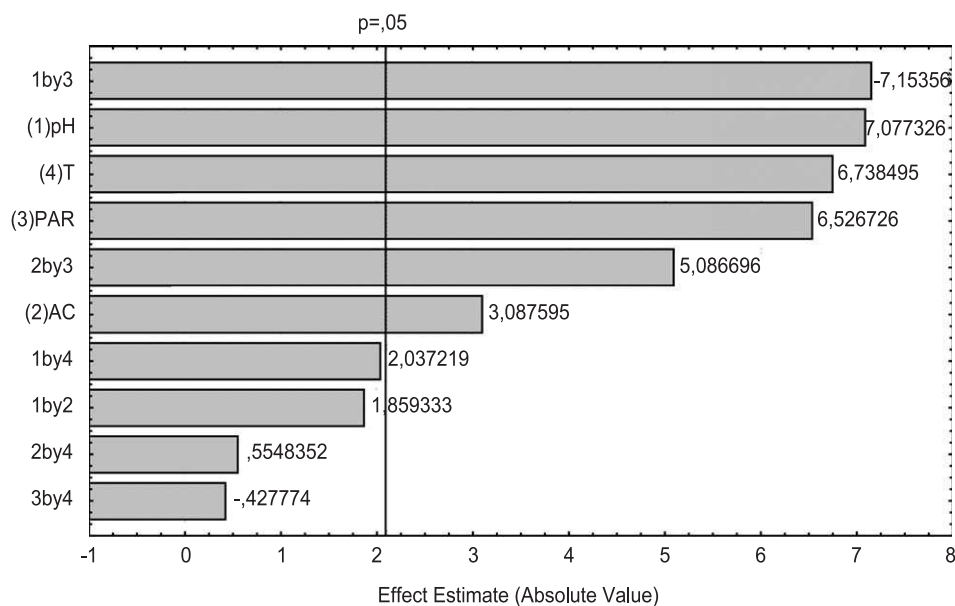
The maximum values are PAR=9194 μg and pH=10.09.

Fig. 1. Pareto chart of standardized effects for variables in the cadmium extraction.

Table 4
Doehlert matrix for design 1

Experiment	PAR mass (μg)	pH	Cadmium recovery (%)	
			Experimental	Expected
1	2550	9.00	92.5	91.4
2	8775	10.00	97.7	97.0
3	15 000	9.00	96.7	93.7
4	15 000	7.00	94.3	92.6
5	8775	6.00	91.1	89.1
6	2550	7.00	84.3	84.6
7	8775	8.00	96.2	94.8

$R=0.979$.

Table 5
Doehlert matrix for design 2

Experiment	Activated carbon mass (mg)	Time (min)	Cadmium recovery (%)	
			Experimental	Expected
1	162.5	10	92.6	93.3
2	200.0	30	93.2	92.8
3	162.5	50	91.3	93.0
4	87.5	50	93.1	93.3
5	50.0	30	86.5	87.6
6	87.5	10	88.7	88.0
7	125.0	30	93.2	93.5

$R=0.950$.

3.2.2. Design 2—conditions of active carbon mass and shaking time for cadmium extraction

To optimize the other variables the activated carbon mass and shaking time were varied, while the pH was fixed at 10.0 and the PAR mass at 9194 μg, considering the results obtained in the design 1. The seven experiments required for this Doehlert design are described in Table 5. Shaking time and activated carbon mass varied from 10 to 50 min and from 50 to 200 mg, respectively.

The obtained data were used in the Doehlert matrix and the equation below illustrates the relationship among activated carbon mass, shaking time and cadmium extraction (%).

$$\% \text{ Cd extraction} = 69.249 + 0.239\text{AC} + 0.418T$$
$$- 5.911 \times 10^{-4}\text{AC}^2 - 0.002\text{AC} \cdot T$$
$$- 0.002T^2 \quad (3)$$

The corresponding surface response is shown in Fig. 3. The determination coefficient for correlation among the values of cadmium extraction (%) experimental and predicted is 0.950, demonstrating a good fit for the model.

The application of Lagrange's criterium in this equation shows that:

$$H(a_o, b_o) = 7.28 \times 10^{-7}$$

$$\delta^2 Y/\delta \text{AC}^2 = -0.004$$

$$\delta^2 Y/\delta T^2 = -1.182 \times 10^{-3}$$

These results indicated that there was a maximum on the surface response, and it was calculated by the following equations:

$$\delta \text{Cd extraction}/\delta \text{AC} = 0 = 0.239 - 1.182 \times 10^{-3}\text{AC}$$
$$- 0.002T \quad (3')$$

$$\delta \text{Cd extraction}/\delta T = 0 = 0.418 - 0.002\text{AC} - 0.004T \quad (3'')$$

The maximum values are AC=168 mg and T=21.2 min.
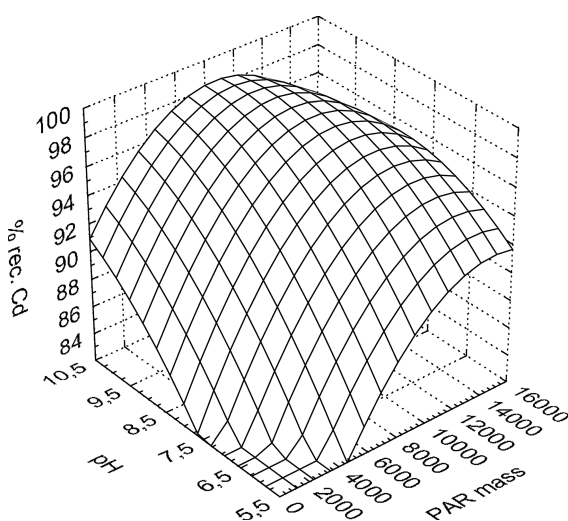

Fig. 2. Surface response for cadmium extraction (%). Cadmium concentration=12.50 μg l^{-1}. Synthetic seawater volume=800 ml, activated carbon mass=200 mg. Shaking time=50 min, pH=6.00–10.00, PAR mass=2550–15,000 μg.
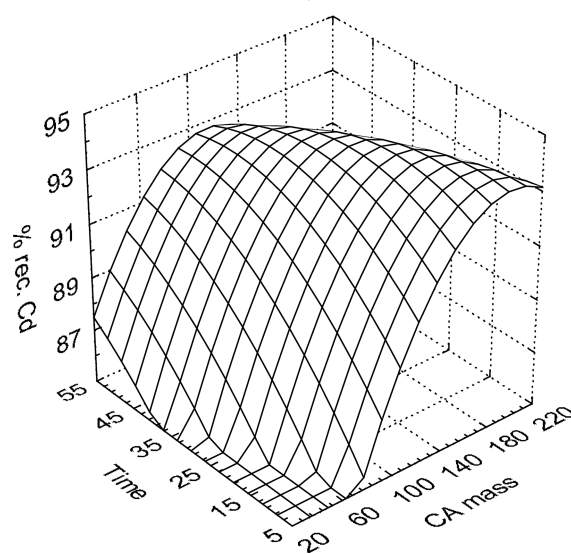

Fig. 3. Surface response for cadmium extraction (%). Cadmium concentration=12.50 μg l^{-1}. Synthetic seawater volume=800 ml, pH=10.0, PAR mass=9194 μg. Activated carbon mass=50–200 mg. Shaking time=10–50 min.
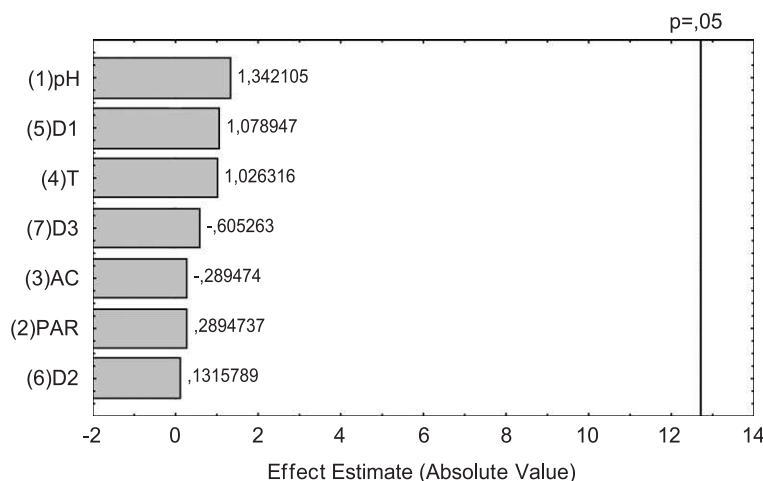
Fig. 4. Pareto chart of standardized effects for robustness study in the cadmium extraction.

3.3. Recommended preconcentration procedure

Evaluating the results obtained, the procedure for cadmium preconcentration in high salt samples recommends the use of the general procedure, described in the experimental part, using a PAR mass of 9194 µg, pH 10.0, activated carbon mass of 168 mg and shaking time of 21.2 min.

3.4. Analytical figures of merit

For a sample volume of 800 ml, the procedure demonstrated a linear calibration curve within the concentration range from 0.0 to 1.25 µg l^{-1}. The calibration graphs obtained were given as (AS)=0.00185+0.0477 [Cd µg l^{-1}] (R^2=0.9984), which compared with data found by using direct aspiration in FAAS without preconcentration (in the concentration range between 0 and 200 µg l^{-1}) (AS) =0.00173+0.00032 [Cd µg l^{-1}] (R^2=0.9997), provides a experimental preconcentration factor [30] of 149.

The precision of procedure proposed, calculated as relative standard deviation (RSD), was 5.4% for cadmium concentration of 62.5 ng l^{-1} in synthetic seawater solution for a series of 11 replicates.

The sensitivity, following IUPAC recommendation, was studied by means of the detection (LOD) and quantification (LOQ) limits, defined as LOD=(3σ)/S and LOQ =(10σ)/S, where S is the slope of the analytical curve, and σ is the standard deviation of 10 consecutive measurements of the blank. LOD and LOQ are 8.3 and 27.7 ng l^{-1}, respectively.

In order to check the efficiency of the proposed procedure, a robustness test was carried. Thus, it was used a saturated fractional factorial design (2^{7-4}), centered on the nominal values of the experimental variables (pH=10.0, activated carbon mass=168 mg, PAR mass=9194 µg and shaking time=21.2 min), with a variation of (±10%). In order not to modify the structure of the design, three dummy variables were added. The results achieved, considering the

analysis of variance (ANOVA) and shown in the Pareto Chart (Fig. 4), demonstrate that the proposed procedure is robust for variation of (±10%) of the variables activated carbon mass, PAR mass and shaking time and (±1.0) units of pH value established as optimum.

3.5. Effect of foreign ions

The influence of some metallic ions in the proposed system was also investigated. Cadmium (1.00 and 10.00 µg) and other metallic ions (all 1.00 and 10.00 µg, respectively) were added to 800 ml of synthetic seawater and the optimized procedure was applied. This experiment was carried out using a multielemental ICP OES solution Quality

Table 6
Determination of cadmium in real samples (*n*=3)

Sample	Location	Added cadmium (µg l^{-1})	Achieved cadmium[a] (µg l^{-1})	Recovery (%)
Seawater	S 13°00′ 08.5″	0	0.035±0.004	–
Porto da Barra	W 38°31′ 56.6″	0.125	0.164±0.024	103.2
Seawater *Ondina*	S 13°00′ 38.0″	0	0.110±0.030	–
	W 38°30′ 38.7″	0.125	0.230±0.020	96.0
Seawater	S 12°56′ 27.9″	0	0.170±0.020	–
Stella Maris	W 38°20′ 10.6″	0.625	0.290±0.030	96.7
Seawater	S 12°59′ 56.8″	0	0.100±0.030	–
Amaralina	W 38°25′ 52.0″	0.125	0.230±0.050	104.0
Seawater	S 13°00′ 39.1″	0	0.070±0.010	–
Rio Vermelho	W 38°30′ 05.2″	0.125	0.200±0.040	106.7
Seawater *Pituba*	S 12°59′ 50.7″	0	0.035±0.004	–
	W 38°26′ 32.0″	0.125	0.146±0.017	98.3
Seawater	S 12°55′ 50.2″	0	0.046±0.002	–
Monte Serrat	W 38°30′ 56.2″	0.125	0.167±0.017	96.7
Saline Effluent 1	–	0	0.19±0.03	–
of *Petroleum*		0.625	0.80±0.18	98.0
Refinery				
Saline Effluent 2	–	0	0.28±0.08	–
of *Petroleum*		0.625	0.90±0.15	99.2
Refinery				

[a] At 95% confidence level.

Control Standards (QCS-19), which had arsenic, antimony, beryllium, cadmium, calcium, chromium, cobalt, iron, molybdenum, nickel, thallium, titanium, zinc, lead, magnesium, manganese and selenium at the concentration of 100 μg ml^{-1} each. The achieved results were 1.26 ± 0.05 μg (n=3) and 12.08 ± 0.33 μg (n=3) for 1.25 and 12.50 μg l^{-1} of cadmium with recoveries of 96.6% and 101.0%, respectively. The results indicate that all studied cations not interfere.

3.6. Application

The studied procedure was applied for the preconcentration and determination of cadmium in surface seawater samples collected from several beaches of Salvador City, Brazil and saline effluents of an oil refinery. The samples were spiked with cadmium at concentrations of 0.125 or 0.625 μg l^{-1}. Table 6 shows that the procedure is not affected by matrix interferences and can be applied satisfactorily for cadmium determination in high salt samples with good accuracy. Found data were consistent with those reported in literature as can be seen in the Table 1. The cadmium content for the seawater samples collected was lower than the maximum permissible level (5.0 μg l^{-1}) for cadmium in seawater as Environment National Advice [31].

4. Conclusions

The use of adsorption of the complex cadmium(II)−PAR on activated carbon has been efficient for preconcentration and determination of cadmium by FAAS. The variable optimization using the Doehlert designs can be performed simply, quickly and with greater efficiency compared to univariated methodology.

A low detection limit, 8.3 ng l^{-1} (3σ, n=10), and an enrichment factor of 149 are the main advantages of this analytical procedure. The preconcentration system proposed is simple, efficient and can be used for cadmium determination in high salt samples with good accuracy and precision.

The results found for cadmium determination in seawater and saline water samples collected in Salvador City, Brazil showed good agreement with other reported data in the literature.

References

[1] M. Zougagh, A.G. Torres, J.M.C. Pavón, Talanta 56 (2002) 753.
[2] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta 58 (2002) 831.
[3] P. Pohl, B. Prusisz, Anal. Chim. Acta 502 (2004) 83.
[4] H. Chen, J. Jin, Y. Wang, Anal. Chim. Acta 353 (1997) 181.
[5] S. Saracoglu, M. Soylak, L. Elci, Talanta 59 (2003) 287.
[6] K. Kongolo, M.D. Mwema, A.N. Banza, E. Gock, Miner. Eng. 16 (2003) 1371.
[7] D. Kara, M. Alkan, Microchem. J. 71 (2002) 29.
[8] A. de Freitas Júnior, M.G.A. Korn, H.V. Jaeger, A.C.S. Costa, Quím. Nova 25 (2002) 1086.
[9] C.J. Cheng, T. Akagi, H. Haraguchi, Anal. Chim. Acta 198 (1987) 173.
[10] S. Saraçoglu, L. Elçi, Anal. Chim. Acta 452 (2002) 77.
[11] U. Divrikli, L. Elçi, Anal. Chim. Acta 452 (2002) 231.
[12] P.J. Statham, Anal. Chim. Acta 169 (1985) 149.
[13] L. Elçi, U. Sahin, S. Oztas, Talanta 44 (1997) 1017.
[14] M.C. Yebra, A. Garcia, N. Carro, A. Moreno-Cid, L. Puig, Talanta 56 (2002) 777.
[15] M.C. Yebra, J. Salgado, L. Puig, A. Moreno-Cid, Anal. Bioanal. Chem. 374 (2002) 530.
[16] E. Carasek, Talanta 51 (2000) 173.
[17] M.C. Yebra, A. García, N. Carro, A. Moreno-Cid, L. Puig, Talanta 56 (2002) 777.
[18] I. Narin, M. Soylak, Anal. Chim. Acta 493 (2003) 205.
[19] A. Ramesh, K.R. Mohan, K. Seshaiah, Talanta 57 (2002) 243.
[20] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, Anal. Chim. Acta 411 (2000) 223.
[21] D.C. Montgomery, Design and Analysis of Experiments, 4th ed., Wiley, New York, 1997.
[22] B.B. Neto, I.S. Scarminio, R.E. Bruns, Como Fazer Experimentos, UNICAMP, Campinas, 2001.
[23] D.H. Doehlert, Appl. Stat. 19 (1970) 231.
[24] S.L.C. Ferreira, W.N.L. dos Santos, C.M. Quintella, B.B. Neto, J.M. Bosque-Sendra, Talanta (2004) (in press).
[25] M. Nechar, M.F. Molina, J.M.B. Sendra, Anal. Chim. Acta 382 (1999) 117.
[26] S.L.C. Ferreira, H.C. dos Santos, M.S. Fernandes, M.S. de Carvalho, J. Anal. At. Spectrom. 17 (2002) 115.
[27] W.N.L. dos Santos, C.M.C. Santos, S.L.C. Ferreira, Microchem. J. 75 (2003) 211.
[28] S.L.C. Ferreira, A.S. Queiroz, H.C. dos Santos, M.S. Fernandes, Spectrochim. Acta, Part B: Atom. Spectrosc. 12 (2002) 1939.
[29] Statistica for Windows, StatSoft, Tulsa, USA, 1999.
[30] M.F. Enriquez-Dominguez, M.C. Yebra-Biurrun, M.P. Bermejo-Barrera, Analyst 123 (1998) 105.
[31] CONAMA—Conselho Nacional do Meio Ambiente, Resolução N. 20 (1986), http://www.mma.gov.br/part/conama.