# *Article*

# Multivariate Optimization of a Simultaneous Cloud Point Extraction Procedure of Cd, Cu and Ni from Sediments Samples and Determination by ICP OES

*Leandro dos Santos, Queila O. dos Santos, Islania Moreno, Cléber G. Novaes,*
*Márcio J. S. dos Santos and Marcos A. Bezerra**

*Laboratório de Química Analítica (LQA), Núcleo de Química Analítica da Bahia (NQA),*
*Universidade Estadual do Sudoeste da Bahia, Campus de Jequié, 45506-191 Jequié-BA, Brazil*

A simultaneous preconcentration method for cadmium, copper and nickel in samples of sediments and determination by inductively coupled plasma optical emission spectrometry was developed. The method is based on the extraction of the metals as complexes formed with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) at cloud point of the nonionic surfactant polyethylene glycol tert-octylphenyl ether (triton X-114). Optimization was performed using a Doehlert design and constrained mixture design. Desirability function was used to provide a simultaneous optimization of the evaluated responses. The developed method presented limits of quantification of 0.066, 0.149 and 0.191 μg g$^{-1}$ and an enrichment factor of 18.4, 16.8 and 18.2 fold for cadmium, copper and nickel, respectively. The proposed method was applied in sediment samples collected in the urban stretch of the Contas River (Jequié, BA, Brazil). Adequate accuracy was found by analysis of two certified reference materials (NIST 1646a estuarine sediments and NIST 2702 marine sediment).

**Keywords:** sediments, cloud point extraction, multivariate optimization, metals, ICP OES

## Introduction

Sediments are deposits of rock debris (resulting from erosion, leaching and chemical precipitation) and organic waste (generated by living or dead organisms) formed in the Earth's surface in layers of loose particles, when the energy of fluid (water, ice or wind) that transport them decreases.[1] Sediments in rivers not only play an important role in understanding regarding water pollution, but can also record the history of the water body contamination by various substances over time.[2]

The determination of metal trace levels in complex matrices, such as sediments, has been a difficult task because of their low concentration levels and matrix effects, requiring the development of separation/pre-concentration procedures before the determination stage. Cloud point extraction (CPE) has been shown to be a powerful analytical tool in the separation and pre-concentration of metal ions and also of organic species in complex matrices, such as environmental and biological samples,[3-6] due to advantages like low cost, safety, speed, simplicity, high factors of pre-concentration and extraction efficiency, and being an

environmentally clean technique, as it does not use toxic organic solvents.[7-9]

The CPE procedure is based on the phenomenon that a aqueous solution of surfactant (non-ionic or amphoteric) in amounts above the critical micelle concentration (CMC) separates into two phases (the solution suddenly starts to get blurred, due to the decreased solubility of the surfactant in water) if some condition, such as temperature or pressure, is changed or if a suitable substance is added to the solution. The solution of the surfactant is separated because the cloud point of the surfactant has been reached. The two phases in which the original solution is separated can be classified into two distinct phases: a surfactant-rich phase (in a smaller volume), containing the desired analyte; and an aqueous phase of greater volume, which contains the original matrix and must be discarded.[10,11]

The importance of knowing the concentration of metals, such as cadmium (Cd), copper (Cu) and nickel (Ni) in sediments is necessary, since monitoring the quality of the sediments is already seen as a necessary extension to the protection of water quality, because sediments are the main recipients of most contaminants deposited in the water column by precipitation. This fact explains the importance of developing faster, more efficient, economic and reliable

*e-mail: mbezerra@uesb.edu.br

analytical methods for determination of these metals in sediment samples.[12]

Inductively coupled plasma optical emission spectrometry (ICP OES) has been widely used for determination of metals in various matrices, such as soils and sediments.[13-15] This technique can be combined with CPE to determine a wide range of analytes of highly variable nature,[16,17] given that it has a number of advantages, such as simultaneous multi element analysis, high sensitivity and accuracy, speed, and a wide linear dynamic range.[11,18] In this work, a methodology based on simultaneous extraction and pre-concentration of Cd, Cu and Ni in sediments and determination by ICP OES using a multivariate experimental design to optimize the experimental extraction conditions was developed.

In this study, it was used multivariate designs (Doehlert and constrained mixture design)[19-21] for the efficient optimization of variables that affect the performance of the extraction/pre-concentration of Cd, Cu and Ni at cloud point of the surfactant triton X-114, aiming to develop a method for determination of these metals at trace levels in sediment samples using ICP OES.

## Experimental

### Instrumentation

A simultaneous ICP OES from Perkin Elmer model Optima™ 7000 DV (Norwalk, CT, USA) with a charge-coupled device (CCD) as a detector was used for determination of Cd, Cu and Ni. The data were stored and processed using the software WinLab32 for ICP-OES. It was used a concentric pneumatic nebulizer and a double-pass Scott type expansion chamber. An axial view was used to determine the studied analytes. The metals' determination was carried out under the conditions shown in Table 1.

A centrifuge model Q022T294 (Quimis, São Paulo, SP, Brazil) was used to accelerate the separation of the surfactant rich-phase from the aqueous phase. An ultrasonic cleaner Maxclean model 1450 (Unique, Indaiatuba, SP, Brasil) was used for the solubilization of the water-surfactant during its preparation. A block digester Tecnal model 040125 (Piracicaba, SP, Brazil) was used for the treatment of the sediment samples and the certified reference materials.

### Reagents and solutions

All reagents used in the analysis were of analytical grade purity (PA). The ultrapure water was obtained using

**Table 1.** Instrumental parameters used for metal determination by inductively coupled plasma optical emission spectrometry (ICP OES) after cloud point extraction

| Parameter | Value |
| --- | --- |
| Radiofrequency power / kW | 1.3 |
| Nebulizer gas flow / (L min⁻¹) | 0.8 |
| Plasma gas flow / (L min⁻¹) | 15 |
| Auxiliary gas flow / (L min⁻¹) | 0.2 |
| Nebulizer pressure / kPa | 620 |
| Stabilization time / s | 15 |
| View | axial |
| Sample flow rate / (mL min⁻¹) | 1.5 |
| Emission wavelength / nm | |
| Cadmium | 228.802 |
| Copper | 327.393 |
| Nickel | 231.604 |

an Elga system model Purelab Classic (High Wycombe, UK). All glassware was decontaminated with 10% $HNO_3$ solution (v/v) for at least 24 h. After this period, it were rinsed with deionized water and dried in air under dust free environment.

Cadmium, nickel and copper solutions were prepared by diluting the respective standard solutions (Merck, Kenilworth, NJ, USA) 1000 µg mL⁻¹ conserved in a 1% hydrochloric acid solution. A solution of 100 mg L⁻¹ (m/v) 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP) was prepared dissolving 0.0100 g in a volume of 100 mL in ethyl alcohol (PA). A 10% (v/v) triton X-114 surfactant solution was prepared from dilution of 10 mL of the concentrated surfactant (Vetec, Rio de Janeiro, RJ, Brazil) to a final aqueous volume of 100 mL followed by solubilization using ultrasound energy. A solution of 10% (v/v) $HNO_3$ was used to decrease the viscosity of the surfactant-rich phase obtained after extraction. Acetate buffer solutions (pH 5 to 6), tris (pH 7 to 8) and borate (pH 9) were used for pH adjustment of the solutions.

### Sample treatment

The sediment samples were collected along the Contas River passing through the urban stretch of the city of Jequié, Bahia, Brazil. They were collected using an artisanal cylindrical sampler made by polyvinyl chloride (PVC), at 2 m distance from the river bank. The samples were placed in plastic bags, transported to the laboratory and dried at 60 °C for 24 h. Next, they were comminuted in mortar and pestle and sifted in sieves of 300 microns. Subsequently, 150 mg of the samples were digested by adding 10 mL of aqua regia in a digester block, for 4 h at 110 °C. Certified

reference materials, NIST 1646a (estuarine sediment) and NIST 2702 (marine sediment), were treated in the same way. After treatment, the samples were transferred to a beaker, had their pH neutralized and were diluted to 40 mL before carrying out the cloud point extraction procedure.

### Multivariate optimization

For the optimization of the cloud point extraction procedure, two types of multivariate experimental designs were applied: (*i*) a Doehlert design, to optimize the method's variables (pH and heating time) and (*ii*) a constrained mixture design, for the optimization of the proportions of the extraction-promoting agents solutions (a 10% triton X-114, 5-Br-PADAP and buffer solution pH 9). The Doehlert matrix used allowed studying the pH variable at five levels (5 to 9) and the heating time at three levels (0 to 20 min). In relation to the mixture design used, it was established some constraints (upper and lower limits) for the levels of the variables. These constricts were necessary to avoid the absence of some extraction, promoting agent in certain experiments set by the experimental matrix. The experiments were performed in random order and duplicated, so the experimental error could be estimated.

To allow the optimization of simultaneous extraction of the three metals studied, an approach developed by Derringer and Suich[22] was used. This optimization approach consists firstly in converting each response $y_i$ in an individual desirability function $d_i$, which varies within the range $0 \leq d_i \leq 1$. If the answer is the wanted one, $d_i = 1$, and if the answer is outside the acceptable region, $d_i = 0$. Accordingly, the levels of the factors are chosen to maximize the overall desirability (D) given by the equation 1, where m is the number of response variables:

$$D = \sqrt[m]{d_1 d_2 ... d_m} \qquad (1)$$

The responses were the emission intensity for each metal and were combined into a single response, overall desirability, using an appropriate mixed function for maximizing the answers.

In the optimization step, 40 mL of a standard solution of 10.0 µg L$^{-1}$ Cd, Cu and Ni was always used. The experimental data were processed using the Statistica® software.

### Cloud point extraction procedure after the optimization process

To carry out the cloud point extraction, a sample volume of 40 mL was set to pH 9 by addition of 1.8 mL

of a borate buffer solution. Then, 350 µL of 5-Br-PADAP (100 µg mL$^{-1}$) and 350 µL of triton X-114 (10%, v/v) were added and the solution was stirred. This system was heated at 60 °C for 20 min. Afterwards, the mixture was centrifuged for 10 min at 3,000 rpm for phase separation. Subsequently, the mixture was ice cooled for 10 min to increase the viscosity of the surfactant-rich phase. The aqueous phase was then discarded by the inversion of the tube. In the last stage, the volume was completed to 2.5 mL with a HNO$_3$ 10% solution (v/v) for the separation of the micellar phase and then the determination of Cd, Cu and Ni was performed by ICP OES.

## Results and Discussion

### Optimization of the experimental conditions

The temperature of the heating stage was fixed at 60 °C and the centrifugation time, in order to obtain separation of the surfactant-poor and -rich phases, was 10 min at 3,000 rpm. The Doehlert design was applied for optimization of two variables, pH and heating time. All experiments were performed through application of the Doehlert design matrix and are shown in Table 2.

To allow for the optimization of simultaneous extraction of the three metals, a desirability function was used to maximize the response. The global desirability value (which can vary from 0 to 1) at the optimum point was equal to 0.9900, showing that the optimum points of the three responses are very close and can be represented by a common point. Linear and quadratic functions were adjusted to obtain overall desirability, in order to describe its behavior in the experimental area and find the optimal conditions. According to analysis of variance (ANOVA, Tables 4a and 4b), both models have presented significant lack of fit ($F_{calculated} > F_{critical}$). However, quadratic model was chosen because shows a better coefficient of determination ($R^2$) and can be used to indicate tendencies. Surface generated by quadratic model is presented in Figure 1.

Using the overall desirability value found and the profile of the surface generated responses, it can be verified that the highest responses are obtained when all variables are at their superior level, that is, with a heating time equal to 20 min and extraction at pH 9. These values were fixed for the application of the mixture design.

The use of mixture design enables simultaneous optimization of the proportion of the promoting components for cloud point extraction, also enabling to evaluate the interactions between them. Such design aimed to optimize the following variables: volume of the solution of the surfactant triton X-114 10% (v/v), volume of the buffer

**Table 2.** Doehlert matrix for the optimization of the variables pH and heating time in simultaneous cloud point extraction of cadmium, copper and nickel

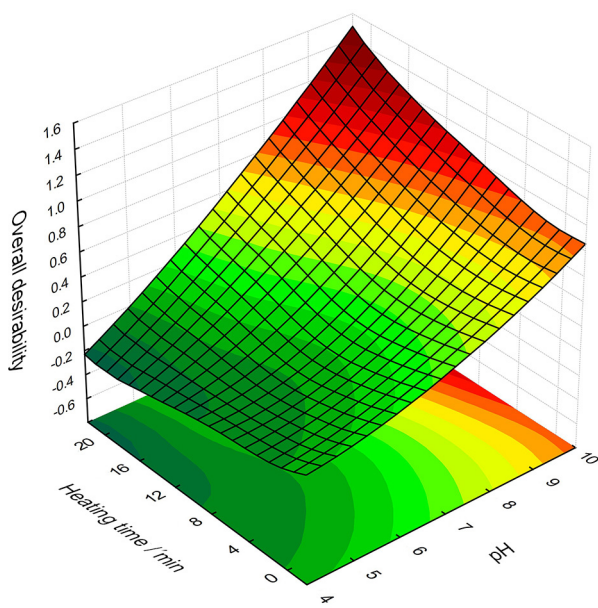| Experiment | pH | Heating time / min | Emission intensity / cps[a] | | |
| --- | --- | --- | --- | --- | --- |
| | | | Cadmium | Copper | Nickel |
| 1 | 6 | 20 | 4583.4 | 8710.4 | 43643.5 |
| | | | 3525.3 | 6632.2 | 64104.7 |
| 2 | 8 | 20 | 39209.1 | 12266.4 | 75759.3 |
| | | | 32313.6 | 10936.7 | 74818.2 |
| 3 | 5 | 10 | 3531.4 | 5332.8 | 48835.6 |
| | | | 3983.7 | 5446.7 | 49751.7 |
| 4 | 7 | 10 | 3921.8 | 5459.1 | 71300.9 |
| | | | 38546 | 5106.1 | 75688 |
| 5 | 9 | 10 | 55771.9 | 6857.4 | 73782.8 |
| | | | 48692.6 | 7384.5 | 78363.2 |
| 6 | 6 | 0 | 3847.5 | 5820.2 | 58184.2 |
| | | | 4602.2 | 6267.7 | 64683.5 |
| 7 | 8 | 0 | 23725.3 | 8273.1 | 70048.7 |
| | | | 23973.3 | 8085.5 | 68349.8 |

[a]Counts *per* second.



**Figure 1.** Response surface obtained through the adjustment of a quadratic function on the overall desirability.

solution and volume of the complexing agent 5-Br-PADAP to be used in the extractions.

Table 3 shows the results obtained after carrying out each experiment in accordance to what was established in the experimental matrix by the applied constraints. The lower and upper constraints established for the components of the mixture were 50 to 350 μL volume for the solution of the surfactant and the complexing agent, and 1800 to 2400 μL for the buffer solution (pH 9).

Linear, quadratic and special cubic models were fitted to describe the behavior of the responses obtained, allowing the calculation of optimal conditions. According to ANOVA

(Table 4) all mathematic models have presented lack of fit ($F_{calculated} > F_{critical}$). Linear functions presented the worst description of the data behavior. Special cubic model presents a slightly improvement in the data description in relation to quadratic model, but this last was chosen due to its simplicity. The surface generated by the quadratic model is shown in Figure 2. This surface has a maximum as critical point. The coordinates of this point are the proportions of the components that generate the greatest response in the studied system. Thus, the optimum conditions obtained for the cloud point extraction were 350 μL of the 10% triton X-114 solution, 350 μL of the 100 μg mL$^{-1}$ (m/v) 5-Br-PADAP solution and 1.8 mL of the pH 9 buffer solution.
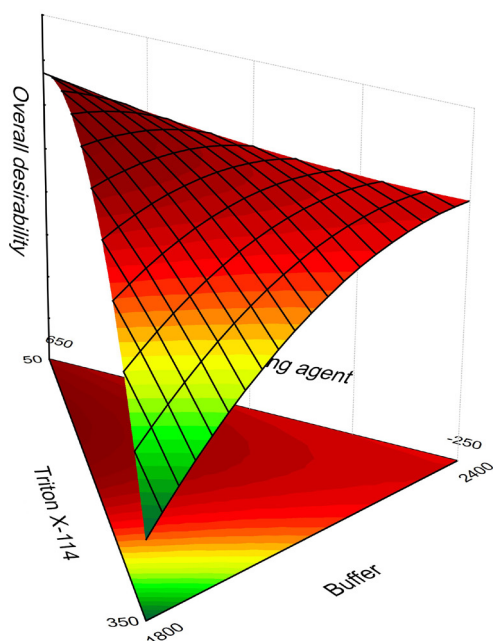
### Analytical characteristics

The equations of regression curves obtained through the process of pre-concentration were determined with standard solutions of Cd, Cu and Ni in a range varying from 5 to 100 μg L$^{-1}$ and the equations obtained through the curves without pre-concentration of these metals were determined with the concentrations of the studied metals varying in a range from 0.1 to 1.5 μg mL$^{-1}$.

The limits of detection (LOD) and quantification (LOQ) are defined as LOD = 3s / a and LOQ = 10s / a, respectively, where a is the inclination of the analytical curve and s is the standard deviation of ten consecutive measurements of the analytical blank sign. Sensitivity corresponds to the fraction of the signal responsible for the addition of a concentration unit to the property of interest (in this case the absorbance) and is numerically expressed by the

**Table 3.** Experimental matrix defined by constraints for the optimization of mixtures of solutions promoting cloud point extraction

| Mixture | Triton X-114 / µL | Buffer / µL | Complexing agent / µL | Signal intensity / cps[a] | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | | Cadmium | Copper | Nickel |
| 1 | 50 | 2400 | 50 | 50288.7 | 2056.4 | 7726.3 |
| | | | | 48320.1 | 2402.9 | 8353.8 |
| 2 | 350 | 2100 | 50 | 22377.4 | 4112.2 | 65103.1 |
| | | | | 24723.6 | 4052.7 | 55235.7 |
| 3 | 50 | 2100 | 350 | 65507.8 | 2408.7 | 12844.9 |
| | | | | 63851.2 | 2531.5 | 13460.8 |
| 4 | 350 | 1800 | 350 | 473923.1 | 8518.2 | 180401.3 |
| | | | | 458631.9 | 8878.7 | 168861.3 |
| 5 | 50 | 2250 | 200 | 22616.6 | 1632.1 | 9333.9 |
| | | | | 22207.7 | 1726.1 | 8860.1 |
| 6 | 350 | 1950 | 200 | 171575.3 | 6443.2 | 225523.7 |
| | | | | 170121.6 | 6393.4 | 218394.2 |
| 7 | 200 | 2250 | 50 | 32032.8 | 4189.1 | 57218.1 |
| | | | | 34929.1 | 3999.2 | 58769.6 |
| 8 | 200 | 1950 | 350 | 441180.4 | 6963.6 | 191328.6 |
| | | | | 441754.4 | 5559.8 | 194308.9 |
| 9 | 200 | 2100 | 200 | 109039.1 | 4062.1 | 163495.5 |
| | | | | 105434.1 | 4032.5 | 146275.8 |

[a]Counts *per* second.



**Figure 2.** Response surface obtained in the second optimization stage of the variables triton X-114 (µL) dependent on complexing agent 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP, µL) and buffer (µL).

inclination of the analytical curve. The enrichment factor (EF) was calculated as the ratio between the slope of the analytical curves with and without pre-concentration. The analytical characteristics of the proposed procedure for the determination of Cd, Cu and Ni were evaluated after optimization of the system and are indicated in Table 5.

## Accuracy and application

Certified reference materials of estuarine sediments (NIST 1646a) and marine sediments (NIST 2702) were used to evaluate the accuracy of the analytical method for the determination of the studied metals in sediments. The values determined by ICP OES in the analyses of the certified reference materials are presented in Table 6.

Concentrations of the studied metals for certified reference material (NIST 1646a) can be considered satisfactory for Ni, since the determination of this metal showed an acceptable pre-concentration relative error of 5.6% (recovery of 94.4%), and for Cu, with a relative error of 18.1% (81.9% accuracy). Cd content was below the limit of quantification of the technique, thereby preventing its determination by the employed method.

The results of the concentrations of the studied metals for the NIST 2702 certified reference material can be considered satisfactory for the three metals, with a relative error of 4% (recovery of 104%), 1.6% (recovery of 106.6%) and 1.9% (recovery of 98.1%) for Cd, Cu and Ni, respectively.

The proposed procedure was applied to the determination of Cd, Cu and Ni in sediment samples collected in the Contas River (Jequié, Bahia, Brazil). The concentrations found for the analyzed metals are shown in Table 7.

Conselho Nacional do Meio Ambiente (CONAMA) established, in resolution 344/2004,[23] a range of acceptable concentrations in sediments for Cd availability

**Table 4.** Analysis of variance (ANOVA) table for mathematical models fitted to experimental data (expressed as overall desirability) obtained from Doehlert and mixture designs

(a) Doehlert design, linear model / ($R^2 = 0.7622$)

|  | Sum of squares | Degree of freedom | Mean square | F-value | Tabled F |
|---|---|---|---|---|---|
| Regression | 0.978987 | 2 | 0.489493 | 14.35 | 3.98 |
| Residual | 0.375266 | 11 | 0.034115 |  |  |
| Lack of fit | 0.361720 | 4 | 0.090430 | 46.73 | 4.12 |
| Pure error | 0.013546 | 7 | 0.001935 |  |  |
| Total sum of squares | 1.354253 | 13 |  |  |  |

(b) Doehlert design, quadratic model / ($R^2 = 0.9637$)

|  | Sum of squares | Degree of freedom | Mean square | F-value | Tabled F |
|---|---|---|---|---|---|
| Regression | 1.219947 | 5 | 0.243989 | 14.53 | 3.69 |
| Residual | 0.134306 | 8 | 0.016788 |  |  |
| Lack of fit | 0.120760 | 1 | 0.120760 | 62.40 | 5.59 |
| Pure error | 0.013546 | 7 | 0.001935 |  |  |
| Total sum of squares | 1.354253 | 13 |  |  |  |

(c) Mixture design, linear model / ($R^2 = 0.7622$)

|  | Sum of squares | Degree of freedom | Mean square | F-value | Tabled F |
|---|---|---|---|---|---|
| Model | 1.546518 | 2 | 0.773259 | 24.04 | 3.68 |
| Total error | 0.482409 | 15 | 0.032161 |  |  |
| Lack of fit | 0.477870 | 6 | 0.079645 | 157.9 | 3.37 |
| Pure error | 0.004539 | 9 | 0.000504 |  |  |
| Total adjusted | 2.028927 | 17 | 0.119349 |  |  |

(d) Mixture design, quadratic model / ($R^2 = 0.9637$)

|  | Sum of squares | Degree of freedom | Mean square | F-value | Tabled F |
|---|---|---|---|---|---|
| Model | 1.955284 | 5 | 0.391057 | 63.72 | 3.11 |
| Total error | 0.073643 | 12 | 0.006137 |  |  |
| Lack of fit | 0.069103 | 3 | 0.023034 | 45.67 | 3.86 |
| Pure error | 0.004539 | 9 | 0.000504 |  |  |
| Total adjusted | 2.028927 | 17 | 0.119349 |  |  |

(e) Mixture design, special cubic model / ($R^2 = 0.9871$)

|  | Sum of squares | Degree of freedom | Mean square | F-value | Tabled F |
|---|---|---|---|---|---|
| Model | 2.002852 | 6 | 0.333809 | 140.8 | 3.09 |
| Total error | 0.026075 | 11 | 0.002370 |  |  |
| Lack of fit | 0.021536 | 2 | 0.010768 | 21.35 | 4.26 |
| Pure error | 0.004539 | 9 | 0.000504 |  |  |
| Total adjusted | 2.028927 | 17 | 0.119349 |  |  |

**Table 5.** Analytical curves with and without pre-concentration and analytical characteristics of the method proposed for the determination of metals in sediments by cloud point extraction and inductively coupled plasma optical emission spectrometry (ICP OES)

| Metal | Cloud point extraction | | Without pre-concentration | | EF | LOD / ($\mu g\ g^{-1}$) | LOQ / ($\mu g\ g^{-1}$) |
|---|---|---|---|---|---|---|---|
|  | Curve[a] | $R^2$ | Curve[b] | $R^2$ |  |  |  |
| Cadmium | y = 15682[Cd] − 1371.7 | 0.9947 | y = 851081[Cd] − 10597 | 0.9956 | 18.4 | 0.020 | 0.066 |
| Copper | y = 15315[Cu] + 18785 | 0.9906 | y = 909987[Cu] − 18598 | 0.9948 | 16.8 | 0.045 | 0.149 |
| Nickel | y = 6513[Ni] + 2158.7 | 0.9980 | y = 356891[Ni] − 6944.5 | 0.9960 | 18.2 | 0.057 | 0.191 |

[a]Concentration interval of 5.0-100.0 $\mu g\ L^{-1}$; [b]interval of 0.1-1.5 $\mu g\ mL^{-1}$; EF = enrichment factor; LOD = limit of detection; LOQ = limit of quantification.

**Table 6.** Cadmium, copper and nickel determination in the certified samples

| Sample | Metal | Found value / ($\mu g \ g^{-1}$) | Certified value / ($\mu g \ g^{-1}$) |
|---|---|---|---|
| | Cadmium | < LOQ | 0.148 ± 0.007 |
| NIST 1646a[a] | Copper | 8.2 ± 0.2 | 10.01 ± 0.34 |
| | Nickel | 21.7 ± 0.2 | 23.0 |
| | Cadmium | 0.85 ± 0.04 | 0.817 ± 0.011 |
| NIST 2702[b] | Copper | 119.6 ± 17 | 117.7 ± 5.6 |
| | Nickel | 74.0 ± 0.8 | 75.4 ± 1.5 |

[a]Estuarine sediment; [b]marine sediment; LOQ = limit of quantification; n = 3.

**Table 7.** Cadmium, copper and nickel determination in the sediment samples

| Sample | Cadmium / ($\mu g \ g^{-1}$) | Copper / ($\mu g \ g^{-1}$) | Nickel / ($\mu g \ g^{-1}$) |
|---|---|---|---|
| Sediment 1 | < LOQ | 47.4 ± 2.0 | 0.49 ± 0.19 |
| Sediment 2 | < LOQ | 35.6 ± 0.4 | 1.07 ± 1.3 |
| Sediment 3 | 0.61 ± 0.3 | 44.9 ± 6.0 | 0.75 ± 0.4 |
| Sediment 4 | 0.94 ± 0.01 | 35.2 ± 5.0 | 3.1 ± 0.5 |
| Sediment 5 | 0.57 ± 0.08 | 44.9 ± 5.0 | 3.6 ± 0.4 |

LOQ = limit of quantification.

(0.6 to 3.5 $\mu g \ g^{-1}$), Cu (35.7 to 197.0 $\mu g \ g^{-1}$) and Ni (18.0 to 35.3 $\mu g \ g^{-1}$). These reference values are not used for sediment classification, but as a contributing factor for the management of the disposal area.

Cadmium concentration found in samples 1 and 2 were below the limit of detection of the method. Cadmium and copper levels found in the analyzed samples are within the acceptable concentration range set by the CONAMA. The concentration of nickel in the sample is below the limit established by the aforementioned agency.

## Conclusions

Cloud point extraction is an attractive alternative for determination of metals in sediment samples followed by quantification through ICP OES, as it can be considered a fast, efficient and economical method, requiring lower volumes of reagents, fitting in the principles of green chemistry. Using multivariate experimental design techniques, such as Doehlert design and constrained mixture design, allowed a fast and efficient optimization of the methodology. In spite of all tested models have presented lack of fit, surfaces obtained with quadratic models were used to find the optimal conditions, because it was the simplest model with an adequate $R^2$ to describe the data behavior. This model become possible to develop a method with confidence and adequate analytical characteristics for application in sediments. The results of this study showed that the obtained values of concentrations of Cd, Cu and Ni in sediment samples are below the maximum extent permitted by the CONAMA, which establishes, among others, the general guidelines and minimum procedures for the assessment and management of sediments and their disposal in Brazilian jurisdictional waters.

## Acknowledgements

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