Article

Determination of Copper and Cadmium in Petroleum Produced Formation Water by Electrothermal Atomic Absorption Spectrometry after Cloud Point Extraction

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Cloud point extraction (CPE) in association with graphite furnace atomic absorption spectrometry (GF AAS) was proposed for preconcentration and quantification of trace amounts of copper and cadmium in samples of saline produced formation water from petroleum exploration. The procedure was based on the formation of hydrophobic complexes of the analytes with 1,5-diphenylthiocarbazone (dithizone) in a micellar media of the surfactant (1,1,3,3-tetramethyl butyl) phenyl-polyethylene glycol (Triton X-114). Constrained mixture design was performed for the optimization of the proportions of the three solutions employed in the CPE: Triton X-114, dithizone, and buffer solution. Under the recommended conditions, the CPE GF AAS procedure allowed to obtain enrichment factors of 18 and 11 times, limits of quantification of 0.030 and 0.12 µg L^{-1} and precision, expressed as relative standard deviation (RSD, n = 8, 2.0 µg L^{-1}), of 1.1 and 4.3% for copper and cadmium, respectively. The CPE GF AAS method was applied to the determination of copper and cadmium in samples of saline produced formation water from petroleum exploration, and its accuracy was accessed by analyzing certified reference material CASS-5 (Nearshore Seawater Reference Material for Trace Metals) from National Research Council (Canada).

Keywords: produced-formation water, constrained mixture design, cloud-point extraction, cadmium, copper

Introduction

Petroleum produced-formation waters (PFW) is typically generated along with oil or effluents resulting from the separation processes in existing gathering and treatment stations in the oil production.[1] The environmental hazards associated with the produced-formation water may vary depending on the composition of the water, the characteristics of the rocks in which it occurs and of its final disposal. It is a practice throughout the oil industry, physically separating water from fluids and then discard them directly into the ocean or injecting it back into the wells or other suitable geological formations, with or without further treatment.[2] The PFW is a complex mixture constituting of the injection water, hydrocarbons residual, metals in the form of inorganic salts, radioactive materials and chemical residues added during the production and treatment process in the extraction.

Toxic metals can influence the biodegradation of organic substances by altering the activity or the microbial population. Various elements such as lead, cadmium, nickel, chromium, copper, and zinc have been studied demonstrating this action.[3-5] Among the metals of environmental interest, copper stands out for problems to the aquatic environment, since they exhibit the same toxicity, persistence, and bioaccumulation in the food

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chain.[6] Cadmium is captured and retained by terrestrial and aquatic plants and can be concentrated in the liver and kidneys of animals that feed on these plants.[4,7] The effects of these toxic metals on aquatic organisms include changes in growth, reproduction, and distribution of the population.[8]

In the final of the past century, there has been a breakthrough in the development of analytical instrumentation with the ability to determine concentrations of the analytes in trace amounts.[9] Several equipments with high sensitivity and low detection limits have been developed; however, there are few analytical techniques that allow sample introduction without pretreatment. The analyzes in environmental chemistry are hampered because usually, the samples to be studied exhibit complex matrices that prevent or hinder the determination of the species of interest.[10] Therefore, sample treatment is considered a crucial step in the chemical analysis process.

Cloud-point extraction (CPE) has been one of the most efficient techniques for separation and pre-concentration of metal ions and traces elements.[11-14] The cloud point is a phenomenon in which an aqueous surfactant solution becomes cloudy by adding an appropriate substance or by changing some of its properties such as temperature or pressure.[15] The use of the CPE has been described in various types of matrices and also coupled to different detection techniques for the determination of inorganic species among which are inductively coupled plasma optical emission spectrometry (ICP OES),[2,16] flame atomic absorption spectrometry (F AAS),[6,17] thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS),[18] spectrophotometry UV-Vis,[19] and graphite furnace atomic absorption spectrometry (GF AAS).[12]

In the present paper, CPE, in association with GF AAS, is proposed for preconcentration and determination of copper and cadmium in samples of PFW. The procedure was based on the formation of hydrophobic complexes of the analytes with 1,5-diphenylthiocarbazone (dithizone) in a micellar media of the surfactant (1,1,3,3-tetramethyl butyl) phenyl-polyethylene glycol (Triton X-114). Constrained mixture design was performed for the optimization of the proportions of the three solutions employed in the CPE: Triton X-114, dithizone, and buffer solution.

Experimental

Instrumentation

Metals determination were made using a AAnalyst 400 graphite furnace atomic absorption spectrometer, equipped with a background corrector with deuterium arc lamp, graphite furnace (with integrated platform and covered with pyrolytic graphite) as an atomizer, hollow cathode lamps and an AS 800 autosampler (PerkinElmer, Norwalk, CT, USA). All measurements were performed at the highest sensitivity wavelength indicated by the equipment for each element: 228.80 nm (Cd) and 283.31 nm (Cu). High purity argon gas (99.99%, Itaox, Brazil) was used for the purging and protection of the graphite furnaces. A centrifuge Quimis Q222T model (São Paulo, Brazil) with a capacity of sixteen tubes of 15 mL was used to accelerate the separation of the surfactant-rich phase from the aqueous phase. A system Elga (Purelab Classic) was used to obtain ultrapure water (conductivity of 18 MΩ cm).

Reagents and solutions

Chemicals used in this work were of analytical purity grade, and the solutions were prepared with ultrapure water. The stock solutions (1000 mg L^{-1}) of copper and cadmium were individually prepared from the dilution 1% HCl (v v^{-1}) of the standard solution (Merck, Darmstadt, Germany). Dithizone (Sigma-Aldrich, Milwaukee, USA, purity > 98%) solution was prepared in the concentration of 0.040% (m v^{-1}) from dissolving a mass of 0.0040 g of the reagent to a volume of 10.0 mL with 95% hydrated ethyl alcohol (Exodo Científica, São Paulo, Brazil). A solution of 10% (v v^{-1}) Triton X-114 (Sigma-Aldrich, Milwaukee, USA) surfactant was prepared by diluting 10.0 mL of the concentrated surfactant to a final volume of 100.0 mL with ultrapure water and solubilized by ultrasound energy. A 1.0% (v v^{-1}) HNO$_3$ solution for decrease the viscosity of the surfactant rich phase was prepared by diluting 1.0 mL of HNO$_3$ in ethanol. Solutions of sodium chloride at concentrations between 1 and 8% (m v^{-1}) were prepared by dissolving an adequate amount of NaCl in deionized water to obtain the desired concentrations. Buffer solutions (0.1 mol L^{-1}) were prepared for the pH values 4.0, 5.0, 6.0, 7.0, 9.0 and 10.0 using acetic acid/sodium acetate, tris-(hydroxymethyl)-aminomethane/HCl or boric acid/sodium borate (Sigma-Aldrich, Milwaukee, USA). Palladium nitrate solution and magnesium nitrate (1000 mg L^{-1}) (Merck, Kenilworth, USA) were used as chemical modifiers to stabilize the analytes in the pyrolysis step, allowing a higher temperature to be used. The proportion of Pd/Mg adopted was 5:3 (v v^{-1}).

Sample collection and treatment

The produced-formation water samples were collected from offshore drilling petroleum platforms using polyethylene bottles pre-decontaminated with a 5% (v v^{-1}) HNO$_3$ solution. The samples were filtered through membranes of pore size 0.45 μm with the aid of a

filtration system that operates under vacuum to remove the suspended particulate matter. These samples were subsequently acidified to pH < 2 with nitric acid and cooled in a refrigerator to ensure the stability of trace elements. Sample salinities were determinate by titration with $AgNO_3$. Samples have presented salinities in the range of 1.5 to 7.5%.

Optimization of the method

The variables volume of the surfactant Triton X-114 10% (v v^{-1}), volume and concentration of the complexing agent (dithizone), pH value, volume of buffer solution, volume of 1% NaCl solution, and volume of the diluent (1% HNO_3 solution) were studied in the optimization process. A constrained mixture design was used for multivariate optimization of the proportions of the mixture components that were added to 10-mL of the sample: solution of surfactant 10% (v v^{-1}) Triton X-114, buffer solution and 0.04% (m v^{-1}) dithizone solution.

Aiming to choose the best conditions for Cu and Cd complexation by dithizone, pH values were evaluated between 4.0 and 10.0. In the optimization of the surfactant volume was studied volumes in the range of 50 to 350 μL. The volume of solution complexing reagent dithizone was studied in the range between 50 and 350 μL considering fixed values of the other variables, except those determined by previous studies of pH and volume of surfactant. It was also studied the optimal value of diluents micellar phase and the influence of the concentration of electrolyte, by determining the optimum amount of 1% NaCl in the range 0-175 μL.

Optimization of the GF AAS heating program

As the surfactant-rich phase has very different characteristics from an aqueous solution usually analyzed by GF AAS, the pyrolysis and atomization temperatures were studied to obtain the best performance. The modifier Pd/Mg was used in the analysis, considering that cadmium is an element of high volatility.

Cloud point extraction procedure

The sample was put in a polyethylene centrifuge tube, buffered with a solution 15 mmol L^{-1} of acetic acid/sodium acetate (pH 5.0) for the extraction of copper and 20 mmol L^{-1} solutions of boric acid/sodium borate (pH 9.0) for extraction of cadmium. A volume of 100 μL of the dithizone solution and a volume of 150 μL of the Triton X-114 10% (v v^{-1}) solution were added to 10 mL of the sample. A 10% (m v^{-1}) NaCl solution was also added to favor the separation of surfactant-rich phase from the aqueous phase. To allow the phases separation, the system was centrifuged for 8 min and then subjected to an ice bath for 10 min. The aqueous phase was discarded by inversion of the tube. The micellar phase was diluted with 1% (v v^{-1}) HNO_3 ethanolic solution and analyzed by atomic absorption spectrometer graphite furnace for the determination of metals.

Results and Discussion

Optimization of the heating temperature

The study of the pyrolysis and atomization temperatures was performed in the micellar phase obtained after application of the CPE for the determination of copper and cadmium in PFW samples (Figure 1). For Cu and Cd, Pd/Mg modifier allows pyrolysis temperatures of 1200 and 500 °C and atomization temperatures of 2400 and 2200 °C, respectively. The heating programming established is presented in Table 1.

Optimization of the method

The pH is a variable that has a significant effect on the extraction in the CPE of metallic analytes. In the case of metals, the extraction is done after the formation of chelates, whose complexation reaction is more effective at a certain pH range. The process is dependent on several factors, such as the distribution of the chelating between the aqueous and micellar phases, acid dissociation of the complexing agent, the formation of the hydrophobic chelate, and its

Table 1. Heating programming for determining copper and cadmium in the micellar phase obtained after cloud point extraction

Step	Temperature for Cu / °C	Temperature for Cd / °C	Ramp / s	Hold / s	Air flow rate / (mL min^{-1})
Drying 1	100	100	5	20	250
Drying 2	140	140	15	15	250
Pyrolysis	1200	500	10	20	250
Atomization	2400	2200	0	5	0
Clean	2600	2600	1	5	250

(a)   (b)
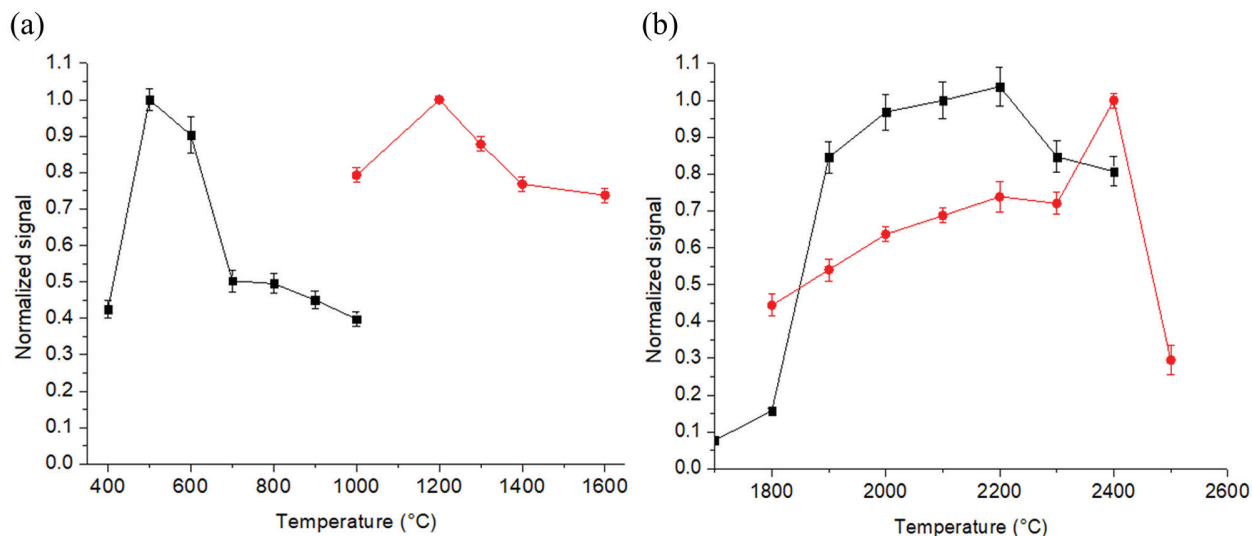
Figure 1. (a) Pyrolysis curves in the surfactant rich phase with atomization temperature at 2200 and 2100 °C for Cu (●) and Cd (■), respectively. (b) Atomization curves in the surfactant rich phase with pyrolysis temperature at 1200 and 500 °C for Cu (●) and Cd (■), respectively.

distribution in the micellar phase. The acid dissociation of the chelating agent is directed as a function of pH, and this will determine whether the metal will be complexed or not.

The effect of pH on the copper and cadmium extraction with dithizone was evaluated. The study of this variable was carried out between pH values 4.0 and 10.0, obtaining the values of absorbance *versus* pH (Figure 2a). The values of the other variables were set at 20 mmol L^{-1} for the buffer solution concentration, 0.020 mmol L^{-1} for the dithizone concentration, 0.2% (v v^{-1}) for the Triton X-114 solution concentration, 50 μL of NaCl (10% m v^{-1}) for a sample final volume of 10.0 mL. Copper and cadmium have better extraction levels at different pH ranges. The best absorbance signal for copper extraction occurred at pH 5.0, while for cadmium, the best pH was between 8.0 and 10.0. Even the cadmium having a broader range of optimum value, the intermediate value 9.0 was chosen because it is more robust and does not affect the absorbance too much if there are variations to its surroundings. Aiming to study the other variables, the optimum pH values of 5.0 and 9.0 were set for copper and cadmium, respectively.

The study of the concentration of buffer solution on the extraction of the metal has the objective of discovering the concentration capable of buffering the sample without causing a decrease in the analytical signal. For copper, for example, the decrease in response after 20 mmol L^{-1} concentration was noted (Figure 2b), probably due to reactions competition of the acetate and the dithizone with the analyte. It is verified that concentrations between 15 and 20 mmol L^{-1} are the optimal values for Cu and Cd extraction.

The enrichment factor of the analyte depends on the ratio between the volume of the surfactant-rich phase and the bulk aqueous phase. A higher volume of the rich phase gives lower enrichment factors and *vice versa*. On the other hand, a very small volume of surfactant may not be sufficient to extract all the metal chelate present in the solution. To study this dependence, the concentration of the surfactant solution added was in the range of 0.05 to 0.35% (v v^{-1}). The optimum Triton X-114 concentration for copper and cadmium was 0.15% (v v^{-1}), as can be seen in Figure 2c, and was adopted for further experiments.

Separation of metallic analytes by CPE demand to form hydrophobic chelates, and they can be extracted by the micellar phase. A hydrophobic neutral chelate is a necessary condition for extraction when non-ionic surfactants are used. The complexing reagent 1,5-diphenylthiocarbazone (dithizone) was used to form stable and neutral complexes with both analytes, copper and cadmium. Figure 2d shows the variation of absorbance intensities along with the concentration variation of dithizone.

A concentration of 0.025 mmol L^{-1} was chosen for both copper and cadmium determination. It is possible to realize that the concentration of the complexing solution considerably affects the extraction of both metals. The excess of complexing solution does not favor extraction due to the salting in effect caused by the solvent (ethyl alcohol) used in the solubilization of the dithizone reagent. This behavior can be noted by reducing the absorbance value when increasing the concentration of the complexing solution in both metals since the increase in dithizone concentration was achieved by increasing the volume of the dithizone solution in ethanol 0.040% (v v^{-1}).

The surfactant phase obtained after extraction at the cloud point has a high viscosity, which makes it difficult to inject in the graphite tube, and it is necessary to dilute
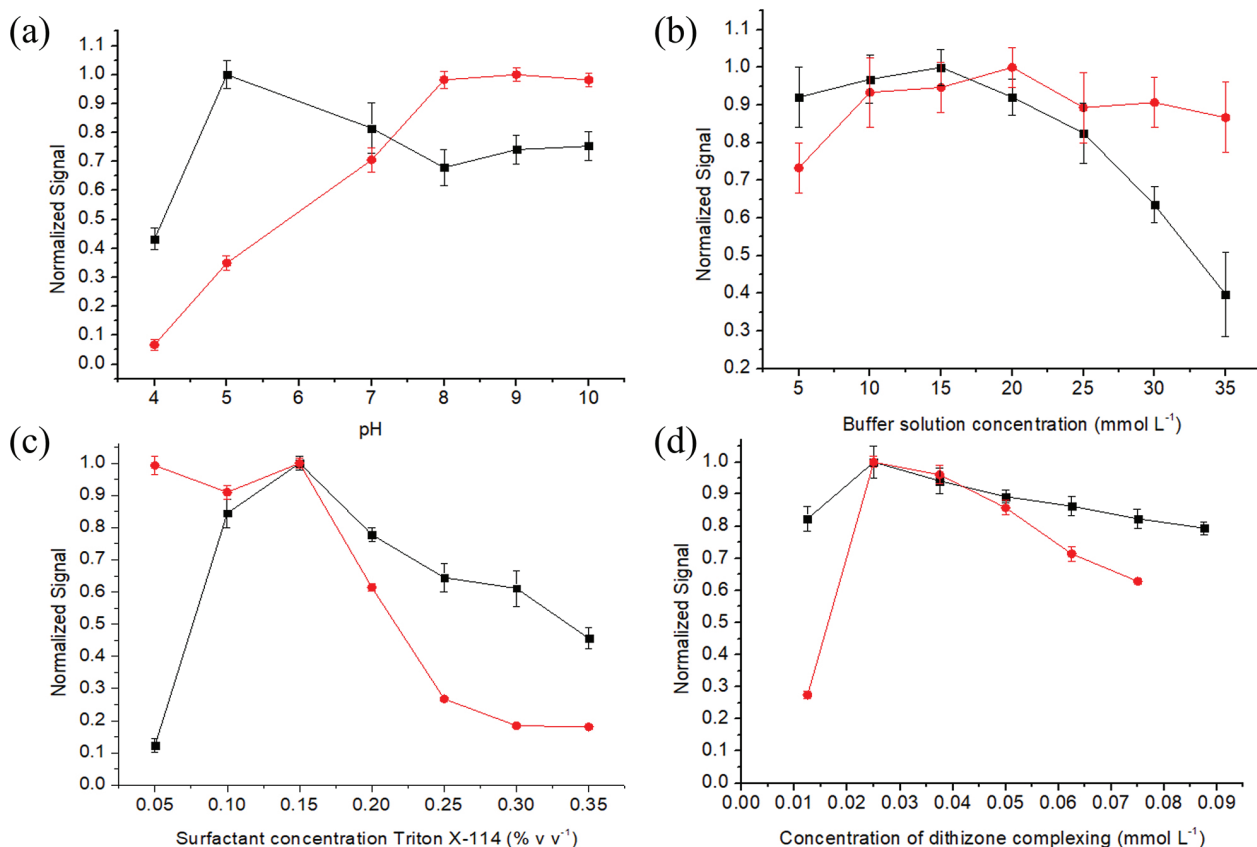
Figure 2. Studies for optimization of the CPE for copper (■) and cadmium (●): (a) effect of pH using 2.0 mL of buffer solution, 100 μL of dithizone complexing, 200 μL of Triton X-114 surfactant and 50 μL of 10% (m v⁻¹) NaCl solution; (b) effect of the concentration of the buffer solution using pH 5.0 and 9.0 for Cu and Cd, respectively, 100 μL of dithizone complexing, 200 μL of Triton surfactant X-114 and 50 μL of 10% (m v⁻¹) NaCl solution; (c) study of Triton X-114 surfactant concentration using 15 mmol L⁻¹ acetate buffer at pH 5.0, 20 mmol L⁻¹ borate buffer at pH 9.0, 100 μL of complex dithizone (0.040%, m m⁻¹) and 50 μL of 10% (m v⁻¹) NaCl solution and (d) effect of the concentration of complexing solution using 15 mmol L⁻¹ acetate buffer solution pH 5.0 (Cu), 20 mmol L⁻¹ borate buffer solution pH 9.0 (Cd), 0.15% (v v⁻¹) Triton X-114 surfactant and 50 μL 10% (m v⁻¹) NaCl solution.

it. The best responses were obtained for values lower than 50 μL and, when no volume of diluent was added, the error caused was very large. Therefore, a volume of 50 μL of the HNO₃ ethanolic solution was chosen for dilution of the surfactant phase.

Multivariate optimization

Aiming to increase the extraction performance, a constrained mixture design was applied to optimize the proportions of the solutions that promote the cloud-point extraction of the analytes. The applied constraints delimited the experimental region avoiding undesirable experimental conditions. Table 2 presents the established constraints for each variable, and Table 3 presents the experimental matrix and obtained responses (absorbances for Cu and Cd).

From the data of Table 3, mathematical functions (linear, quadratic, and special cubic) were fitted to describe the behavior of the data and to allow the location of the optimal experimental conditions. The linear models for the responses of both extracted metals leaving residuals (the

difference between the value found experimentally and that predicted by the mathematical function) were very large and therefore present a low predictive capacity.

For copper data, the quadratic and special cubic models were also fitted. These two models adequately described the experimental region. However, because the quadratic model is simpler, it was chosen to optimize copper extraction (equation 1):

$$y_{Cu} = -0.0710x_1 + 0.0202x_2 + 0.00868x_3 + 0.133x_1x_2 + 0.169x_1x_3 + 0.0173\ x_2x_3 \quad (1)$$

where y_{Cu} is the predicted response, x_1 is the proportion of the surfactant solution, x_2 is the proportion of the buffer solution, and x_3 is the proportion of the complexing solution. Figure 3a shows the response surface described by this quadratic model. This surface has a maximum point as a critical point. The coordinates of this point (indicated by the black arrow in Figure 3a) are the proportions of the components that generate the highest response (absorbance) for the studied system. The optimum volumes found for

Table 2. Low and high constraints for mixture design

Mixture variable	Symbol	Low constraint (−1)	High constraint (+1)
Surfactant volume / μL	SV	50	350
Buffer volume / μL	BV	1800	2400
Complexing volume / μL	CV	50	350

copper extraction were 155 μL (6.2%) of the surfactant solution, 2140 μL (85.6%) of the acetate buffer solution, and 205 μL (8.2%) of the complexing solution.

For the cadmium data, only the special cubic model described the data behavior. Therefore, it was chosen to optimize the extraction of cadmium (equation 2):

$$y_{Cd} = -0.0950x_1 + 0.033x_2 - 0.252x_3 + 0.336x_1x_2 + 1.132x_1x_3 + 1.5x_2x_3 - 2.176x_1x_2x_3 \qquad (2)$$

where y_{Cd} is the predicted response, x_1 is the proportion of the surfactant solution, x_2 is the proportion of the buffer solution, and x_3 is the proportion of the complexing solution. Figure 3b shows the response surface described by the cubic model. This surface has a cell point as a critical point. The coordinates of this point cannot be taken with

the optimal proportions of the components since the cell point is only an inflection point between the regions of greatest and lowest surface response. As the intention is to maximize the response, the optimal condition (point indicated by black arrow in Figure 3b) was found by visual inspection and the recommended volumes found for the extraction of cadmium were 50 μL (2%) of the surfactant solution, 2100 μL (84%) of the acetate buffer solution and 350 μL (14%) of the complexing solution.

Studies of interferences

The influence of some metal ions that form complexes with dithizone was investigated to identify possible interferents of the CPE method. The studied metal ions were Ca^{2+}, Mg^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+} and Zn^{2+}. The atomic absorption spectrometry is a very selective technique and, in general, does not suffer appreciable influence due to the presence of other metals than the one of interest. However, metals complexes with the dithizone and can compete with the complexation of the metal of interest and decrease the extraction efficiency. The tests were performed in the presence of 10 μg L^{-1} of the analytes.

An interference was considered when the signal in the presence of the potential interfering ion caused a

Table 3. Experimental matrix and responses used for the optimization of the proportions of the solutions used in the CPE

Experiment	Variables			Analytical signal[a]	
	SV	BV[b]	CV	Cu	Cd
1	50	2400	50	0.072	0.031
				0.081	0.027
2	350	2100	50	0.040	0.067
				0.028	0.052
3	50	2100	350	0.068	0.270
				0.076	0.232
4	350	1800	350	0.048	0.112
				0.048	0.099
5	50	2250	200	0.08	0.273
				0.102	0.250
6	350	1950	200	0.041	0.098
				0.032	0.111
7	200	2250	50	0.088	0.058
				0.096	0.065
8	200	1950	350	0.101	0.153
				0.084	0.165
9	200	2100	200	0.088	0.155
				0.101	0.137

[a]Measurements made in duplicate; [b]buffer acetate (pH 5.0) for Cu and buffer borate (pH 9.0) for Cd. SV: surfactant volume; BV: buffer volume; CV: complexing volume.
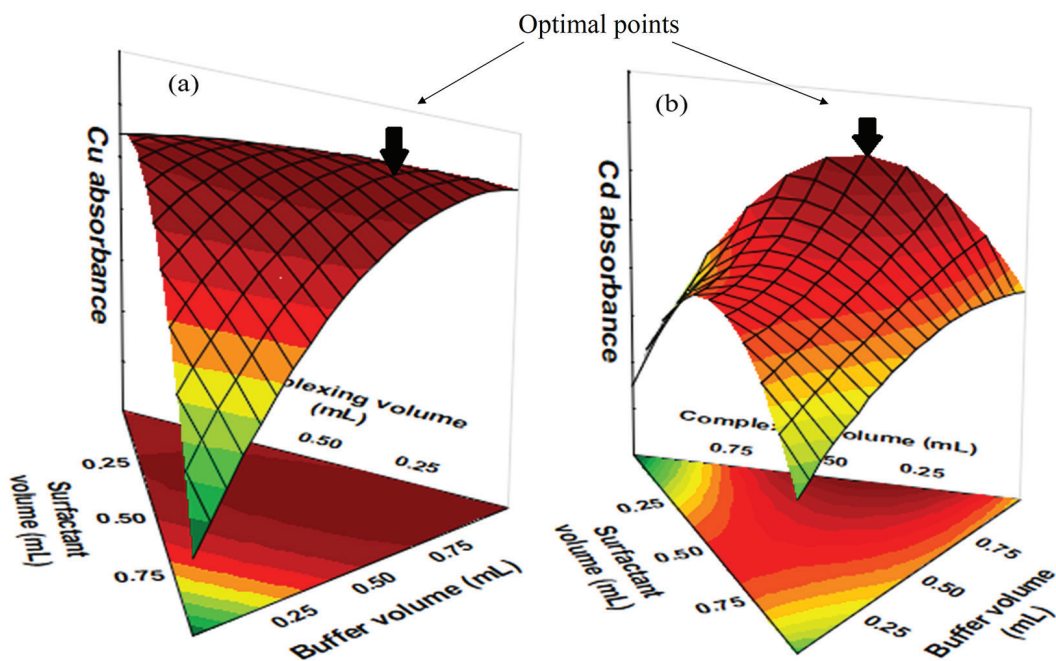
Figure 3. Response surfaces obtained by (a) quadratic model to the data of copper and (b) special cubic model to the data of cadmium.

change of 10% in the analytical signal, compared with the signals of Cu and Cd determination in the absence of interfering metals. For Ca and Mg, concentrations greater than 200 µg mL^{-1} affected the signal magnitude. For the other tested species, no interference was observed until concentrations of 300 µg mL^{-1}.

Analytical characteristics

After established the conditions for extraction of copper and cadmium from saline samples using the CPE, the analytical characteristics of the method were accessed. Enrichment factors were calculated by the ratio of the angular coefficients of the curve obtained by the preconcentration process and the curve obtained by direct aspiration of the standard solutions (without preconcentration). Linearity for the determination of each element was evaluated, accessing their determination coefficients (R^2). Limits of detection (LOD) and limits of quantification (LOQ) were calculated based on the standard deviation (s) of ten measures of the blank solution, according to the following expressions: LOD = 3s / m and LOQ = 10s / m, where m is the slope of the analytical curve. Precision was investigated in the form of repeatability using ten measurements for each element at 2.0 µg L^{-1} and expressed as relative standard deviation (RSD, in percentage). Values found for these and other analytical characteristics are presented in Table 4.

The accuracy of the proposed method was evaluated by analysis of the certified reference material

Table 4. Analytical characteristics of the developed method based on cloud-point extraction of analytes and determination by GF AAS

Analytical characteristics	Analytes	
	Cu	Cd
Worked concentration range / (µg L^{-1})	0.030-5.0	0.12-5.0
Linearity (R^2)	0.9990	0.9860
Sensitivity / (L µg^{-1})	0.201	0.231
Limit of detection / (µg L^{-1})	0.010	0.041
Limit of quantification / (µg L^{-1})	0.030	0.12
Enrichment factor	18.0	10.6
Repeatability (RSD, 20 µg L^{-1}) / %	1.1	4.3

CASS5 (Nearshore Seawater Reference Material for Trace Metals) from National Research Council (Canada). For copper, found values by application of the CPE GF AAS methodology (0.395 ± 0.035 µg L^{-1}) were not statistically different from the certified value (0.380 ± 0.03 µg L^{-1}). Cadmium was below the limit of detection in this material, and it was not determinate. An addition/recovery test was carried out in one PFW sample for both metals. Recoveries between 91 to 107% were obtained.

The analytical method was applied in the determination of Cu and Cd in ten petroleum formation-water samples and results are presented in Table 5. Copper concentrations ranged from < 0.030 to 2.29 µg L^{-1}, and cadmium ranged from < 0.12 to 2.14 µg L^{-1}. The concentrations of copper and cadmium found in the samples are in the range of concentration below the limit established by CONAMA

Table 5. Results of the determination of Cu and Cd in produced-formation waters samples applying the developed CPE GF AAS method

Sample	Cu / (μg L^{-1})	Cd / (μg L^{-1})
1	1.96 ± 0.05	2.1 ± 0.2
2	1.8 ± 0.1	1.41 ± 0.01
3	1.71 ± 0.08	1.4 ± 0.2
4	1.5 ± 0.3	< 0.12
5	< 0.030	< 0.12
6	1.5 ± 0.4	< 0.12
7	1.15 ± 0.02	1.41 ± 0.04
8	1.07 ± 0.01	1.32 ± 0.02
9	2.3 ± 0.1	< 0.12
10	< 0.030	1.3 ± 0.2

Resolution No. 357, of March 17, 2005,[20] which calls for a maximum value of 5 μg L^{-1} of copper and cadmium in seawater where oil extraction takes place.

Conclusions

The proposed cloud-point extraction for cadmium and copper and the determination by graphite furnace atomic absorption spectrometry of trace amounts of these metals from matrices with high saline content such as produced-formation water proved to be an efficient method. The optimization studies allied with the use of constrained mixture design have to aid in finding the experimental conditions to extract efficiently these metals. The concentrations of copper and cadmium found in the samples were in the range of concentration below the limits established by the Brazilian environmental agency.

Acknowledgments

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